Biobased step-growth polymers : chemistry, functionality and applicability

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chemistry, functionality and applicability

Bart A. J. Noordover

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Biobased step-growth polymers

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PROEFSCHRIFT

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"… it is well known that boiled linseed oil has for many centuries constituted the fundamental raw material of our art. It is an ancient art and therefore noble: its most remote testimony is in Genesis 6:14, where it is told how, in conformity with a precise specification of the Almighty, Noah coated (probably with a brush) the Ark's interior and exterior with melted pitch. But it is also a subtly fraudulent art, like that which aims at concealing the substratum by conferring on it the color and appearance of what it is not: from this point of view it is related to cosmetics and adornment, which are equally ambiguous and almost equally ancient arts (Isaiah 3:16). Given therefore its pluri-millenial origins, it is not so strange that the trade of manufacturing varnishes retains in its crannies (despite the innumerable solicitations it modernly receives from kindred techniques) rudiments of customs and procedures abandoned for a long time now."

Primo Levi – *The Periodic Table*

Voor mijn ouders

Table of Contents

1

Introduction

1.1 Step-growth polymers

Step-growth polymers, also referred to as condensation polymers or polycondensates, make up an important part of the total amount of polymeric materials utilized today. Examples of such polymers are polyesters, polycarbonates, polyamides, polyurethanes and epoxy resins. Polycondensates find their way into countless applications, depending on the specific properties of the material. Polyesters, for example, are widely used in clothing, packaging (for example: poly(ethylene terephthalate) bottles), toner and coating applications. In addition, fiber-reinforced polyesters are used as engineering plastics in the automotive industry and in many types of domestic and office appliances and electronic devices. Polycarbonates can be found in applications where toughness and transparency are required, such as windshields, bulletproof glass, safety helmets and glasses. Also, polycarbonates are used in food and medical packaging and in consumer products such as ski poles, compact discs and power tool housings. Polyamides, such as the well-known Nylons, can be found in clothing, fibers, carpets and parachutes. Another field of application for these materials is the engineering plastics area, covering the automotive, electronics and aviation industries. Various consumer goods, such as ski boots and toys, also contain polyamides. Polyurethanes are used in flexible foams, elastomeric materials, adhesives and coatings. Examples include seat cushions, mattresses, insulation foams, automobile parts and sporting goods.[1]

An increasingly important application of step-growth polymers, especially of polyesters, epoxy resins and polyurethanes, is their use in coating systems. One of the more recent developments in the coating field is the successful implementation of the powder coating technology, which was used for the first time in the 1950s. In these systems, the paint formulation is applied onto the substrate as a fine solid powder instead of from solution, followed by thermally induced flow and subsequent cooling. Initially, only thermoplastic powder coatings were used, which do not involve curing reactions but rely solely on melting and sintering of the powder particles. These systems are suitable for some applications, but prove to be limited by poor solvent resistance and high application temperatures (and, thus, to metallic or other heat-resistant substrates). In the 1970s, thermosetting powder coatings gained importance. This technology makes use of polymer resins with relatively low molecular weights that can be cross-linked by curing agents to form a polymer network during the application process.[2] The major types of polymers used in such systems are carboxylic acid-functional polyesters, hydroxy-functional polyesters, epoxy resins, epoxy-polyester hybrids and acrylic resins.[3]

Most commonly used step-growth polymers are prepared using monomers derived from fossil fuels (i.e. petrochemicals). In recent years, there is a strongly increasing drive to search for monomers from alternative sources such as agricultural crops. Several examples of polymers based on renewable resources have been investigated, including materials based on monosaccharides, fatty acids, starch, cellulose, lactic acid and natural amino acids.[4-7] Also in the coatings field, research efforts are spent on introducing alternative, biobased monomers into performance materials.[8-10]

1.2 Thermosetting powder coatings

The focus of this thesis is on step-growth polymers of moderate molecular mass, with suitable thermal properties and functionalities for thermosetting coating systems. Such materials are widely used in industry to make coating formulations for a broad variety of products, such as metal and wooden furniture, tools, domestic appliances as well as automotive and industrial applications.[2] In Europe, about 10 % of the total paint consumption consists of powder coatings, while waterborne paints account for approximately 55 % of the market. In addition, one third of all the paint used in Europe is still solvent borne. In the coming years, the yearly growth rate for powder coatings is expected to be approximately 7 % world-wide. The fact that powder coating technology is a solvent-free, relatively clean and easily accessible technology will stimulate its growth at the expense of solvent borne systems.[11]

Basically, a thermosetting paint system consists of a polymeric binder of moderate molecular weight having functional end-groups, which react with a cross-linking agent during the coating application. Polymers used in thermosetting powder coating systems typically have number average molecular weight ($\overline{M}_n$) values between 2000 and 6000 g/mol. With increasing molecular weight of the polymer, the melt viscosity increases, leading to problems in processing and poor flow during powder coating application. The polymers are often synthesized via classical melt polycondensation procedures. Ideally, all polymer chains have a functionality $\overline{F}_n$ equal to or larger than two. This means that each chain should have at least two end-groups that can react with the selected curing agent present in the powder paint formulation. In this way, all chains participate in the network formation upon curing and are considered to be elastically active network chains.[12,13] So-called 'dangling ends' (e.g. linear chains that only have one functional group) as well as cyclic chains generally have a negative influence on the coating performance and their presence should be minimized. The molecular weight of the resin, together with its functionality, determines the cross-link density of the final cured network. The average functionality of a polymer sample can be increased by increasing the number of (pendant) functional groups per polymer chain. This can be achieved by using monomers with functionalities larger than two, often resulting in branched polymer chains. Another option is to lower the polymer molecular weight, which automatically means that more functional end-groups are present per gram of sample. When the functionality of a resin is high, more cross-linker is needed to cure the formulation. The resulting polymer network will have a lower molecular weight between the cross-linkages. During curing, the powder paint particles have to flow and coalesce to form a continuous film on the substrate. Therefore, the polymeric binder should have a flow temperature (T_{flow}) well below the curing temperature. Also, the resins should have a relatively low melt viscosity, to facilitate good film formation. In systems with high resin functionalities, the viscosity of the melt increases rapidly during curing, shortening the time available for flow to occur. In powder coating systems, it is therefore crucial to balance the rate of curing and the time available for film formation.[2]

The predominant type of polymer end-groups (e.g. carboxylic acid or hydroxyl groups) is determined by the stoichiometry of the monomers present in the reaction mixture. The thermal properties, on the other hand, can be tuned by the choice of different aromatic and aliphatic building blocks as well as by the average molecular weight of the polymer. The glass transition temperature (T_g) is an important thermal characteristic for such resins. The T_g of the powder paint should be at least 40 °C, to ensure the storage stability of the material at room temperature as well as to obtain coatings with suitable T_g values. Upon gelation of the coating formulation, the T_g of the system increases due to the increase of the cross-link density and the $\overline{M}_n$, as well as due to the decrease of the number of free chain ends.[14,15] There are two main methods to influence the T_g of the polymer. First of all, the monomer selection (i.e. their inherent flexibilities and conformations) determines the minimum and maximum boundaries of the T_g. More flexible monomers decrease the T_g, while rigid structures lead to a stiffer polymer chain and therefore to a higher T_g. In addition, the average molecular weight and the molecular weight distribution have an important influence on the T_g, as was described by Fox and Flory with equation 1.1.[16]

$$T_g = T_g^{\infty} - \frac{K}{\overline{M}_n} \qquad \text{(Equation 1.1)}$$

In this equation, T_g^{∞} is the glass transition temperature of a polymer of infinite molecular weight and K is a constant related to the thermal expansion coefficients above and below T_g. This equation demonstrates that the T_g will increase with the number average molecular weight $\overline{M}_n$ of the polymer, leveling off at a certain plateau value (T_g^{∞}). Polymer resins, used as binders in thermosetting powder coatings or toner systems, have relatively low number average molecular weights. K is in the order of 10^4 to 10^5.[16,17] Therefore, the glass transition temperatures of these polymers strongly depend on their $\overline{M}_n$ values. The free volume created by the polymer end-groups plays a very important role in this respect.

Commercially available powder paints consist of many different constituents. The main ingredients are the polymeric binder with reactive chain-ends, the curing agent and, often, the pigments. Other compounds present in these systems are flow agents, degassing agents, stabilizers and catalysts, a.o. In a typical industrial process, the different components are premixed and fed to an extruder, usually operated at 90 – 120 ˚C. It is crucial that the curing reaction does not take place at an appreciable rate during this extrusion step. One of the ways to prevent pre-reaction is by using blocked curing agents, which become deblocked at temperatures well above the extrusion temperature. The resulting extrudate is ground to a fine powder. This powder paint can be electrostatically applied onto the pretreated substrate, which is then placed in a curing oven. During this curing step, carried out between 150 and 220 ˚C depending on the curing chemistry, thermally induced flow and cross-linking occur simultaneously.

1.3 Renewable resources

For centuries, natural and agricultural products have been used in the production of non-food products such as clothing, paper, soap, greases and paints. The important advances made in science with respect to catalysis and polymer chemistry resulted in the rapid development of the petrochemical industry in the beginning of the 20th century.[18] At the time, oil reserves were abundant and seemed inexhaustible, leading to cheap production of more and more high-performance materials. Alongside this newly developed petrochemical infrastructure, the production of chemicals from agricultural sources remained intact. Vegetable oils, fatty acids, starch, cellulose and natural rubber are important examples of such products. Nowadays, the increasing oil prices and the public as well as the political awareness of the rapid depletion of the global fossil feedstock, have sparked new initiatives towards high performance biobased products. Apart from the well-known traditional renewable materials, a new class of biobased starting compounds has become available. As a result of the tremendous increase of the research efforts in this field, an expanding range of chemicals, suitable for e.g. polymer synthesis, can be produced in an efficient way from renewable resources such as starch, cellulose and vegetable oils. Improved production processes to obtain various biobased monomers on large scales as well as the development of a sustainable economy should make the use of renewable feedstock even more economically attractive in the future.[19,20]

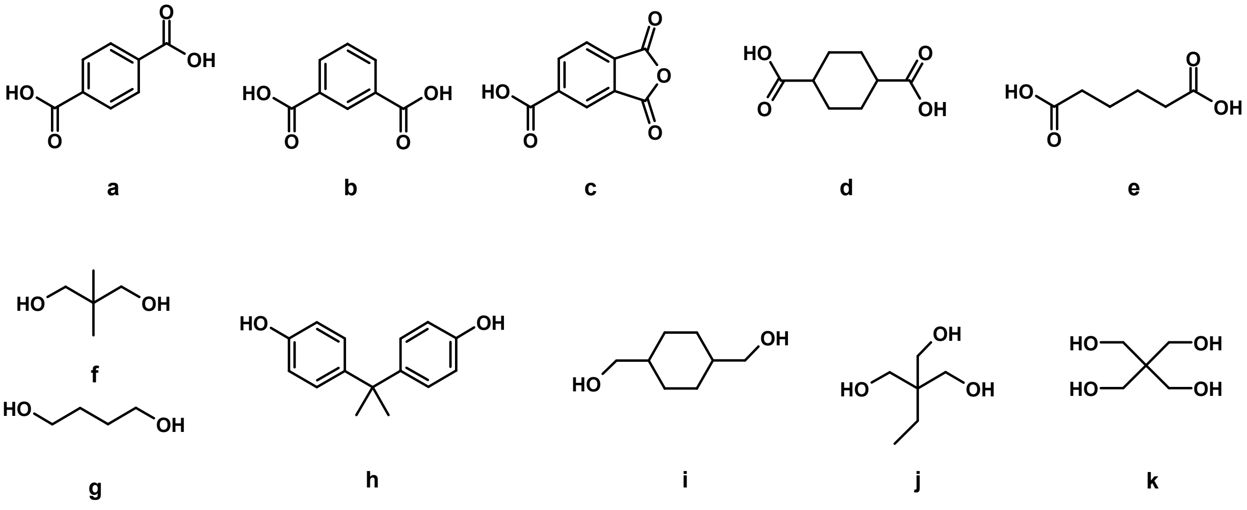
Terms like ‘biobased’, ‘renewable’ and ‘green’ have become more and more popular in scientific, governmental as well as commercial publications. It is important to realize, however, that such designations are by no means interchangeable. According to the United States Department of Agriculture, the word ‘biobased’ refers to chemicals, energy sources and other materials that utilize biological or renewable agricultural materials. The term ‘renewable’ indicates that a certain material or energy source is inexhaustible or rapidly replaceable by new growth. Obviously, the regeneration of a certain resource should occur on a time-scale that matches the time-scale of its use. Important examples of renewable resources are starch from corn or potatoes (harvested annually), plants and trees as well as energy sources such as water, sunlight and wind. These resources replenish themselves and should not run short when managed properly, making sure that the world’s food supply is not compromised. ‘Green’ chemistry can be defined as the design, manufacture and application of chemical products and processes that reduce or eliminate substances hazardous to human health or the environment.[21]

It is important to realize that the monomers and polymers described in this thesis are still very much at the beginning of a development process. The materials are obtained from renewable resources, but at the moment some of these biobased products cannot be produced without making use of conventional chemicals derived from fossil fuels. We do expect, however, that benefits for the environment can be realized with the development and maturation of biobased chemical processes and products.

1.4 Conventional and biobased step-growth polymers and curing agents

1.4.1 Conventional polyesters used in thermosetting powder coatings

As mentioned already, most of the currently available polymers are based on starting materials derived from petrochemicals. Conventional polyester resins for coating applications often contain aromatic carboxylic acid-functional monomers, such as (derivatives of) terephthalic acid, isophthalic acid and trimellitic anhydride. These monomers provide rigidity to the polyester chains, increasing their T_gs and enhancing their thermal performances. These acid-functional monomers are often combined with, for example, neopentyl glycol, linear alkane diols, bisphenol-A and polyols such as trimethylolpropane or pentaerythritol.[2,22] Aliphatic monomers such as adipic acid, 1,4-cyclohexane dicarboxylic acid and 1,4-cyclohexane dimethanol can also be used in polyester resins.[23,24] The fossil fuel derivatives commonly used for polyester synthesis are depicted in Scheme 1-1.



Scheme 1-1. Hydroxy- and carboxylic acid-functional monomers commonly used in powder coating resins: (**a**) terephthalic acid (TPA), (**b**) isophthalic acid (IPA), (**c**) trimellitic anhydride (TMA), (**d**) 1,4-cyclohexanedicarboxylic acid (CHDA), (**e**) adipic acid, (**f**) neopentyl glycol (NPG), (**g**) 1,4-butanediol (1,4-BD, other linear alkane diols such as ethylene glycol are also used), (**h**) bisphenol-A, (**i**) 1,4-cyclohexanedimethanol (CHDM), (**j**) trimethylolpropane (TMP) and (**k**) pentaerythritol.

Polycarbonates are known for their toughness, excellent transparency, hydrolytic stability as well as solvent resistance. Nonetheless, conventional aromatic polycarbonates, such as poly(bisphenol-A carbonate), are hardly used in coating applications, due to their high T_gs, poor scratch resistance and poor UV-stability. In particular, aromatic monomers have the disadvantage that they are susceptible to photodegradation, leading to embrittlement and possibly also yellowing of the coating in time.[25-27] It is therefore desirable to develop fully aliphatic systems with better UV stability, suitable for outdoor applications. However, due to the high chain flexibility of most aliphatic polymers, these materials generally have a too low T_g for practical powder coating applications.

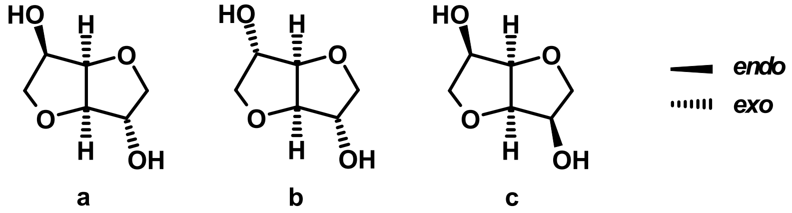
1.4.2 Conventional curing agents derived from petrochemicals

Hydroxy-functional polyesters are usually cured using polyisocyanate cross-linkers, resulting in poly(ester urethane) networks. To prevent premature curing from taking place and to limit the health risks involved in using isocyanates, the –NCO groups of these curing agents are often protected by blocking agents such as ε-caprolactam or methyl ethyl ketoxime or through reversible internal blocking using uretidiones (i.e. isocyanate dimers).[2] Carboxylic acid-functional polymers can be cured using epoxides, such as triglycidyl isocyanurate (TGIC), or by compounds containing activated hydroxyl groups, such as β-hydroxyalkylamides. TGIC is currently under pressure, since it is classified as a category 2 mutagen.[28] Alternative epoxy compounds are also in use, such as mixtures of diglycidyl terephthalate and triglycidyl trimellitate. All the mentioned conventional curing agents and their curing chemistries will be discussed in chapters 2 and 4 of this thesis.

1.4.3 Monomers from renewable resources

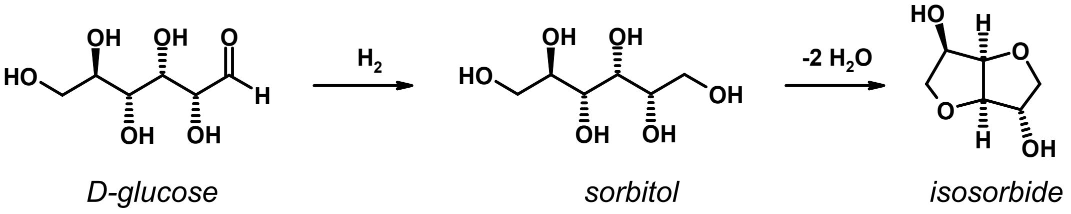
During our investigations, several existing as well as new biobased monomers were used to synthesize step-growth polymers and cured networks based on such polymers. An important partner in this respect was Agrotechnology and Food Innovations (also referred to as A&F). This company, part of the Wageningen University and Research Centre (WUR), ran a project parallel to our research, dealing with the synthesis and development of biobased monomers (diols, carboxylic diacids and diamines) and a number of novel curing agents from renewable

resources. In addition, new monomers were supplied to us by Roquette Frères, a company located in the north of France, active in the field of renewable resources and bio-refining.
Most of the polymeric systems described in this thesis contain one or more of the so-called 1,4:3,6-dianhydrohexitols (DAH), shown in Scheme 1-2.



Scheme 1-2. The 1,4:3,6-dianhydrohexitols: (**a**) 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS), (**b**) 1,4:3,6-dianhydro-L-iditol (isoidide, II) and (**c**) 1,4:3,6-dianhydro-D-mannitol (isomannide, IM).

These rigid, bicyclic molecules are derived from starch. For example, isosorbide (IS) is obtained in the following way: first, starch is extracted from corn (or another starch source) and enzymatically hydrolyzed to its basic mono- and oligomeric units, i.e. D-glucose (or: dextrose), the disaccharide maltose and other oligosaccharides. D-glucose is then separated from the mixture of sugars and hydrogenated to yield sorbitol (or: D-glucitol). By a subsequent acid-catalyzed dehydration step, the desired product is obtained (Scheme 1-3).

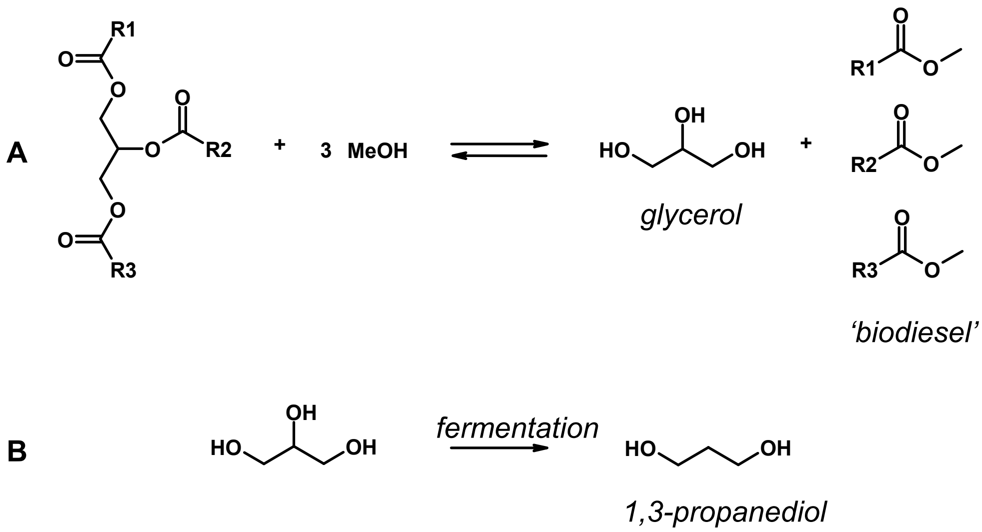


Scheme 1-3. Synthesis of 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) from D-glucose.[29]

Already in 1884, Fauconnier described 1,4:3,6-dianhydro-D-mannitol (or isomannide).[30] In 1929, a dianhydride of sorbitol was mentioned for the first time in a German patent assigned to the I.G. Farbenindustrie A.G.[31] At that time, the exact structures of such compounds were not known. In the 1940s, the structures of isosorbide, isomannide and isoidide (i.e. the presence of the 1,4 and the 3,6 anhydro rings as well as the secondary OH-groups) were determined.[32-35] Their five-membered rings are nearly planar and do not undergo conformational changes such as those taking place in cyclohexane moieties. The angle between the two rings is 120 °. The hydroxyl groups of the DAHs, located at the C_2 and C_5

positions, are either *exo-* or *endo*-oriented, indicating their configurations with respect to the V-shape formed by the two *cis*-fused rings. Isosorbide thus has one *endo*-OH and one *exo*-OH, while isoidide has two *exo*-oriented hydroxyls and isomannide has two hydroxyl groups in the *endo* configuration.[36-38] Nowadays, isosorbide is the only 1,4:3,6-dianhydrohexitol that is commercially available on an appreciable scale. This hygroscopic molecule has a melting temperature between 61 and 64 ºC and it is known to be thermally stable up to 270 ºC and can, thus, be used in polycondensation reactions in the melt.[39,40] Several research groups have investigated the 1,4:3,6-dianhydrohexitols as monomers in polymer synthesis and their work will be referred to in the several chapters of this thesis. The highlights of the research performed until 1997, concerning polycondensates containing 1,4:3,6-dianhydrohexitols, were summarized in a review by Kricheldorf.[41] Another application of the 1,4:3,6-dianhydrohexitols can be found in the medical world, where mono- and dinitrates of isosorbide are used to treat *Angina Pectoris.*[42]

In addition to the DAHs, many other monomers[43] can be obtained from biomass, such as 1,3-propanediol, glycerol, 2,3-butanediol and succinic acid.[44] Glycerol can be obtained by the fermentation of glucose. Nowadays, however, glycerol is mainly obtained as a side-product of biodiesel (i.e. monoalkyl esters of long chain fatty acids) produced by transesterification of triglycerides with methanol (Scheme 1-4, **A**).[45]



Scheme 1-4. (**A**) Synthesis of glycerol through transesterification of triglycerides with methanol[45,46] and (**B**) 1,3-propanediol by fermentation of glycerol.[47]

For every ton of biodiesel produced, roughly 100 kg of glycerol is obtained[48], which has led to a surplus of glycerol on the world market and to a drop in its price. Therefore, using glycerol as a feedstock for, e.g., polymer production, has become more interesting. From glycerol, 1,3-propanediol can be obtained through fermentation using, for example, the microorganisms *Escherichia coli* or *Klebsiella pneumoniae* (Scheme 1-4, **B**).[46,47,49] Another compound that can be derived through fermentation of glucose, is 2,3-butanediol (2,3-BD).[50] This diol is an important intermediate in the synthesis of methyl ethyl ketone. In addition, it can be used as a monomer in polycondensation reactions.[51]

Apart from hydroxyl-functional monomers, carboxylic acid-functional monomers were used to synthesize polyesters. Succinic acid (SA), for example, can be obtained via fermentation of glucose with yields up to 1.1 kg succinic acid/kg of glucose (with CO_2 incorporation). Currently, SA is produced from butane via maleic anhydride. Improvements in the production of SA through fermentation have made its biological production competitive to the butane-based route. Interestingly, hydrogenation of succinic acid can lead to products such as 1,4-butanediol, tetrahydrofuran (THF) and γ-butyrolactone. The latter is used as a solvent and as an intermediate for agrochemicals and pharmaceuticals.[44,52] Citric acid (CA) is another biobased compound, useful as a functionality-enhancing monomer in polyester systems. CA is produced commercially from glucose or sucrose at low cost via fermentation, with an approximate annual production of 7×10^5 tons.[53]

The renewable monomers described in this paragraph were used to synthesize fully aliphatic polyester and polycarbonate resins, as well as polyester, poly(ester urethane) and poly(carbonate urethane) networks. Their chemistries, characteristics and performances will be described in detail in Chapters 2 - 7 of this thesis.

1.5 Aim and scope of this study

The main motivation for this work is the scientific curiosity to synthesize and characterize new polymers and to apply these materials in technically relevant polymeric systems. The overall objective of the investigations described in this thesis, is to demonstrate the feasibility of using biobased monomers to synthesize step-growth polymers with suitable properties for, e.g., thermosetting coating applications. An additional aim was to show that biobased polymeric systems can perform as good as or even better than materials derived from petrochemicals. To achieve these goals, a detailed understanding of the chemistry and functionality of the different monomers and the resulting polymers was required. In order to develop sound synthetic procedures, in-depth studies into the chemistry of the several polymerization and modification reactions were performed. Crucial polymer characteristics, such as functionality, glass transition temperature, molecular weight (distribution) as well as rheological behavior, were investigated to be able to design polymeric architectures and networks that perform well with respect to chemical and mechanical resistance.

This research project included a broad array of disciplines, ranging from monomer synthesis and modification to polymerization via several synthetic routes as well as different analytical and materials testing techniques. To achieve the objectives stated previously, a chain-of-knowledge approach was chosen, encompassing the following steps (not necessarily performed in this order):

1. Synthesis and modification of renewable monomers
2. Polymerization of said starting materials to prepare step-growth polymers such as polyesters, polycarbonates and polyurethanes
3. Development of novel biobased chain extenders and curing agents
4. Design of the total polymeric architectures of coating and toner systems having different chemistries and performances

Steps 1 and 3 were mainly carried out by our partner Agrotechnology and Food Innovations (part of the Wageningen University and Research Centre). Polymer synthesis, characterization, application and testing were carried out at the Eindhoven University of Technology, the latter two in close collaboration with DSM Resins (Zwolle, the Netherlands).

1.6 Outline of this thesis

This thesis consists of 8 chapters concerning the research on step-growth polymers and cross-linked networks thereof, based partly or fully on monomers from renewable resources.

Chapter 2 discusses a broad range of linear as well as branched co- and terpolyesters, based on 1,4:3,6-dianhydro-D-glucitol (isosorbide) and succinic acid in combination with several comonomers. The chemistry and reactivity of the biobased monomers were studied and the polymerization procedures were optimized. The characteristics of the various polyesters obtained are described in detail. Many of the synthesized polymers were applied as coating systems from solution as well as through powder coating application. The results with respect to the mechanical and chemical stability of the afforded coatings are also discussed.

To clarify the influence of the configuration of the different 1,4:3,6-dianhydrohexitol isomers on the polymer properties, **Chapter 3** describes co- and terpolyesters based on

1,4:3,6-dianhydro-D-mannitol and 1,4:3,6-dianhydro-L-iditol. A comparison is made with regard to reactivity, thermal stability of the monomers, synthetic procedures and polymer as well as poly(ester urethane) coating properties.

In order to enhance the functionality of 1,4:3,6-dianhydrohexitol-based polyesters and to prepare carboxylic acid-functional materials, citric acid was evaluated as a renewable modifier to react with the secondary hydroxyl groups at the polyester chain ends. The chemistry of these citric acid modifications, the characteristics of the resulting polyesters as well as the subsequent curing chemistry and coating properties are described in **Chapter 4**.

Besides polyesters, polycarbonates prepared from the different 1,4:3,6-dianhydrohexitol isomers were studied, as discussed in **Chapter 5**. Three different synthetic routes were investigated, to optimize the functionality, composition, molecular weight (distribution) and thermal properties of the various targeted linear and branched (co)polycarbonates. These polymers were also applied as constituents of fully aliphatic poly(carbonate urethane) coating systems, of which the mechanical and chemical performances are presented.

High molecular weight poly(cyclohexene carbonate), prepared from the oxirane cyclohexene oxide and CO_2, was broken down and functionalized *in situ*, by alcoholysis of its carbonate linkages by polyols such as trimethylolpropane and 1,3,5-cyclohexanetriol. The resulting aliphatic, hydroxy-functional resins were applied in solvent cast poly(carbonate urethane) coating systems. The chemistry and properties of these polymeric systems are disclosed in **Chapter 6**.

In **Chapter 7**, fully biobased polyester, poly(ester urethane) and poly(carbonate urethane) coatings are revealed, obtained by curing several biobased, branched polyester and polycarbonate resins with novel bifunctional blocked isocyanate and epoxy curing agents based on renewable resources.

The final section of this thesis, **Chapter 8**, is an epilogue that highlights the most important results and conclusions resulting from the research described in Chapters 2-7. Furthermore, it contains a technology assessment concerning the industrial relevance of the work performed as well as suggestions for future research in the field of step-growth polymers from renewable resources.

Appendices A-C consist of additional information, serving as supporting documentation for the results presented in the different chapters.

References

(1) Odian, G. *Principles of polymerization* 3rd ed: John Wiley & Sons, Inc.: New York, 1991.

(2) Misev, T. A. *Powder coatings - chemistry and technology* 1st ed: John Wiley & Sons: New York, 1991.

(3) Richart, D. S. *Coating processes, powder technology*, in *Kirk-Othmer Encyclopedia of Chemical Technology*. 2001, John Wiley & Sons, Inc.: New York.

(4) Soderqvist Lindblad, M.; Liu, Y.; Albertsson, A.-C.; Ranucci, E.; Karlsson, S. *Adv. Polym. Sci.* **2002**, *157,* 139.

(5) Guner, F. S.; Yagci, Y.; Erciyes, A. T. *Prog. Pol. Sci.* **2006**, *31,* 633.

(6) Datta, R.; Henry, M. *J. Chem. Technol. Biotechnol.* **2006**, *81,* 1119.

(7) Mecking, S. *Angew. Chem. Int. Ed.* **2004**, *43,* 1078.

(8) Derksen, J. T. P.; Cuperus, F. P.; Kolster, P. *Prog. Org. Coat.* **1996**, *27,* 45.

(9) Overeem, A.; Buisman, G. J. H.; Derksen, J. T. P.; Cuperus, F. P.; Molhoek, L.; Grisnich, W.; Goemans, C. *Ind. Crop. Prod.* **1999**, *10,* 157.

(10) Van Haveren, J.; Oostveen, E. A.; Micciche, F.; Noordover, B. A. J.; Koning, C. E.; Van Benthem, R. A. T. M.; Frissen, A. E.; Weijnen, J. G. J. *J. Coat. Technol. Res.* **2007**, *4,* 177.

(11) Busato, F. *Macromol. Symp.* **2002**, *187,* 17.

(12) Flory, P. J. *Chem. Rev.* **1944**, *35,* 51.

(13) Treloar, L. R. G. *Rep. Prog. Phys.* **1973**, *36,* 755.

(14) Simon, S. L.; Gillham, J. K. *J. Appl. Polym. Sci.* **1992**, *46,* 1245.

(15) Mafi, R.; Mirabedini, S. M.; Attar, M. M.; Moradian, S. *Prog. Org. Coat.* **2005**, *54,* 164.

(16) Fox, T. G. J.; Flory, P. J. *J. Appl. Phys.* **1950**, *21,* 581.

(17) Kollodge, J. S.; Porter, R. S. *Macromolecules* **1995**, *28,* 4089.

(18) Coombs, J.; Hall, K. *Renew. Energy* **1998**, *15,* 54.

(19) Koutinas, A. A.; Wang, R.; Webb, C. *Ind. Crop. Prod.* **2004**, *20,* 75.

(20) Van Dam, J. E. G.; De Klerk-Engels, B.; Struik, P. C.; Rabbinge, R. *Ind. Crop. Prod.* **2005**, *21,* 129.

(21) Gonzalez, M. A.; Smith, R. L. *Environ. Prog.* **2004**, *22,* 269.

(22) Belder, E. G.; Van der Linde, R.; Schippers, J. (DSM Resins B.V.). US4528341, 1984.

(23) Awasthi, S.; Agarwal, D. *J. Coat. Technol. Res.* **2007**, *4,* 67.

(24) Marsh, S. J. *JCT CoatingsTech* **2005**, *2,* 32.

(25) Decker, C.; Moussa, K.; Bendaikha, T. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29,* 739.

(26) Allen, N. S.; Edge, M.; Mohammadian, M.; Jones, K. *Polym. Degrad. Stab.* **1993**, *41,* 191.

(27) Luda, M. P.; Tauriello, R.; Camino, G. *Eur. Coat. J.* **2000**, *10,* 74.

(28) HSE. *Revised guidance on control of exposure to TGIC in coating powders*. 2003 [cited 18th of May 2007]; Available from: http://www.hse.gov.uk/press/2003/e03081.htm.

(29) Stoss, P.; Hemmer, R. *Adv. Carbohydr. Chem. Biochem.* **1991**, *49,* 93.

(30) Fauconnier, A. *Bull. Soc. Chim. Fr.* **1884**, *41,* 119.

(31) Muller, J.; Hoffmann, U. (I.G. Farbenindustrie A.G.). DE488602, 1929.

(32) Bell, F. K.; Carr, J.; Krantz, J. C. *J. Phys. Chem.* **1940**, *44,* 862.

(33) Hockett, R. C.; Fletcher, H. G.; Sheffield, E. L.; Goepp, R. M. *J. Am. Chem. Soc.* **1946**, *68,* 927.

(34) Hockett, R. C.; Fletcher, H. G.; Sheffield, E. L.; Goepp, R. M.; Soltzberg, S. *J. Am. Chem. Soc.* **1946**, *68,* 930.
(35) Fletcher, H. G.; Goepp, R. M. *J. Am. Chem. Soc.* **1946**, *68,* 939.
(36) Wright, L. W.; Brandner, J. D. *J. Org. Chem.* **1964**, *29,* 2979.
(37) Cope, A. C.; Shen, T. Y. *J. Am. Chem. Soc.* **1956**, *78,* 3177.
(38) Cecutti, C.; Mouloungui, Z.; Gaset, A. *Bioresour. Technol.* **1998**, *66,* 63.
(39) Fleche, G.; Huchette, M. *Starch* **1986**, *38,* 26.
(40) Majdoub, M.; Loupy, A.; Fleche, G. *Eur. Polym. J.* **1994**, *30,* 1431.
(41) Kricheldorf, H. R. *J.M.S. - Rev. Macromol. Chem. Phys.* **1997**, *C37,* 599.
(42) Hennig, L.; Andresen, D.; Hennig, A.; Levenson, B.; Bruggemann, T.; Schroder, R. *J. Clin. Pharmacol.* **1991**, *31,* 636.
(43) Gandini, A.; Belgacem, M. N. *Prog. Pol. Sci.* **1997**, *22,* 1203.
(44) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107,* 2411.
(45) Hoydonckx, H. E.; De Vos, D. E.; Chavan, S. A.; Jacobs, P. A. *Topics Cat.* **2004**, *27,* 83.
(46) Meher, L. C.; Vidya Sagar, D.; Naik, S. N. *Ren. Sust. Energ. Rev.* **2006**, *10,* 248.
(47) Mu, Y.; Teng, H.; Zhang, D. J.; Wang, W.; Xiu, Z. L. *Biotechnol. Lett.* **2006**, *28,* 1755.
(48) Dasari, M. A.; Kiatsimkul, P.-P.; Sutterlin, W. R.; Suppes, G. J. *Appl. Cat. A General* **2005**, *281,* 225.
(49) Cheng, K. K.; Zhang, J. A.; Liu, D. H.; Sun, Y.; Liu, H. J.; Yang, M. D.; Xu, J. M. *Proc. Biochem.* **2007**, *42,* 740.
(50) Qin, J. Y.; Xiao, Z. J.; Ma, C. Q.; Xie, N. Z.; Liu, P. H.; Xu, P. *Chinese J. Chem. Eng.* **2006**, *14,* 132.
(51) Syu, M.-J. *Appl. Microbiol. Biotechnol.* **2001**, *55,* 10.
(52) Shekhawat, D.; Nagarajan, K.; Jackson, J. E.; Miller, D. J. *Appl. Cat. A General* **2002**, *223,* 261.
(53) Ikram-ul, H.; Ali, S.; Qadeer, M. A.; Iqbal, J. *Bioresour. Technol.* **2004**, *93,* 125.

2

Hydroxy-functional polyesters based on isosorbide

Abstract

Co- and terpolyesters based on 1,4:3,6-dianhydro-D-glucitol (isosorbide) and succinic acid in combination with other renewable monomers such as 2,3-butanediol, 1,3-propanediol and glycerol were synthesized and characterized. Linear OH-functional polyesters were obtained via melt polycondensation of non-activated dicarboxylic acids with OH-functional monomers. The type of end-group was controlled by the monomer stoichiometry. The glass transition temperatures of the resulting polyesters could be effectively adjusted by varying polymer composition and molar mass. By adding poly-functional monomers such as trimethylolpropane or glycerol, polyesters with enhanced functionality were obtained. These bio-based polyesters displayed functionalities and T_g *values in the appropriate range for (powder) coating applications. The polyesters were cross-linked using conventional curing agents through solvent casting as well as powder coating procedures. Coatings from branched polyesters showed significantly improved mechanical and chemical resistance compared to those formulated from linear polymers. These renewable polyesters proved to be suitable materials for coating applications with respect to solvent resistance, impact resistance and hardness. Accelerated weathering experiments showed that chain scission occurs under the influence of UV radiation. Functional groups such as hydroxyl groups, carboxylic acids, anhydrides and peroxides are formed in time. The weathered coatings have reduced impact stability. On the other hand, the appearance of the coatings does not change significantly.*

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2.1 Introduction

Aliphatic polyesters have been investigated as binder resins for thermosetting coating and toner systems. Most aliphatic polyesters have low T_gs due to their flexible building blocks, which limits their use in applications were the resins are to be applied as powders. However, there are exceptions to be found. For example, polyesters based on 1,4-cyclohexanedimethanol, 1,4-cyclohexane dicarboxylic acid or other cyclo-aliphatic monomers such as hexahydrophthalic acid have been shown to afford T_gs sufficiently high for powder coating applications and to lead to coatings with good weathering resistance.[1-3] Another way to circumvent the low T_g values of aliphatic polyesters is to modify the molecular architecture. Hyperbranched aliphatic polyesters can be used in thermoset (powder) coatings, also if these polyesters have low T_gs, when semi-crystalline segments are introduced to achieve suitable rheological properties.[4-6]

Stimulated by the growing concern for the environment and the rapid depletion of the mineral reserves, partially bio-based thermosetting systems have also been considered, such as coating formulations with aliphatic oxiranes from vegetable oils[7,8] or containing monomers from renewable resources.[9] In this respect, 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) is a very interesting monomer, since it is a rigid aliphatic moiety originating from corn starch. It has already shown to give T_g increasing effects in, for example, poly(ethylene terephthalate) (PET).[10-12] With isosorbide providing enough rigidity to obtain T_g values in the appropriate range[13-15] already for the typically low molecular weights required for thermosetting coating applications, we anticipated that fully aliphatic polyesters can be obtained using this monomer in combination with others, resulting in properties sufficient for (powder) coating and toner applications. As biobased diacid components, linear aliphatic diacids such as succinic acid (SA) or adipic acid (AA) can be used in these polyesters. The combination of these renewable monomers would ultimately give access to technically applicable polymers from bio-based raw materials.

The use of isosorbide in polymer systems has previously been reported by several authors in scientific journals and patents.[16-23] Also, some publications describe polyesters based on isosorbide for coating applications.[24-29] Numerous papers on dianhydrohexitol-based polyesters were published by the groups of Kricheldorf[15,16,30-32] and Okada.[17,33-36] In most of these papers, the interesting properties of dianhydrohexitol-based liquid crystalline polymers as well as the biodegradability of several types of dianhydrohexitol-based polymers are emphasized, whereas coating applications are not specifically mentioned or elaborated upon.

Synthesis of polyesters containing isosorbide is often carried out in the melt or in solution, exclusively using activated diacid components like acid chlorides or anhydrides. A disadvantage of using acid chlorides might be that the HCl, formed during the reaction at high temperatures, can attack the cyclic ethers present in isosorbide, leading to a triol moiety. This triol could then afford non-controlled branched or even cross-linked systems.[25] These side reactions, however, were not observed at temperatures up to 230 ºC.[30,37,38]

This chapter describes the chemistry and characteristics of isosorbide-based co- and terpolyesters. Monomers such as isosorbide, 1,3-propanediol, 2,3-butanediol, glycerol and succinic acid were used in the polymer synthesis. We present a systematic investigation of a synthetic protocol for the melt polymerization of non-activated monomers, the evaluation of the polymer properties and application tests. Coatings were applied from solution as well as from the corresponding powder paints.

2.2 Experimental section

Materials. Isosorbide (IS) was obtained as a gift from Agrotechnology and Food Innovations (98+ %) as well as from Roquette (98.5+ %, trade name: Polysorb® P). Succinic acid (SA), 2,3-butanediol (2,3-BD), neopentyl glycol (NPG), trimethylolpropane (TMP), titanium(IV) n-butoxide, 4-dimethylaminopyridine (DMAP) and acetic anhydride were purchased from Acros Organics. Normalized solutions of KOH in methanol, 1,3-propanediol (1,3-PD), glycerol (99.5+ %, GLY), glycerol-$^{13}C_3$ (99 atom% ^{13}C) and dibutyltin dilaurate (DBTDL) were obtained from Aldrich. All solvents were purchased from Biosolve. Chloroform-*d* was obtained from Cambridge Isotope Laboratories, DMSO-d_6 was bought from Campro Scientific. Irganox HP2921, a mixture of phenolic and phosphonic anti-oxidants[39], was a gift from Ciba Specialty Chemicals. An isophorone diisocyanate-based, ε-caprolactam blocked polyisocyanate (trade name: Vestagon B1530) was a gift from Degussa GmbH. Hexamethylene diisocyanate-based polyisocyanate (trade name: Desmodur N3600) and its corresponding ε-caprolactam blocked polyisocyanate (trade name: Desmodur BL3272) were gifts from Bayer AG. Flow agent Resiflow PV5 was purchased from Worlée Chemie, benzoin was obtained from DSM Special Products. All chemicals were used as received.

Polymerization of renewable monomers to form copolyesters. A typical polymerization was carried out according to the following procedure. Succinic acid (44.9 g, 0.38 mol) and isosorbide (63.4 g, 0.43 mol) were weighed into a 250 mL round bottom glass flange reactor. The reactor was fitted with a vigreux column and a Dean-Stark type condenser to collect the condensation product. During the first part of the synthesis, the setup was continuously flushed with inert gas to limit oxidation and facilitate transport of water vapor. While stirring, the mixture was heated to 180 ºC using a heating mantle. Titanium(IV) n-butoxide (0.02 mol% relative to succinic acid), dissolved in toluene, was added to the melt. Subsequently, the reaction temperature was increased stepwise to maintain distillation of the formed water. The maximum reaction temperature was 230 ºC. After 4 hours, vacuum processing was started at 230 ºC, with typical pressures ranging from 1 – 5 mbar. Vacuum was applied for 4 hours, after which the polymer was discharged from the reactor and left to cool and solidify.

Solvent casting and curing of hydroxy-functional polyesters. Hydroxy-functional polyesters were cured using conventional polyisocyanate curing agents: (1) an *ε*-caprolactam blocked trimer of isophorone diisocyanate (trade name: Vestagon B1530, NCO equivalent weight = 275 g/mol), (2) a trimer of hexamethylene diisocyanate (trade name: Desmodur N3600, NCO equivalent weight = 183 g/mol) and (3) an *ε*-caprolactam blocked trimer of hexamethylene diisocyanate (trade name: Desmodur BL3272, NCO equivalent weight = 410 g/mol).
Ad 1 & 3: A solution of 0.3 – 0.5 g of polyester, 1.05 molar equivalent of the cross-linker (calculated from the OH-value, determined by titration) and 0.5 wt% (relative to solid resin) of dibutyltin dilaurate in 1 mL N-methyl-2-pyrrolidone (NMP) was prepared. Subsequently, a wet film of approximately 250 µm thickness was applied onto an aluminum panel, using a doctor blade. The film was left to dry at room temperature followed by curing at 200 ºC during 30 minutes under nitrogen, resulting in films having thicknesses between 30 and 100 µm. Ad 2: A solution of 0.3 – 0.5 g of polyester in 0.7 mL of NMP was prepared, as well as a separate solution of Desmodur N3600 (1.05 molar equivalent, calculated from titration data) in 0.3 mL of NMP. The two solutions were mixed and applied directly to the aluminum substrate as a wet film with a thickness of 250 µm. After drying at room temperature, the film was cured at 180 ºC under N_2 during 20 minutes. Coatings were also applied through a powder coating process, which typically proceeds as follows: a polyester resin was co-extruded with the curing agents in a 1 to 1 ratio at approximately 100 ºC, using a twin-screw mini-extruder. In addition, 1.5 wt% flow agent (Resiflow PV5, Worlée) and 0.75 wt% degassing agent (benzoin) were added to the formulation. The obtained extrudate was ground to particles smaller than 90 µm and powder coated onto an aluminum gradient panel using corona spraying, followed by curing in a gradient oven at temperatures ranging from 100 to 250 ºC.

Measurements. SEC analysis in tetrahydrofuran (THF) was carried out using a Waters GPC equipped with a Waters 510 pump and a Waters 410 refractive index detector (at 40 °C). Injections were done by a Waters WISP 712 auto injector, with an injection volume of 50 µL. Two linear columns, Mixed C, Polymer Laboratories, 30 cm, 40 °C, were used. The eluent flow rate was 1.0 mL/min. Calibration curves were obtained using polystyrene standards (Polymer Laboratories, M = 580 g/mol to M = 7.1×10^6 g/mol). Data acquisition and processing were performed using WATERS Millennium32 (v3.2 or 4.0) software. SEC analysis in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was carried out using a set-up equipped with a Shimadzu LC-10AD pump and a WATERS 2414 differential refractive index detector (at 35 ºC). Injections were done by a MIDAS auto-injector, the injection volume being 50 µL. PSS (2× PFG-lin-XL, 7 µm, 8×300 mm, 40 °C) columns were used. The eluent flow rate was 1.0 mL/min. Calibration curves were obtained using PMMA standards. In this case, data acquisition and processing were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer, chloroform-*d* being used as the solvent (unless stated otherwise). The thermal stabilities of polymer samples were determined using a Perkin Elmer Pyris 6 TGA apparatus. Approximately 10 mg of polymer was heated from 40 ºC to 700 ºC at a heating rate of 10 ºC/min under a N_2 flow of 20 mL/min. Results were analyzed using Pyris 4.01 software. Glass transition temperatures were determined by DSC measurements, carried out with a DSC Q100 from TA Instruments. Curing of powder coating formulations was also followed by DSC, using a Perkin Elmer DSC Pyris 1 device, calibrated using indium and tin. The measurements were carried out at a heating rate of 10 ºC/min. Data acquisition was carried out using Pyris 7 software. MALDI-ToF-MS measurements were performed on a Voyager DE-STR from Applied Biosystems. Calibrations were carried out with poly(ethylene oxide) standards for the lower mass range and polystyrene standards for the higher mass range. The mass accuracy was better than 0.2 Dalton and the mass resolution was approximately m/z 12,000. DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as matrix. Potassium trifluoroacetate (Aldrich, >99 %) was used as cationization agent. Solutions of the matrix (40 mg/mL), potassium trifluoroacetate (5 mg/mL) and the polyester sample (1 mg/mL) in THF were premixed in a ratio of 5:1:5. The mixture was subsequently hand-spotted on the target and left to dry. Spectra were recorded in reflector mode at positive polarity. Potentiometric titrations were carried out using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The carboxylic acid functionality was measured by titration with a normalized 0.1 N methanolic KOH solution. The acid value (*AV*) is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize 1 g of polymer resin (Equation 2-1).

$$AV = \frac{V_s \times N \times 56.1}{W_s} \qquad \text{(Equation 2-1)}$$

With AV = acid value (mg KOH/g), V_s = volume of methanolic KOH solution needed to titrate the sample (mL), N = normality of KOH solution (mol/L), 56.1 = molar mass of KOH (g/mol) and W_s = sample weight (g).

Polyester hydroxyl end-groups were acetylated in solution (NMP) with acetic anhydride at room temperature (4-dimethylaminopyridine was used as catalyst), followed by titration of the resulting acetic acid with a normalized 0.5 N methanolic KOH solution. Blank measurements were necessary to obtain the hydroxyl values. The hydroxyl value (*OHV*) is the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of material (Equation 2-2). All titrations were carried out in duplo.

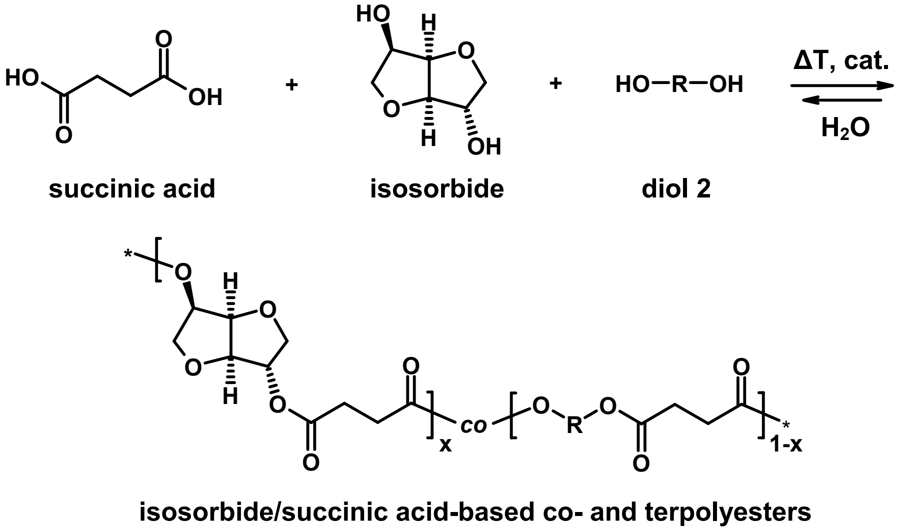
$$OHV = AV + \frac{(V_b - V_s) \times N \times 56.1}{W_s} \qquad \text{(Equation 2-2)}$$

With OHV = hydroxyl value (mg KOH/g), AV = acid value (mg KOH/g), V_b = volume of methanolic KOH solution needed to titrate the blank (mL), V_s = volume of methanolic KOH solution needed to titrate the sample (mL), N = normality of KOH solution (mol/L), 56.1 = molar mass of KOH (g/mol) and W_s = sample weight (g).

Curing reactions were followed using Attenuated Total Reflection Fourier-Transform Infrared spectroscopy (ATR-FTIR), on a Bio-Rad Excalibur FTS3000MX spectrophotometer. A golden gate set-up was used, equipped with a diamond ATR crystal. The resolution was 4 cm^{-1}. Dynamic Mechanical Analysis (DMA) was carried out using a TA Instruments AR1000-N Rheolyst rheometer, having a parallel plate geometry. Samples were prepared by compression molding (at 400 bar) of powder paint formulations at room temperature.[40,41] Solid, opaque disks of approximately 500 μm thick were obtained. Temperature as well as time sweeps were performed, using the following parameter settings: temperature range = 70 - 250 ºC, temperature ramp rate = 2 ºC/min., strain = 1 %, frequency = 1 Hz (= 6.283 rad/s). Data acquisition was done with Rheology Advantage Instrument Control software, data analysis with Rheology Advantage Data Analysis software. Cross-linking and coating performance at room temperature were evaluated using several characterization methods: acetone rub test (solvent resistance test: the sample is rubbed back and forth with a cloth drenched in acetone. If no damage is visible after more than 150 rubs (i.e. 75 ‘double rubs’), the coating has good acetone resistance), reverse impact test (a rapid deformation test, performed by dropping a certain weight (in kg) on the back of a coated panel from a certain height (in cm), described in ASTM D 2794) and pendulum damping test (ASTM D 4366, to determine König hardness). The thicknesses of the obtained coatings were measured using a magnetic induction coating thickness measuring device (Twin-Check by List-Magnetik GmbH). Accelerated weathering was performed using an Atlas Suntest XXL+ xenon arc apparatus. The experiments were carried out at an irradiance of 60 W/m^2 at 45 ºC and a relative humidity of 25 %.

2.3 Results and discussion

In this study, several series of isosorbide-based polyesters were synthesized. All polyesters were obtained from dicarboxylic acid and diol monomers, polymerized in bulk (Scheme 2-1). The functional polymer end-groups were used in a subsequent curing process for coating formation. The syntheses of the polyesters were performed following three approaches: (1) Synthesis of isosorbide/succinic acid copolymers using isosorbide (IS) as the only diol component (§2.3.1); (2) Systematic partial replacement in these copolymers of isosorbide by, for example, neopentyl glycol (NPG), 2,3-butanediol (2,3-BD) or 1,3-propanediol (1,3-PD), leading to terpolyesters (§2.3.2); (3) Synthesis of branched IS-based polyesters, having enhanced functionalities (§2.3.3). In the first approach, the goal was the optimization of the reaction conditions, while approach 2 was aimed at obtaining insight into detailed structure-property relationships. The third series of syntheses was aimed at improving the performance of the final coating systems.



Scheme 2-1. Renewable co- and terpolyesters based on isosorbide and succinic acid and, optionally, other diols (with $0 < x \leq 1$).

2.3.1 Poly(isosorbide succinate)

Initial polycondensation experiments

A series of polymerization experiments was conducted with succinic acid and isosorbide in bulk. It was noted that the reaction proceeds without the addition of a catalyst up to a conversion of approximately 60 % at 180 °C. A strong discoloration of the polyester was observed during the course of the reaction. The discoloration was prevented to a large extent by polymerizing under inert gas and optimization of the reaction time, leading to yellow polymers. Furthermore, significant improvements with respect to polyester color were obtained using a special polymer grade of isosorbide (Polysorb® P, Roquette Frères, 98.5+ %), which finally yielded a colorless polymer.

A reaction of isosorbide with succinic acid, carried out at 180 ºC, was monitored in detail. In this study we aimed at obtaining a hydroxyl-functional polymer with a molecular weight of 2500 g/mol. A convenient way to follow the progress of the reaction is end-group titration. As can be seen in Figure 2-1, the titrated acid and hydroxyl values (AV and OHV, respectively: measures for the amount of functional groups per gram of polymer sample) decrease during the course of the reaction due to the esterification reaction, as expected. However, the theoretical OHV of 38 mg KOH/g (AV = 0 mg KOH/g), corresponding to the target molecular weight, was not reached, not even at an extended reaction time (Table 2-1, entry **A**). This suggests that the reaction stops at a certain conversion under these reaction conditions. This was confirmed by SEC results obtained from samples withdrawn during the reaction. The number average molecular weight ($\overline{M}_n$) of the final sample (Table 2-1, entry **A**) was estimated to be between 2000 and 2500 g/mol (polystyrene calibration). However, the SEC traces contain several separate low molecular weight peaks that are probably caused by oligomers and residual monomer. The titration data also suggest that the molecular weight obtained from SEC is overestimated. A $\overline{M}_n$-value of 800 - 900 g/mol was calculated from the total amount of titrated end-groups per gram of sample (i.e. $AV + OHV$), see Table 2-1. This discrepancy is probably caused by differences in hydrodynamic volume between polyesters and the polystyrene chains used for the calibration of the SEC apparatus.[42-44] Considering the low molecular weight of the material it is surprising that still a T_g of 43 °C is obtained (Figure 2-1).

A similar molecular weight limit was observed in all reactions performed under these conditions. One explanation for this phenomenon could be found in the structure of isosorbide, which is a chiral bicyclic ether having two secondary hydroxyl groups. However, these two functionalities have different reactivities, since they differ in orientation. The hydroxyl group connected to C5 is in the *endo* position and is involved in intramolecular hydrogen bonding[45,46], while the other is in the *exo* position. The latter is more reactive in polycondensation reactions in the melt, since it does not participate in internal hydrogen bonding and is less sterically hindered.[47,48] The *endo*-oriented hydroxyl group probably causes the conversion limitation under these reaction conditions. Similar observations were made for polyethers based on isosorbide.[21]

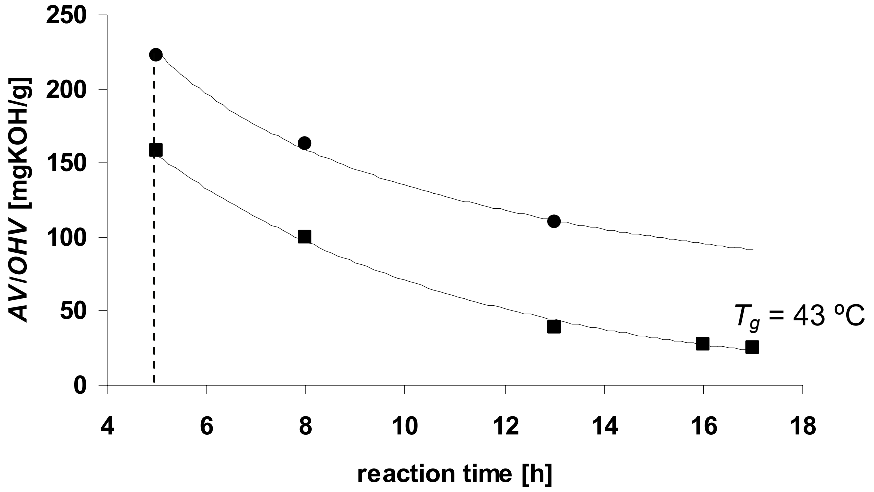


Figure 2-1. Development of acid value (*AV*, ■) and hydroxyl value (*OHV*, ●) as a function of reaction time of the bulk polymerization of isosorbide with succinic acid. The vertical dashed line indicates the start of the evacuation of the vessel (180 °C, 30 mbar) at t = 5 hours. Initial *AV*: 402 mg KOH/g, initial *OHV*: 440 mg KOH/g.

Optimization of the reaction conditions

In order to increase the conversion and, as a result, the molecular weight, the synthetic procedure was modified by raising the reaction temperature (to 230 °C) and lowering the pressure (to 1-5 mbar). In addition, titanium(IV) n-butoxide was used as an esterification and transesterification catalyst. The resulting polyesters have slightly higher molecular weights, as determined from SEC data. Titration data confirm this increase: polyesters **1a, 1b** and **1c** (Table 2-1) have significantly lower acid and hydroxyl values than entry **A**. Still, we cannot exclude that the formation of cyclic structures contributes to this reduction of available functional groups (Figure 2-2). Further information about the end-group structure was obtained from MALDI-ToF-MS analysis. It has to be noted that this technique does not afford quantitative data. Moreover, one has to be aware that ionization efficiencies can be significantly different for acid and hydroxyl end-groups.[44,49] Nevertheless, MALDI gives information concerning the types of end-groups present in a polymer sample and the monomer residues present in the individual polyester chains. MALDI-ToF-MS spectra for succinic acid/isosorbide copolyesters show individual molecular peaks between 800 and 4000 g/mol, separated by the mass of one succinic acid/isosorbide repeating unit (228 Da) (Figure 2-2). The peaks with the highest intensities are attributed to polymer chains having hydroxyl end-groups and only low intensity peaks attributed to cyclic structures or carboxylic acid end-groups are present.

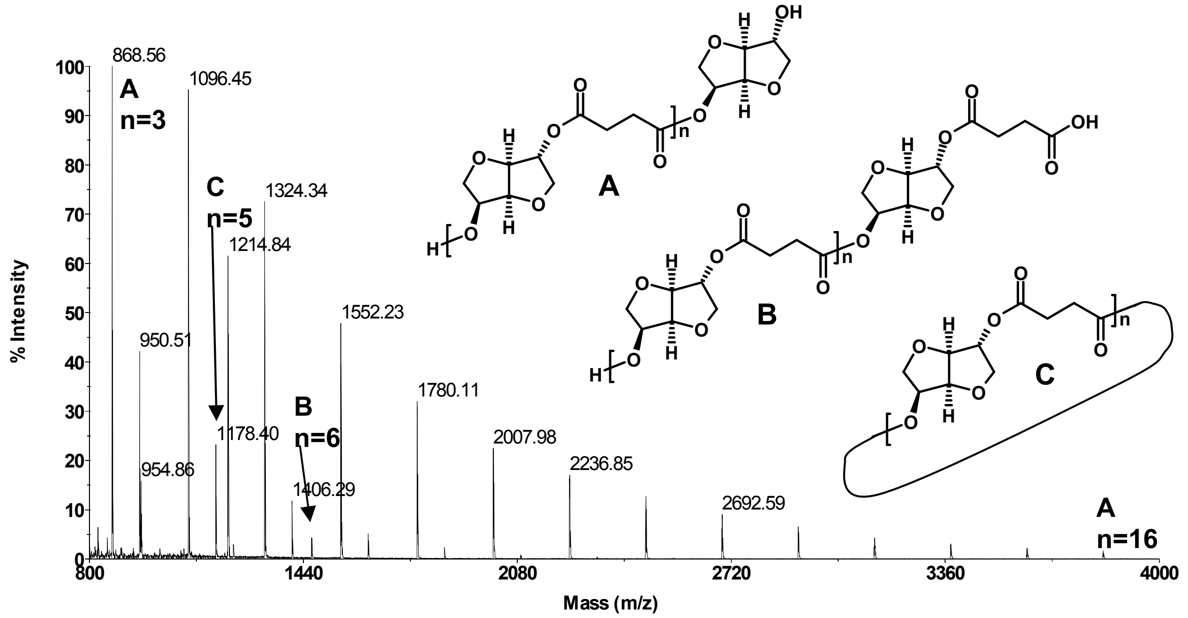


Figure 2-2. MALDI-ToF-MS spectrum of polyester **1b**, showing peaks attributed to (**A**) linear chains with two hydroxyl end-groups, (**B**) linear chains with one hydroxyl and one carboxylic acid end-group as well as (**C**) cyclic chains.

As expected in this low molecular weights regime[50], the T_g of the polymer increases with molar mass (Table 2-1), which is advantageous for the envisioned application of these copolyesters. No melting peaks were observed in the DSC thermograms, indicating that this copolyester is an amorphous material.

Table 2-1. Linear copolyesters from succinic acid (SA) and isosorbide (IS).

entry	feed composition	composition (NMR) [1]	T_g [°C]	$\overline{M_n}$ [2] [g/mol]	*PDI*	*AV* [3] [mg KOH/g]	*OHV* [3] [mg KOH/g]
A	SA/IS [1:1.09]	SA/IS [1:1.09]	43.0	n/a	n/a	25	110
1a	SA/IS [1:1.10]	SA/IS [4] [1:1.06]	67.7	3100	1.6	8.8	40.0
1b	SA/IS [1:1.14]	SA/IS [1:1.11]	56.5	2400	1.8	1.5	65.0
1c	SA/IS [1:1.12]	SA/IS [1:1.11]	52.8	2200	1.7	14.8	71.9

[1] Composition data obtained from ^{1}H NMR spectra.
[2] Determined by SEC in THF, using PS standards.
[3] *AV* = acid value, *OHV* = hydroxyl value.
[4] Data obtained after dissolution/precipitation from $CHCl_3$/MeOH.

Assuming that all the polyester end-groups are IS moieties, it is possible to estimate the molecular weight of poly(isosorbide succinate) from the ^{1}H NMR spectra. In the ^{1}H NMR spectrum of copolyester **1b**, the signals corresponding to IS and to IS end-groups can be clearly discerned (Figure 2-3). The ratio SA:IS = 1:1.11 was determined by integration of IS signals **c** and **k** (or: **d**, **l** and **n**) relative to SA signals **g,h**. From this ratio, the $\overline{M}_n$ was estimated to be 2200 g/mol (i.e. an average of 9.1 SA-IS repeating units and one IS moiety as end-group). From titration as well as MALDI-ToF-MS data, it is clear that there are also small amounts of acid-functional chains (approximately 2-3 % of all end-groups are carboxylic acids) and cyclic chains. These are not taken into account in this calculation, which means that the actual $\overline{M}_n$ is probably somewhat lower than determined from NMR. From the total amount of titrated end-groups per gram of sample (i.e. $AV + OHV$), a $\overline{M}_n$-value of 1700 g/mol is obtained. In this case, only the cyclic oligo- and polyester chains are not considered.

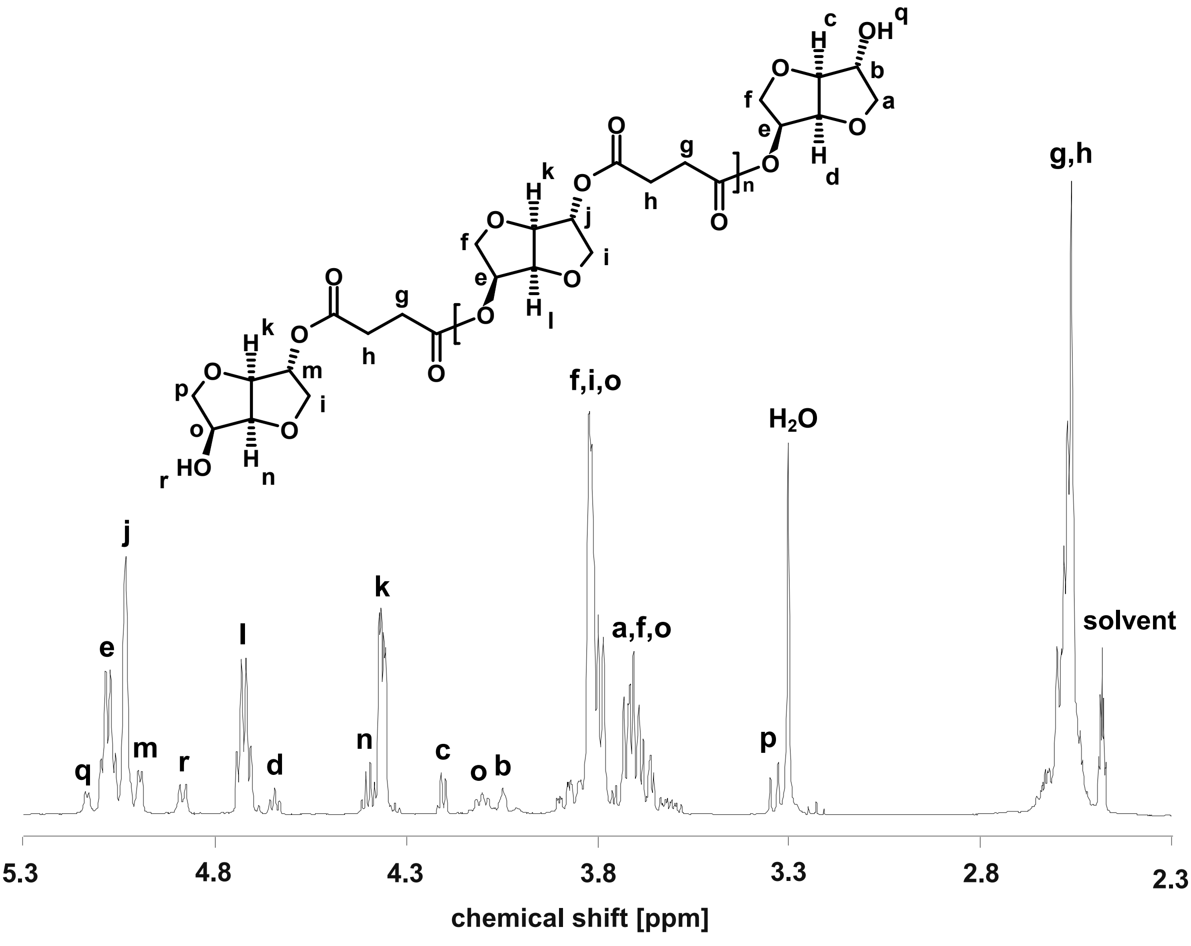


Figure 2-3. ^{1}H NMR spectrum of copolyester **1b**, recorded in DMSO-d_6.

The ratio *endo*:*exo* hydroxyl end-groups was determined from Figure 2-3. In DMSO-d_6, these two different OH-groups give doublet signals at 4.90 ppm (**r**, *endo*) and at 5.15 ppm (**q**, *exo*). Their ratio is approximately 6:4. This was confirmed by comparing signals **n**:**c** as well as **e**:**j**+**m**. From this ratio, we conclude that the majority of the hydroxyl end-groups have the *endo* orientation. This observation confirms the difference in reactivity between the two IS hydroxyl functionalities under these reaction conditions: the *endo*-oriented hydroxyl group is significantly less reactive than its *exo*-oriented counterpart.

The situation is different when acid-functionalized polymers are targeted. Even after using an excess of succinic acid, a combination of all possible end-groups can be identified in the MALDI spectrum. Although the majority of the high intensity peaks can be assigned to carboxylic acid-functionalized chains, peaks of moderate to high intensity corresponding to hydroxyl end-groups are present in the polymer samples as well (Figure 2-4).

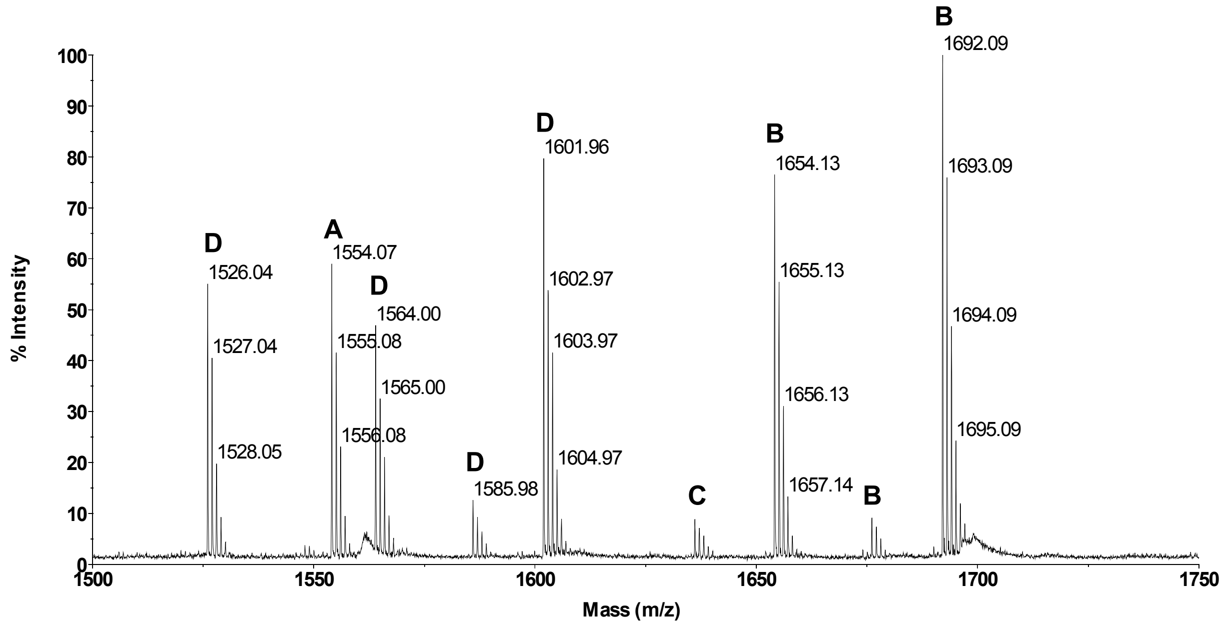


Figure 2-4. Section of the MALDI-ToF-MS spectrum of poly(isosorbide succinate), obtained after polymerization with an excess of succinic acid: (**A**) linear chains having two hydroxyl end-groups; (**B**) linear chains having one carboxylic acid and one hydroxyl end-group; (**C**) cyclic chains; (**D**) linear chains having two carboxylic acid end-groups. *N.B. Acid-functionalized species produce several peaks due to proton replacement by sodium and potassium, originating from the cationization agent.*

Since MALDI-ToF-MS is not a quantitative technique, titrations were performed to verify these results. Several co- and terpolyesters, prepared using excesses of succinic acid amounting to 0.1 – 0.2 molar equivalents relative to the diol(s), were titrated and all of them had high hydroxyl values of a comparable order of magnitude as their acid values. This observation can only be explained by a reduced reactivity of the secondary hydroxyl groups in the chain growth steps, in particular at chain ends when additional steric constraints are present (i.e. *endo*-orientation of the OH-group). Therefore, the synthesis of fully acid-functional linear isosorbide polymers cannot be achieved under these reaction conditions, when using non-activated diacid species.

In summary, we have shown that poly(isosorbide succinate)s can be synthesized having appropriate molecular weights, T_gs and functionalities. The grade of isosorbide used for the polymerizations as well as the processing atmosphere and temperature are important factors, determining conversion and the color of the resulting polyester. Furthermore, it appears that the *endo*-oriented OH-groups of isosorbide are responsible for the limitation of the conversion of the melt polycondensations and thus the molecular weights of the polyesters. The fact that it seems to be impossible to prepare carboxylic acid-functional polyester by using an excess of dicarboxylic acid monomers is another consequence of the low reactivity of these sterically hindered OH-groups.

2.3.2 Isosorbide-based terpolyesters

An important incentive for the use of isosorbide as a rigid monomer in polyesters is its T_g increasing effect (contrary to the T_g reducing effect of most linear aliphatic monomers), which opens possibilities to replace aromatic monomers. We therefore synthesized several series of linear and branched polyesters, containing isosorbide in combination with various comonomers. The T_gs of low molecular weight polymers, as those synthesized in this study, strongly depend on their $\overline{M}_n$ values and the presence of low molecular weight species. For example, copolymer **1a** based on succinic acid and isosorbide with a molecular weight of $\overline{M}_n$ = 3100 g/mol (relative to PS standards) has a T_g of 67.7 ºC. For virtually the same copolymer, but with an $\overline{M}_n$ of 2400 g/mol, the T_g is only 56.5 ºC (copolyester **1b**) and 52.8 ºC at an $\overline{M}_n$ of 2200 g/mol. The Fox-Flory equation (Equation 1-1, Chapter 1) describes this phenomenon, stating that polymer T_g increases with molecular weight, leveling off at a certain plateau value (T_g^{∞}).[50] Figure 2-5 shows the effect on T_g and $\overline{M}_n$ of systematic replacement of neopentyl glycol (NPG) by isosorbide in a succinic acid based polyester synthesized at constant reaction times and temperature (≠ constant conversion).

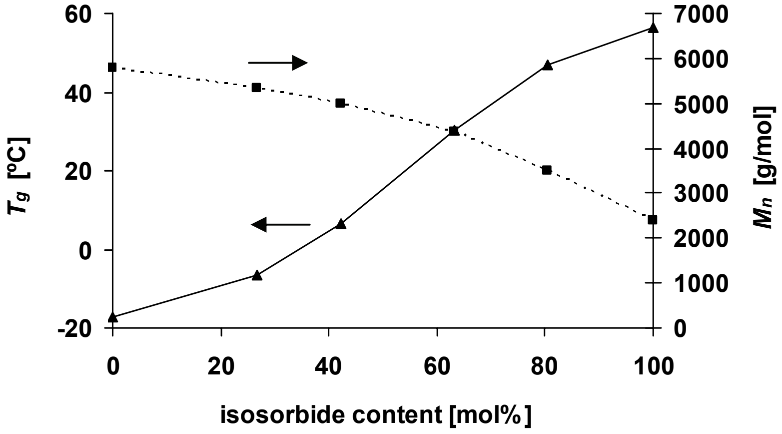


Figure 2-5. T_g (▲) and $\overline{M}_n$ (■) as a function of isosorbide content for a polyester based on succinic acid, neopentyl glycol and isosorbide (isosorbide mol% relative to total diol content). *The lines in this figure are meant only as guides to the eye.*

The plot shows a decrease of $\overline{M}_n$ with increasing isosorbide content. This is probably due to the decreased reactivity of the secondary hydroxyl groups of this monomer, compared to the primary OH-groups of NPG. Nevertheless, a significant increase in T_g with increasing isosorbide content can be observed. Taking into account the T_g decreasing effect of lowering the molecular weight, one can expect that the increase in T_g should be even more pronounced when comparing materials of equal molecular weights. Figure 2-5 does therefore not provide maximum values for the glass transition temperatures of these polyesters. The results of these experiments demonstrate that it is possible to synthesize aliphatic polyesters containing isosorbide with sufficiently high T_g values, which are potential candidates for application in powder coatings. Within the molecular weight range of 3000 – 6000 g/mol (Figure 2-5), a minimum isosorbide content of approximately 70-80 % of the total diol amount is required to obtain materials with T_g values above the minimally required level (> 45 ºC) for powder coating applications.

Based on the above conclusion, several terpolyesters were synthesized from succinic acid (SA), isosorbide (IS) and either 1,3-propanediol (1,3-PD), 2,3-butanediol (2,3-BD) or NPG (Table 2-2). 1,3-PD and 2,3-BD are biobased monomers, while NPG is petroleum-based. The isosorbide content was kept between 60 and 100 mol%, relative to the total amount of diols present.

Table 2-2. Linear terpolyesters based on succinic acid (SA), isosorbide (IS), 2,3-butanediol (2,3-BD), 1,3-propanediol (1,3-PD) and neopentyl glycol (NPG).

entry	feed composition	composition (NMR) [1]	T_g [°C]	$\overline{M}n$ [g/mol]	*PDI*	*AV* [mgKOH/g]	*OHV* [mgKOH/g]
2a	SA/IS/2,3-BD [1:0.92:0.23]	SA/IS/2,3-BD [1:0.87:0.19]	50.6	2700	1.9	0.2	48.6
2b	SA/IS/2,3-BD [1:0.69:0.46]	SA/IS/2,3-BD [1:0.65:0.36]	46.8	4600	1.6	2.0	32.0
3a	SA/IS/1,3-PD [1:0.85:0.20]	SA/IS/1,3-PD [1:0.83:0.25]	45.2	2700	2.0	4.7	43.9
3b	SA/IS/1,3-PD [1:0.69:0.46]	SA/IS/1,3-PD [1:0.63:0.45]	20.6	3500	1.5	1.5	37.7
4a	SA/IS/NPG [1:0.80:0.20]	SA/IS/NPG [1:0.76:0.20]	47.1	3500	1.5	13.6	33.5
4b	SA/IS/NPG [1:0.60:0.40]	SA/IS/NPG [1:0.62:0.40]	30.5	4300	1.5	7.5	34.0

[1] Composition data obtained from ^{1}H NMR spectra. For example: entry **3b** (see Figure 2-6): composition is determined by integration of peaks **h** (4H, SA), **c** + c' (1H, IS) and **i** (2H, 1,3-PD).

The polyester composition as determined by the corresponding ^{1}H NMR spectrum (see e.g. Figure 2-6) is in good agreement with the monomer feed ratio. Isosorbide end-groups can be readily distinguished (for example: resonances **a'**, **b'**, **c'**, **d'**) in these low molecular weight polyesters.

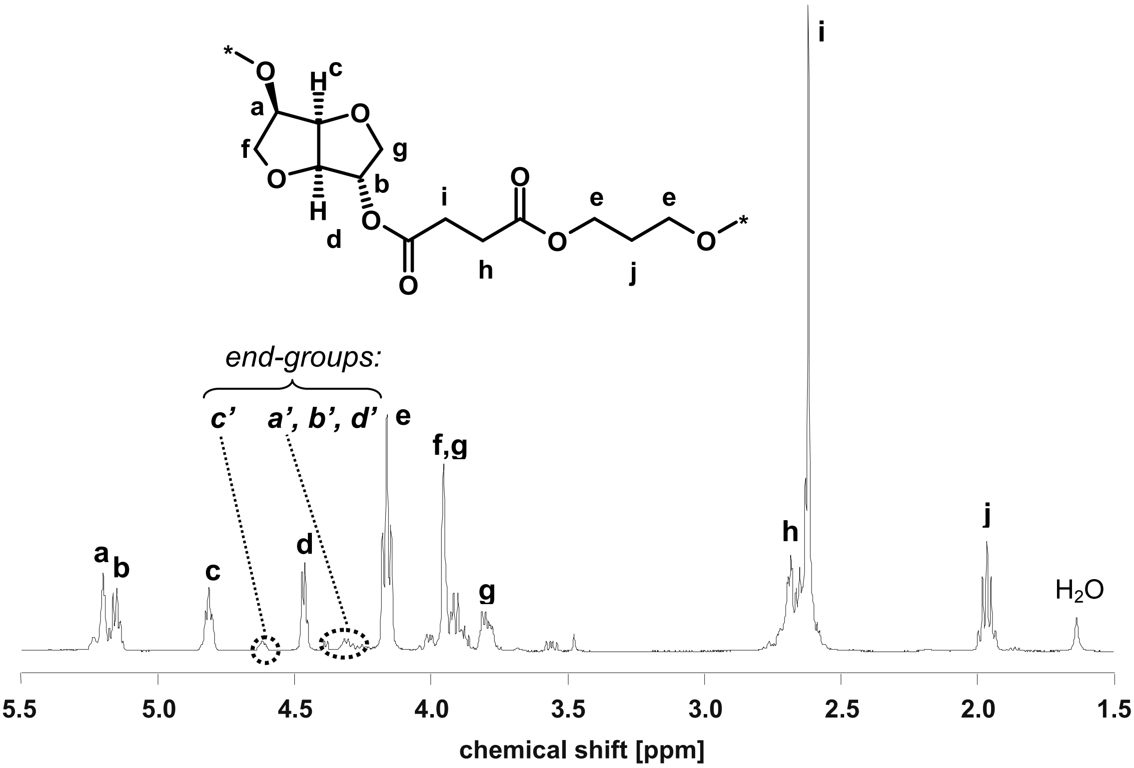


Figure 2-6. ^{1}H NMR spectrum of terpolyester **3b** in Table 2-2: poly(isosorbide-*co*-propylene succinate).

The differences in shifts between resonances **a** and **b** as well as between resonances **c** and **d** in Figure 2-6 are direct results of the *endo* and *exo* orientations of the two OH-groups of isosorbide. The broadening of the CH_2 signal of succinic acid at 2.6 – 2.8 ppm (peaks **h** and **i**) is caused by the presence of two different diol moieties (IS and 1,3-PD), as well as by the *endo* and *exo* character of the isosorbide OH-groups, leading to different chemical shifts.[48]

When comparing the feed compositions with the final polyester compositions in Table 2-2, it becomes clear that the diols with primary OH-groups (i.e. 1,3-PD and NPG) are built into the polymer more readily. This difference in reactivity between the secondary hydroxyl groups of isosorbide and the primary hydroxyl groups of 1,3-propanediol could potentially lead to blocky terpolyesters if randomization by transesterification does not occur to a sufficient extent. However, the catalyst used for these terpolyester syntheses, $Ti(OBu)_4$, is known to be an efficient transesterification catalyst.[51-53] Moreover, ^{13}C NMR spectra do not give any indication that blocky structures are present in the final products. This was determined by comparing the integrals of signals corresponding to the carbonyls of the different repeating units present in the terpolyesters, as demonstrated here for terpolyester **3b**.

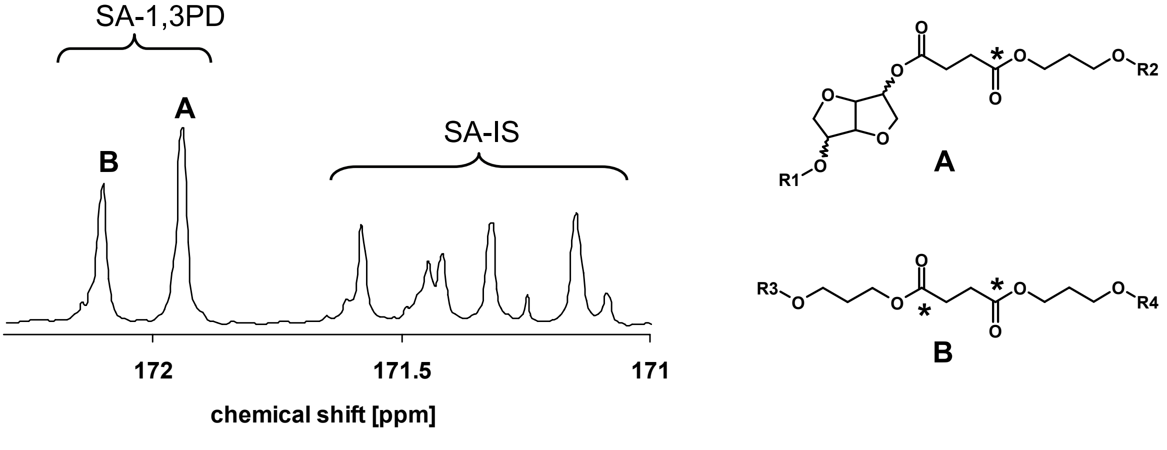


Figure 2-7. Carbonyl region of the ^{13}C NMR spectrum of terpolyester **3b** in Table 2-2: poly(isosorbide-*co*-propylene succinate).

In Figure 2-7, the carbonyl section of the ^{13}C NMR spectrum of polyester **3b** is shown, in which two clusters of resonances are present: signals assigned to succinate carbonyls attached to 1,3-propanediol moieties (SA-1,3-PD) and succinate carbonyls bonded to isosorbide units (SA-IS). The ratio SA-IS:SA-1,3-PD was 0.58:0.42, as estimated by integration of the two clusters of peaks. This matches the ratio isosorbide:1,3-PD present in the polymer, which is also 0.58:0.42. The two carbonyl resonances present in the SA-1,3-PD cluster (**A** and **B**) correspond to the carbonyls labeled by asterisks. The chemical shifts of species **A** and **B** differ significantly and, thus, appear as separate peaks in the ^{13}C NMR spectrum. For a random terpolyester, the ratio **A**:**B** is expected to be the same as the ratio isosorbide:1,3-PD, while this ratio should deviate from the terpolyester composition for blocky terpolymers. The ratio **A**:**B** was determined by integration of the two corresponding resonances: **A**:**B** = 0.57:0.43. This corresponds well to the ratio isosorbide:1,3-PD, so it appears that random terpolyesters were obtained using the described polymerization procedure under the influence of $Ti(OBu)_4$. Of course, we have to take into account the fact that integration of ^{13}C NMR resonances is not a very precise method, so these observations give an indication rather than hard evidence.

Figure 2-8 shows an example of a part of a MALDI-ToF-MS spectrum of terpolyester **2a** (SA/IS/2,3-BD = 1:0.87:0.19, composition determined from ^{1}H NMR analysis).

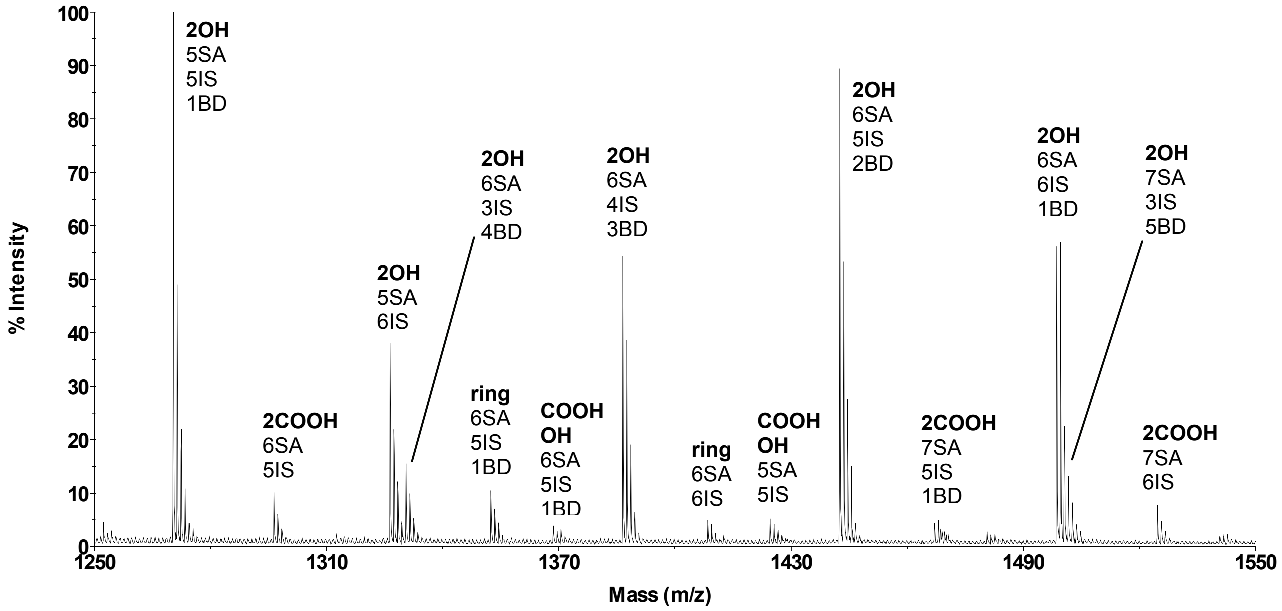


Figure 2-8. Section of the MALDI-ToF-MS spectrum of terpolyester **2a**.
Peak labeling (example): **2 OH** = number and type of end-groups
5 SA = number of SA moieties
5 IS = number of IS moieties
1 BD = number of 2,3-BD moieties

The main species observed in the spectrum are hydroxy-functional chains. However, chains having one hydroxyl and one carboxylic acid end-group are also visible, as well as chains with two carboxylic acid end-groups. As expected, cyclic oligo-esters are also observed. These rings do not participate in the network formation during cross-linking and can act as plasticizers for the cured coating, lowering its T_g. Carboxylic acid functionalities are undesirable as well, since they do not participate in the curing reaction, realizing that curing agents designed for hydroxy-functional resins will be applied in this specific case.

Terpolymer series **2, 3** and **4** (Table 2-2) have lower glass transition temperatures than the poly(isosorbide succinate)s, due to the increase in chain flexibility. Moreover, it can be seen that 1,3-PD and NPG (series **3** and **4**, respectively) affect T_g more than 2,3-BD (series **2**). This can be explained by the more flexible nature of 1,3-PD and NPG as compared to 2,3-BD. Hence, by selecting different diols and diol-ratios, the T_g values of the polyesters can be effectively tuned. Figure 2-9 shows the T_g development of these terpolyester series as a function of isosorbide content (relative to the total diol content). Again, $\overline{M}_n$ has an effect on polyester T_g. However, the number average molecular weights of the polyesters described in Figure 2-9 are within the same range in order to make a fair comparison.

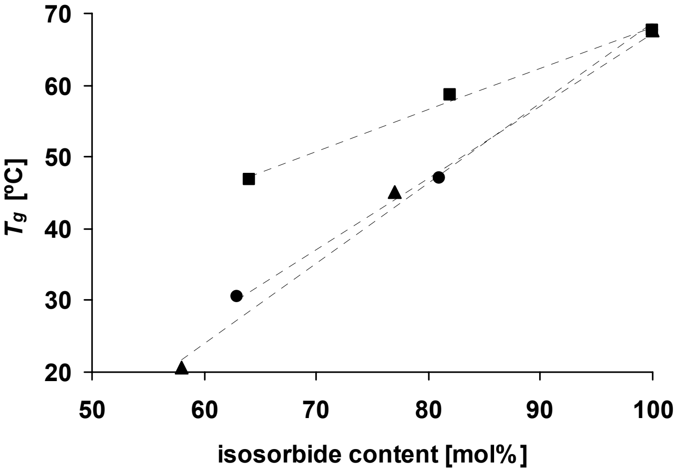


Figure 2-9. T_g as a function of isosorbide content for copolyester: SA/IS/diol 2, with diol 2: 1,3-propanediol (▲), neopentyl glycol (●) and 2,3-butanediol(■).

An important parameter for polyesters used in powder coatings is their thermal stability. Curing of powder coating formulations occurs at temperatures between 160 and 200 ºC. The thermal stability of the polyesters was investigated by thermogravimetric analysis (TGA). No significant weight loss was observed up to 250 ºC (Figure 2-10). Some weight loss occurs above 250 ºC, which is thought to be caused by evaporation of residual monomer and/or oligomeric species. Around 350 ºC, rapid degradation is observed.

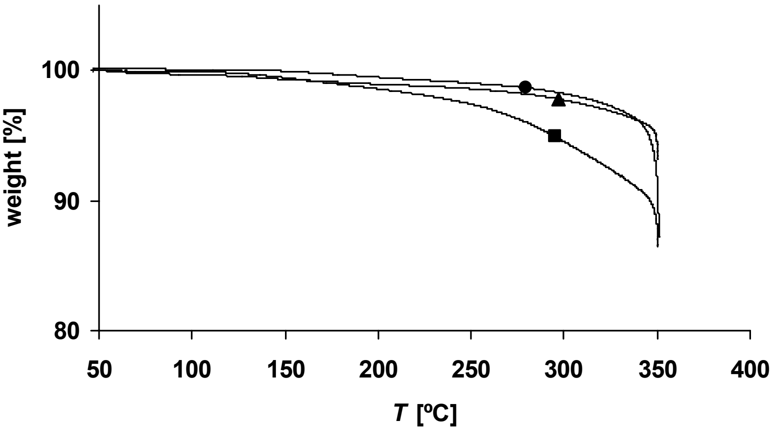


Figure 2-10. Results of thermogravimetric analysis (TGA) for poly(isosorbide succinate) (■), poly(isosorbide-*co*-propylene succinate) (▲) and poly(isosorbide-*co*-1,2-dimethylethylene succinate) (●).

In this paragraph, linear OH-functional terpolyesters were presented, based on succinic acid and isosorbide. Their T_gs can be tuned by varying the content of isosorbide relative to the other diol(s) present in the terpolyester. These thermally stable polymers appear to have suitable properties for application in coating systems, with respect to T_g and functionality.

2.3.3 Branched isosorbide-based polyesters with enhanced functionality

Polyester functionality ($\overline{F_n}$) is a crucial parameter in thermosetting polymer systems. Depending on the applied curing agent, the polyester should either be mainly carboxylic acid or hydroxy-functional ($\overline{F_n} \geq 2$). Besides the chain functionality, the concentration of functional end-groups (*OHV* or *AV*) has a strong influence on the cross-link density and, thus, on coating properties such as toughness, hardness and solvent resistance. The linear copolyesters reported in Table 2-2 mainly have hydroxyl end-groups due to the excess of diol monomers added during their syntheses. However, as was discussed already, not all chains have two hydroxyl end-groups. To increase the functionality of the hydroxy-functional polymers, branched polyesters were synthesized by addition of trimethylolpropane (TMP) or the renewable monomer glycerol (GLY) in the polymer synthesis. This led to polyesters with increased hydroxy-functionality, as can be seen in Table 2-3. The broadening of the molecular weight distribution indicates that branching has occurred. A disadvantage of using TMP or GLY is the pronounced lowering of the polyester T_g (compare polymers **5a** and **5b** with **1b** and **2a**, respectively). This effect is partly due to the increase of chain flexibility by incorporating these polyols. In addition, branching is known to lead to a drop in polymer T_g as well as a decrease of the melt viscosity.[54,55]

Table 2-3. Copolyesters with increased functionality, obtained by adding trimethylolpropane or glycerol during the polyester synthesis.

entry	feed composition [1]	composition (NMR)	T_g [ºC]	$\overline{M}_n$ [g/mol]	*PDI*	*AV* [mgKOH/g]	*OHV* [mgKOH/g]
5a	SA/IS/TMP [1:1.1:0.1]	SA/IS/TMP [1:1.03:0.09]	43.5	2100	2.3	1.3	91.7
5b	SA/IS/2,3-BD/TMP [1:0.86:0.24:0.1]	SA/IS/2,3-BD/TMP [1:0.83:0.18:0.1]	44.3	3100	3.8	0.5	74.1
5c	SA/IS/GLY [1:1.1:0.1]	SA/IS/GLY [1:1.06:0.1]	38.4	2300	3.5	8.4	114.7

[1] SA = succinic acid, IS = isosorbide, TMP = trimethylolpropane, 2,3-BD = 2,3-butanediol and GLY = glycerol.

Based on the molecular weight data, it was estimated that the branched polyester chains each contain approximately one TMP or GLY unit. The MALDI-ToF-MS spectrum of polyester **5c** (Figure 2-11) shows signals of branched chains containing one GLY moiety as well (peaks **E**), but at a rather low intensity. In addition, low intensity signals of polyester chains containing two GLY units (i.e. having four hydroxyl end-groups) and cyclic chains with GLY (peaks **F**) and without GLY (peaks **C**) units are observed. On the other hand, the main signals are attributed to linear chains (peaks **A**), having only two hydroxyl end-groups. The structures **E**, **F**, **C** and **A** are drawn in Scheme 2-2. Judging from the content of the branching monomer (approximately 10 mol% of GLY relative to isosorbide), it seems unlikely that these linear chains are the main product. The explanation of the lower intensities of the branched chains might be due to differences in ionization efficiency during the MALDI-ToF-MS analysis, demonstrating once more that MALDI should be considered as a qualitative technique.

The introduction of trifunctional monomers into polyesters based on isosorbide significantly enhances the functionalities of these polymers, as becomes clear from the hydroxyl values (*OHV*) listed in Table 2-3. A disadvantage of introducing branching by addition of glycerol or trimethylolpropane is that the T_g of the polyesters drops significantly.

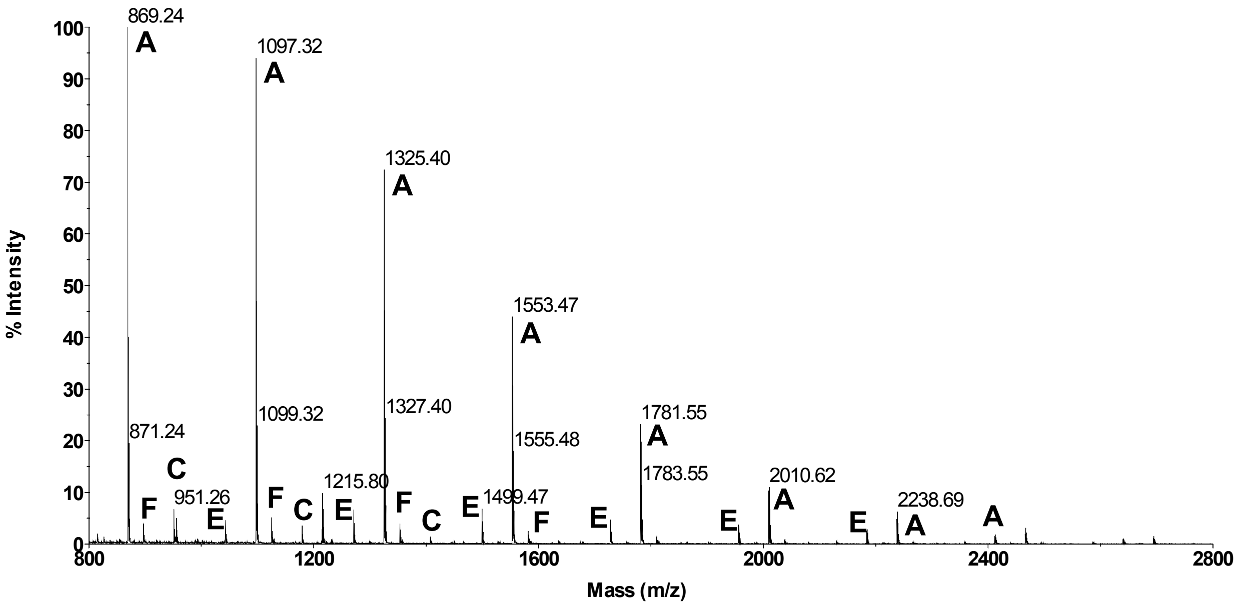
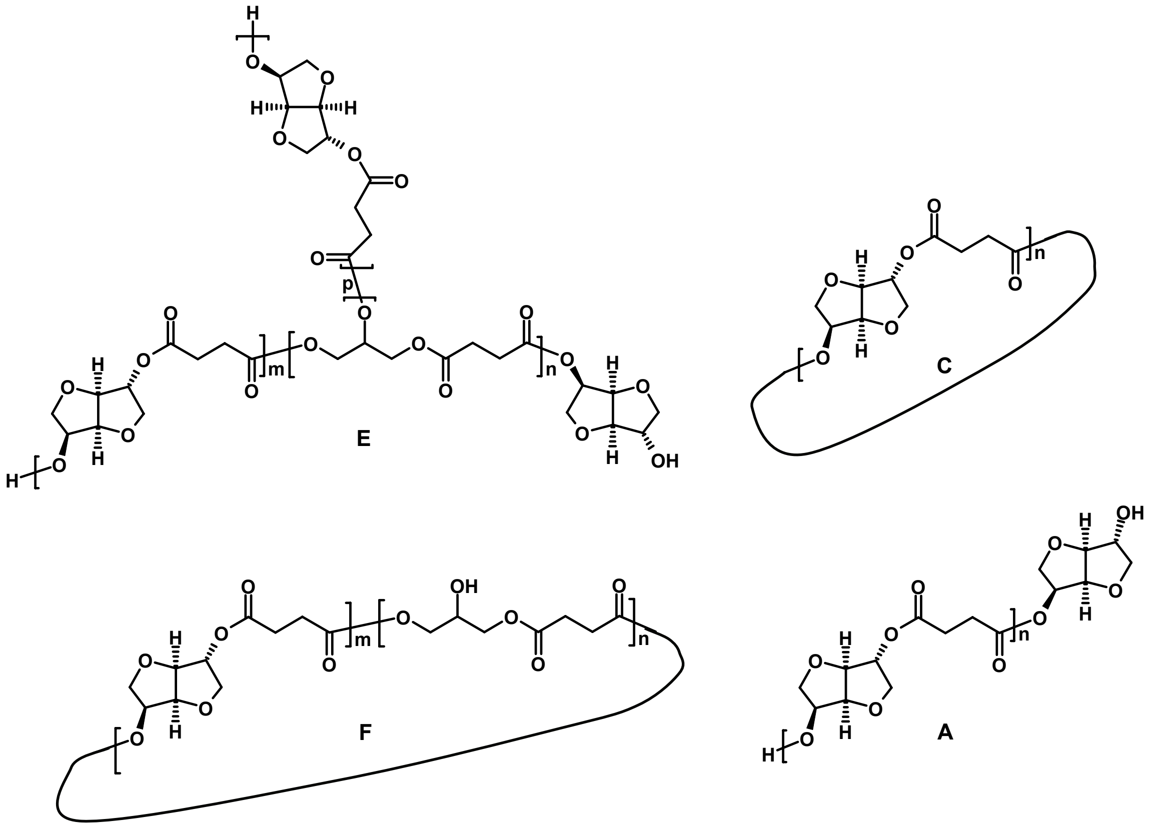


Figure 2-11. MALDI-ToF-MS spectrum of polyester **5c**, a poly(isosorbide-*co*-glyceride succinate). Scheme 2-2 depicts the structures referred to by the peak labels.

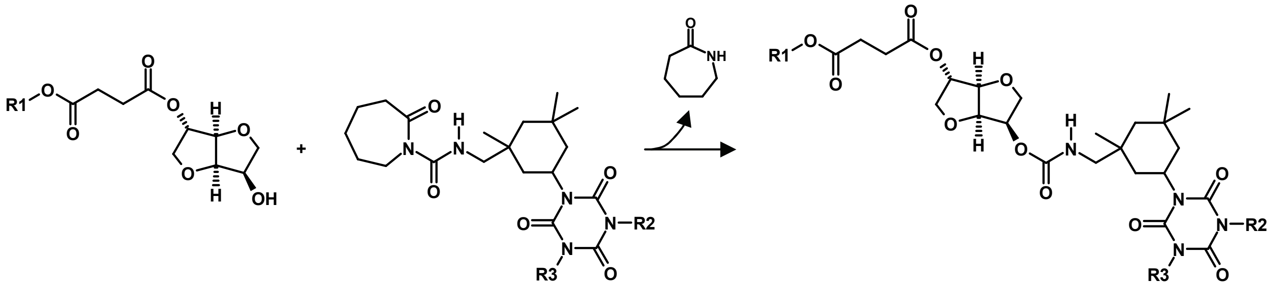


Scheme 2-2. Observed products of the polycondensation of succinic acid, isosorbide and glycerol.

2.3.4 Curing of IS-based polyesters cast from solution

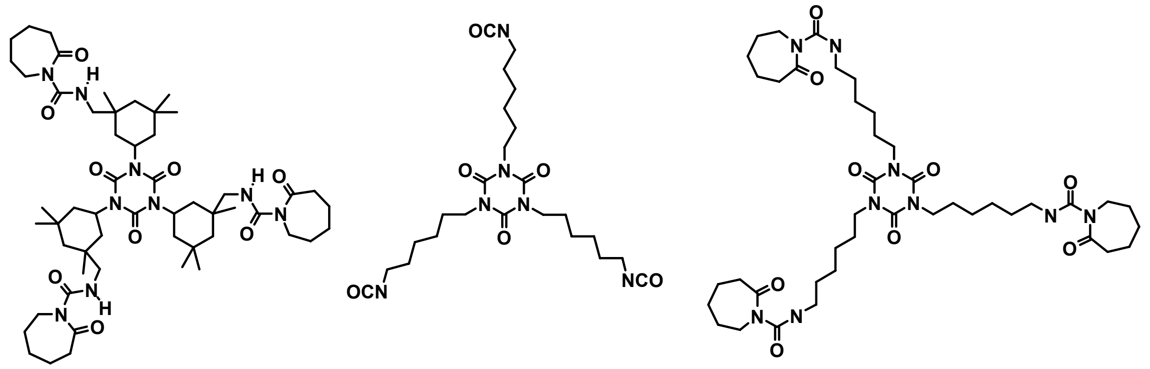
Curing chemistry and characterization

The linear and branched OH-functional copolyesters, described previously, were cured with conventional polyisocyanates to evaluate their applicability in thermosetting coating systems. The reaction between the polyester polyols and the polyisocyanates results in poly(ester urethane) networks, as schematically depicted in Scheme 2-3.



Scheme 2-3. Schematic representation of the curing reaction between an OH-functional poly(isosorbide succinate) and a IPDI-based blocked polyisocyanate, resulting in a poly(ester urethane) network. R1, R2 and R3 are polymer chain fragments.

The hydroxy-functional polyesters were cured using three different commercially available curing agents (Scheme 2-4): a polyisocyanate based on isophorone diisocyanate (IPDI), blocked with ε-caprolactam, a hexamethylene diisocyanate (HMDI)-based polyisocyanate and its ε-caprolactam blocked version. In Table 2-4, the most important characteristics of these curing agents are given.



I **II** **III**

Scheme 2-4. Conventional curing agents: (**I**) ε-caprolactam blocked isophorone diisocyanate-based polyisocyanate (trade name: Vestagon B1530, approximate structure), (**II**) hexamethylene diisocyanate-based polyisocyanate (trade name: Desmodur N3600, approximate structure), (**III**) ε-caprolactam blocked hexamethylene diisocyanate-based polyisocyanate (trade name: Desmodur BL3272, approximate structure).

Table 2-4. Curing agents used in coating formulations in combination with OH-functional bio-based polyester resins.

curing agent	based on	blocking agent	T_g [ºC]	T_m [ºC]	NCO-eq. weight [g/mol]	NCO content (total) [wt%]
I	IPDI	ε-caprolactam	41-53	62-82	~275	14.8-15.7
II	HMDI	-	n/a	n/a	~183	22.5-23.5
III	HMDI	ε-caprolactam	n/a	n/a	~412	~10.2

Data obtained from product data sheets, available online from the suppliers Degussa GmbH (**I**) and Bayer AG (**II** and **III**).

Curing agent **I** is a common component in powder coating formulations, while curing agent **II** is often used in two-component solvent-borne systems for exterior applications.[3] To be able to work on small scale, polymer films were initially applied from solution, rather than by powder application. Formulation of the various coating compositions was based on data from end-group titrations. A slight excess (0.05 molar equivalent) of curing agent with respect to titrated polyester end-groups was used. Curing reactions carried out with **I** and **III** (Scheme 2-4) were catalyzed with dibutyltin dilaurate (DBTDL, 0.5 wt% with respect to the amount of polyester). These curing reactions were performed at relatively high temperature during 30 minutes, to facilitate deblocking of the isocyanate moieties and removal of ε-caprolactam. Deblocking of these curing agents commences at a temperature of approximately 170 ºC, as shown in the DSC thermogram of curing agent **I** in Figure 2-12. The T_g, the melting range and the deblocking exotherm are clearly discernable from this plot.

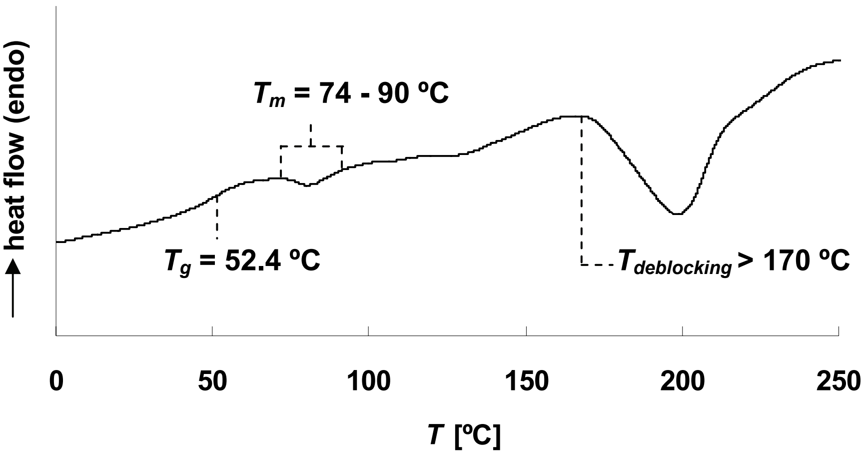


Figure 2-12. DSC thermogram of curing agent **I**, a polyisocyanate based on isophorone diisocyanate (trade name: Vestagon B1530, producer: Degussa GmbH).

The curing of the polyester resins with the different cross-linkers was monitored by ATR-FTIR spectroscopy. For OH-functional polyesters cured with **II**, disappearance in time of the isocyanate absorption peak at 2271 cm^{-1} could be observed (Figure 2-13). After 4.5 minutes of curing at 180 ºC, most of the –NCO moieties had reacted, as is evident from the disappearance of the isocyanate signal in the IR spectrum. It should be mentioned that at *t* = 0, the sample was already heated up to reaction temperature, which took approximately 30 seconds. This means that reaction had already started shortly before the first measurement was carried out. All obtained films were glossy and transparent, ranging from almost colorless to slightly yellow. The coating color strongly depends on the purity of the isosorbide grade used for the polyester synthesis as well as the type of curing agent and the curing conditions.

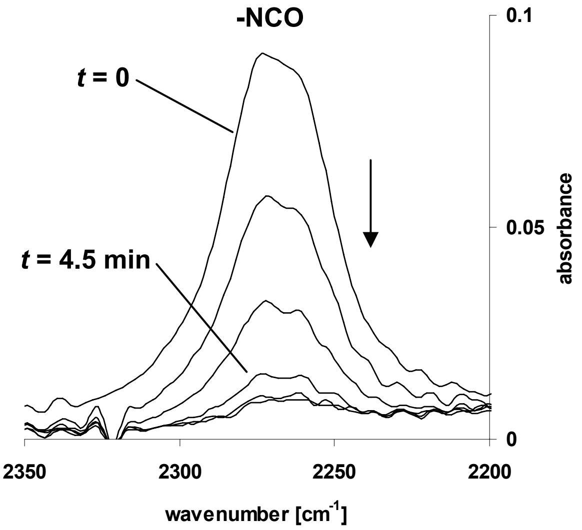


Figure 2-13. ATR-FTIR absorption peak for isocyanate (2271 cm^{-1}) functionalities during the curing reaction between OH-functional polyester **5a** and curing agent **II** (Scheme 2-4). Spectra measured at *t* = 0, 1, 2, 4.5, 7.5 and 10 minutes at 180 ºC.

Curing was also followed by taking samples for SEC analysis. The results are in line with the IR data, since they show rapid gelation of the coating formulations. The weight average molecular masses of the coating formulations increase exponentially towards infinity, leading to insolubility of the networks in THF. For OH-functional branched polyesters, cured with the free isocyanate groups of **II**, this occurs within 5 to 6 minutes. When curing the same polymers with the corresponding ε-caprolactam blocked curing agent **III** in the presence of 0.5 wt% of dibutyltin dilaurate (DBTDL), gelation occurs within 4 minutes. The catalyst DBTDL seems to play an important role in accelerating the reaction of the polymer end-groups with curing agent **III**, since gelation occurs within a shorter time than for curing with curing agent **II** that has free isocyanate groups.

Formulations and coating properties

To determine the effect of enhanced polyester functionality on coating properties such as chemical resistance and mechanical performance (i.e. impact resistance and hardness), both linear and branched OH-functional polyesters were cured with the same cross-linkers. Characteristics of the resulting coatings based on OH-functional polyesters are given in Table 2-5.

Table 2-5. Coatings based on hydroxy-functional polyesters (applied from solution).

film	polyester	curing agent [1]	T_{cure} [°C]	t_{cure} [min]	acetone resistance [2]	impact test [100 kg×cm] [2]	König hardness [s]	av. film thickness [µm]
				linear OH-functional polyesters				
F1	1b	II	180	20	+	+	204	43
F2	2a	I	200	30	-	-	222	40
F3	2a	II	180	20	-	+/-	n.d.	38
F4	2a	III	200	30	-	-	216	69
F5	3a	II	180	20	-	-	211	27
F6	3b	II	180	20	-	+	61	34
				branched OH-functional polyesters				
F7	5a	I	200	30	+	+/-	211	103
F8	5a	II	180	15	+	+	n.d.	44
F9	5a	III	200	30	+	+	200	72
F10	5b	II	180	20	+	+	205	41
F11	5c	II	180	15	+	+	n.d.	42

[1] See Scheme 2-4.
[2] + = good, +/- = moderate, - = poor

Film **F1** shows the best characteristics of all the coatings based on the linear hydroxy-functional copolyesters. With respect to chemical and mechanical properties, it was the only coating that passed all the different tests. This is thought to be the result of the relatively low molecular weight of polyester **1b** and, as a result, its high hydroxyl number (*OHV* = 65.0 mg KOH/g) compared to polyester series **2** and **3**. The degree of cross-linking and, hence, the amount of urethane linkages increase with decreasing molecular weight, which improves the performance. Apart from entry **F1**, all films from linear polyesters have poor to moderate acetone resistance. The main reason for this is probably poor network formation due to insufficient polymer functionality. **F1**, **F3** and **F6** show intermediate to good impact resistance, which is mainly due to the flexible nature of cross-linker **II**. Surprisingly, curing with the *ε*-caprolactam blocked version (**III**) of this HMDI-trimer leads to poor results.

Optimization of curing conditions and / or catalysis is necessary to further investigate this observation. Values for the König hardness of these coatings are rather high (König hardness of glass, measured on the same pendulum tester is approximately 235 s). **F6** is much softer at room temperature, which can be explained by the low T_g of polyester **3b** (T_g = 20.6 ºC). The film thicknesses of the dry coatings vary considerably. This is a result of the method of application and the solvent used.

The results in Table 2-5 clearly show that increasing the polyester functionality by adding trifunctional monomers such as TMP (**F7-F10**) or the renewable glycerol (**F11**) leads to improved coating properties. Acetone resistance is significantly improved when using branched polyesters, due to increased cross-link density. Coatings based on polymer **5a** all pass the reverse impact test (i.e. impact applied to the back of the coated panel), which means that resistance against rapid deformation is also increased, compared to films based on linear polyesters. Impact resistance, however, greatly depends on film thickness. Thick coatings are damaged easier upon impact, which is probably the main reason why coating **F7** shows some slight cracking. These results can be optimized by making sure that film thicknesses are homogeneous. As expected, the T_g of the cured films is significantly higher than that of the corresponding polyesters. For example, the T_g of **F8** is 76.1 ºC, compared to 43.5 ºC for its corresponding polyester **5a**.

The observations described in this section demonstrate that it is possible to synthesize and apply thermosetting coatings based on renewable aliphatic polyesters with satisfactory properties. The films combine good solvent resistance with a good ability to withstand rapid deformation. In addition, the pendulum damping test (i.e. König hardness test) shows that the coatings are also resistant against slow deformation / indentation.

2.3.5 Application and curing of IS-based polyesters as powder paints

Based on the results obtained when applying and curing coatings from solution, a limited number of resins were used in powder coating formulations. The resins were synthesized on a 300-400 g scale, to facilitate application experiments on a larger scale. In Table 2-6, key data for these polyesters are given.

Table 2-6. IS-based terpolyesters (linear and branched), synthesized on 300-400 g scale.

entry	feed composition [1]	composition (NMR)	T_g [ºC]	$\overline{M}_n$ [g/mol]	*PDI*	*AV* [mg KOH/g]	*OHV* [mg KOH/g]
6	SA/IS/2,3-BD [1:0.92:0.23]	SA/IS/2,3-BD [1:0.92:0.22]	56.3	4000	1.6	7.6	51.4
7	SA/IS/GLY [1:1.08:0.08]	SA/IS/GLY [1:1.05:0.1]	40.3	2000	2.2	13.6	106.9

[1] SA = succinic acid, IS = isosorbide, 2,3-BD = 2,3-butanediol, GLY = glycerol.

Polyester **6** is a linear polymer, while polyester **7** is a branched material with significantly higher OH-functionality. The powder paints were formulated with the help of industrial powder coating specialists. Curing agent **I** (Scheme 2-4) was used in these formulations, since this is the only cross-linker that is a solid at room temperature (melting range: 62-82 ºC). In addition to the polyester resin (**6** or **7**), the curing agent (**I**) and the catalyst (DBTL, 1 wt%), some standard additives such as benzoin (0.75 wt%, degassing agent) and Resiflow PV5 (1.5 wt%, acrylic resin, used as flow agent) were added to the formulations, to improve the film formation and, thus, the final coating appearance and properties.

The curing behavior of these formulations was also investigated through dynamical mechanical analysis (DMA) using a rheometer with parallel plate geometry. From these measurements, important variables, such as the onset temperature of the curing reaction, the gel-point (indicated by the point at which $G' = G''$ or $\tan\delta = 1$) and the degree of cure can be determined. The minimum modulus or viscosity of the molten formulation determines the flow and leveling of the coating. Information concerning the cross-link density of the final network can be deduced from the shear modulus of the rubbery plateau. According to the kinetic theory of rubber elasticity, the cross-link density can be calculated using Equation 2-3.

$$\nu_e = \frac{G_r'}{RT_r} \qquad \text{(Equation 2-3)}$$

In this equation, ν_e is the concentration of elastically effective network chains (mol/m^3), G_r' (Pa) is the equilibrium shear modulus of the rubbery network, R is the gas constant (8.314 m^3 Pa K^{-1} mol^{-1}) and T_r (K) is the temperature at the beginning of the rubbery region of the G' versus T plot. This equation is valid for unpigmented systems, subjected to small strains.[56,57] Figure 2-14 contains the plots of the shear modulus (G') and the temperature (T) versus time (t) for the following two formulations: **F12** (resin **6**, curing agent **I**, DBTL) and **F13** (resin **7**, curing agent **I**, DBTL). This plot was measured in a temperature ramp experiment, followed by an isothermal period.

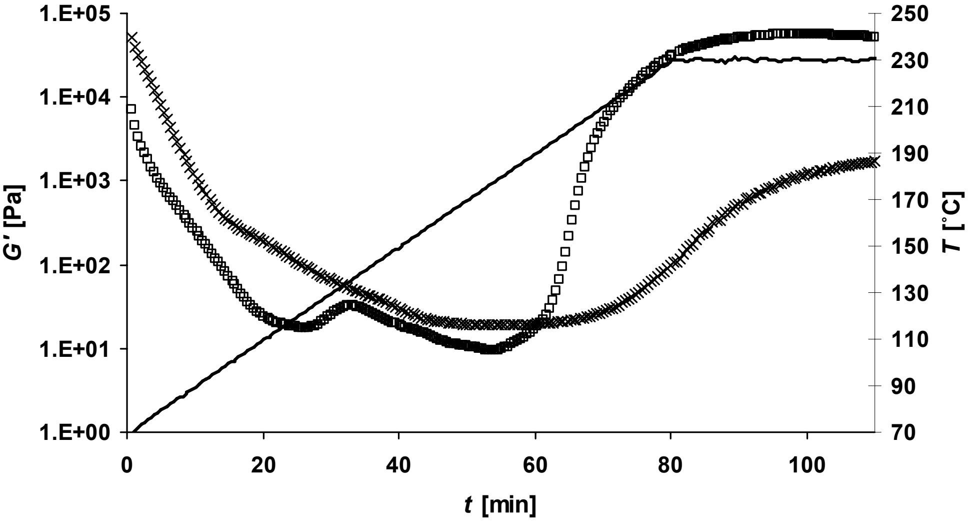


Figure 2-14. Shear modulus *G'* (for formulations **F12** (x) and **F13** (□)) and temperature *T* (▬) as functions of time *t* during IS-based poly(ester urethane) network formation. The temperature sweep was performed at 2 °C/min.

At $t = 0$ (and $T = 70$ °C), the shear modulus *G'* of **F12** is significantly higher than of **F13**, which is due to the higher T_g of the linear resin present in **F12.** Another explanation for this observation could be the lower amount of curing agent (relative to the amount of resin) in formulation **F12**, which is related to the lower concentration of functional groups in this polymer. After all, the curing agent can act as a plasticizer at the starting temperature of 70 °C, since it is well mixed with the polyester resin through extrusion. Upon heating, the moduli of both formulations drop rapidly. Between 100 and 180 °C, these formulations have quite low complex viscosities in the order of 10^0–10^1 Pa.s, facilitating flow of the coating onto the substrate. **F13** shows a rapid increase in *G'*, starting at approximately 175 °C. At this temperature, deblocking of the curing agent has already started and it is clear that the increase in modulus is caused by the formation of the polymeric network. Formulation **F12**, however, only shows a moderate increase in modulus at higher temperatures than **F13**. The moduli of both formulations level off at a rubbery plateau value which is much higher for **F13** (~ 55 MPa) than for **F12** (~ 1.5 MPa). This difference is caused by the fact that resin **7** has a lower $\overline{M}_n$ and a higher functionality, resulting in a lower molecular weight between cross-links M_c and, therefore, a higher cross-link density of **F13**. Using Equation 2-3, the cross-link densities can be estimated, using $T_r = 503$ K. It should be noted that these calculations were performed using the shear modulus determined at a frequency of 1 Hz. The cross-link density v_e is indeed much higher for **F13** (13.2 mol/m^3) than for **F12** (0.4 mol/m^3). The obtained values for v_e are of the same order of magnitude as data described in literature.[58,59] Apparently, the formation of a 3-dimensional network occurs at a significantly lower rate and to a much lesser extent in system **F12** than in system **F13**. This is confirmed by the coating performances of these formulations. Formulation **F12** shows very poor solvent and impact resistance over the whole curing temperature range, while **F13** is solvent resistant after curing at temperatures between 180 and 250 ºC. However, resistance to fast impact (determined by the reverse impact test performed at 160 pound×inch, equivalent to 184 kg×cm) is also poor for **F13**.

Several factors determine whether coatings are ductile or brittle, such as the T_g of the system, its yield stress and the cross-link density. For systems **F12** and **F13**, it might be that the network formed is not dense enough, attributing to reduced impact resistance. Insufficient cross-link density can be partly caused by the relatively large amount of residual carboxylic acid end-groups present in resin **7**, as indicated by the *AV* (Table 2-6). Another possible explanation could be that the curing reaction between the bulky IPDI-based curing agent **I** with the (often *endo*-oriented) secondary hydroxyl functionalities of the polyester resin does not proceed to completion. In general, thermosetting systems applied from solution tend to perform better than when the same system is applied as a powder paint. Therefore, resins **6** and **7** were also evaluated as binders in solvent-cast coatings. Experiments with curing agent **I** as well as with the free polyisocyanate **II** in combination with resin **6** demonstrated that it was not possible to obtain a fully cured, solvent and impact resistant network when using this linear polyester. For the branched resin **7**, on the other hand, curing with cross-linker **II** gave solvent and impact resistant films. As for **F13**, also the solvent-cast coating consisting of resin **7** and curing agent **I** showed good solvent resistance but poor mechanical stability. Possibly, the brittle behavior of resins **6** and **7** in combination with the isophorone diisocyanate-based curing agent **I** is not related to the network formed, but rather to the inherent properties of these particular molecular structures.

2.3.6 Accelerated weathering of biobased poly(ester urethane) coatings

An important property of thermoset coating systems is their outdoor durability. When coatings are applied for exterior purposes, they are subjected to many factors causing weathering. These factors include UV radiation, thermal cycles, moisture, acid rain, mechanical stresses and biological attack. Weathering causes degradation of polymers through oxidation, hydrolysis and physical ageing. UV degradation leads to chain scission in polymers, as well as yellowing (especially in aromatic systems) and fading of coating color. Chain scission has several consequences, such as embrittlement and erosion of the polymeric film, which becomes apparent by loss of gloss, for example. To test the UV stability of polymers in general and of coatings in particular, many methods are available. The most reliable method is to test the coating under its actual service conditions and during the required service period. Examples of such tests are natural weathering experiments performed at locations with high UV exposure, such as the well-known Florida tests. This type of evaluation is obviously time-consuming, which has sparked the interest in accelerated weathering measurements. Well-known accelerated weathering methods make use of xenon arc lamps, emitting light having a spectral distribution resembling that of sunlight, albeit at a much higher intensity. In addition, the relative humidity can be controlled during these measurements. Translating accelerated weathering results to a lifetime prediction for a certain coating system is very difficult, since many factors may play a role in the rate of weathering.

An isosorbide-based, branched OH-functional polyester (Table 2-3, entry **5a**) was applied to an aluminum Q-panel and cured with curing agent **II** from NMP solution. The same procedure was followed for a branched isophthalic acid (IPA)/neopentyl glycol (NPG)/trimethylolpropane (TMP)-based terpolyester ($\overline{M}_n$ = 4100 g/mol, *PDI* = 6.7, T_g = 49.9 ºC, *AV* = 5.1 mg KOH/g, *OHV* = 85.3 mg KOH/g). In addition, a branched terephthalic acid (TPA)/NPG/TMP-based terpolyester ($\overline{M}_n$ = 5000 g/mol, *PDI* = 2.3, T_g = 61.9 ºC, *AV* = 35.7 mg KOH/g, *OHV* = 5.4 mg KOH/g), containing only low levels of IPA, was cured with triglycidyl isocyanurate (TGIC) after solution casting from NMP. The three coatings were subjected to accelerated weathering in a xenon arc testing device at a relative humidity of 25 %. The isosorbide-based system will be referred to as **W1**, the IPA-based weathered coating as **W2** and the TPA-based system as **W3**. **W2** is known to have the best resistance to weathering of all commercial poly(ester urethane) systems used as powder coatings. **W3**, containing mainly TPA as the diacid constituent, is one of the most commonly used systems, even though it is significantly less resistant to UV irradiation.[3,60] Another important reason**,** apart from its excellent weathering stability, why we selected system **W2** to compare the isosorbide-based system with, is that it has a similar hydroxyl value as resin **5a**, which means that the ratio polyester / cross-linker is approximately the same. Also, the initial glass transition temperatures of the resins are similar. System **W3** was selected to be able to evaluate **W1** in relation to a very stable (**W2**) and a less stable, commercial system (**W3**). The three coating systems did not contain any stabilizing additives.

The weathered samples were characterized at intervals of 1000 hrs (which is roughly comparable to one year of outdoor exposure). IR spectra of the different samples were collected and the appearance of the coatings was evaluated. Figure 2-15 shows the FTIR spectra of **W1**, **W2** and **W3** as functions of time.

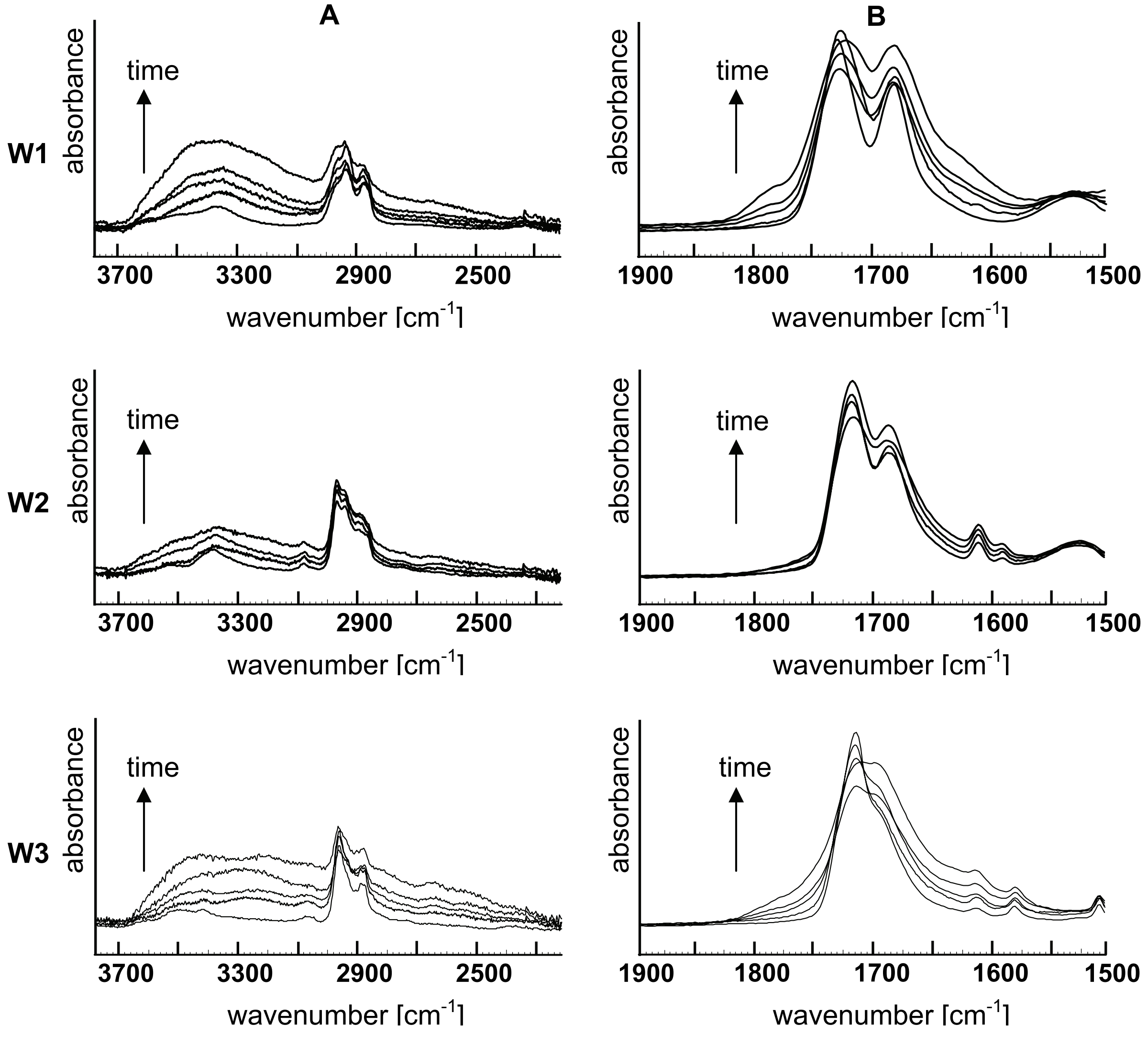


Figure 2-15. FT-IR spectra of **W1**, **W2** and **W3** as functions of weathering duration at *t* = 0 (bottom curves), 1000, 2000, 3000 and 4000 (top curves) hrs: (**A**) alcoholic and carboxylic -OH and -NH regions and (**B**) carbonyl regions.[61,62] *N.B. for weathered sample **W2**, the spectrum at t = 3000 hrs was omitted for clarity reasons.*

In time, increases in absorbance can be observed, indicating increases of the amounts of functional groups in the coatings, such as hydroxyl, carboxyl, hydroperoxyl and anhydride groups. These changes already occur in the early stages of UV-exposure, while the coating appearance remains the same.[63] From the IR-plots, it is clear that the increase in functional groups is more rapid for systems **W1** and **W3** compared to **W2**. The plots **A** show the increase of the amount of –OH groups as a function of time, where the bottom curve represents the situation at $t = 0$ and the top curve shows the situation at $t = 4000$ hrs. In both systems, a significant increase of the amount of hydroxyl, hydroperoxyl and/or carboxyl groups is observed and this increase is most pronounced for system **W1**. In plots **B**, the carbonyl regions of the FT-IR spectra are shown. An increase of the band at 1770-1780 cm^{-1} is observed, which again is more pronounced for systems **W1** and **W3**. This band is attributed to anhydride carbonyls. These results indicate that these systems degrade through photo-oxidation mechanisms occurring during UV-exposure. Apparently, **W1** and **W3** are more susceptible to UV-degradation than **W2**. There are some differences between **W1** and **W3** in the –OH regions of their spectra (plots **A**), where weathering of **W1** seems to generate slightly more functionality than **W3**. From the carbonyl regions (plots **B**), no clear distinction can be made between the two coatings.

One other important factor should be taken into account when comparing weathering results of polyester systems, which is their susceptibility to hydrolysis. In general, aliphatic polyesters tend to be hydrolyzed more rapidly than aromatic polyesters. When polyester chains hydrolyze, hydroxyl and carboxyl absorptions will increase as they would do upon degradation of the polyester by UV-irradiation. It is therefore difficult to distinguish between the effects of the UV-light and hydrolysis. These weathering experiments were performed at a moderate relative humidity (25 %), so it was expected that the influence of hydrolysis would not be too important but still we cannot exclude the influence of hydrolytic degradation of the polymeric networks.

The appearance of the coatings did not change dramatically during the accelerated weathering experiments. The films did not show strong decreases in gloss (not quantified) and no cracking or other film defects were observed. Initially, the coating **W1** was slightly more yellow than **W2** and **W3**, which is probably due to the presence of low levels of chromophores (most likely impurities) in the isosorbide monomer. With increasing weathering duration, the color of **W1** vanished. This is thought to be due to degradation and removal of (part of) the chromophores from the coating (i.e. bleaching). A slight reduction in color was also observed for system **W3**. This phenomenon is known to occur during weathering experiments.

2.4 Conclusions

Linear and branched polyesters based on renewable resources were synthesized via bulk polycondensation from isosorbide and succinic acid to yield hydroxy-functional polymers. Biobased terpolyesters from succinic acid, isosorbide and either 2,3-butanediol or 1,3-propanediol, containing at least 60 - 70 % of isosorbide, have molecular weights and glass transition temperatures suitable for thermosetting powder coating applications. Coatings formulated from linear polymers in combination with non-renewable conventional curing agents show moderate solvent resistance and mechanical performance. On the other hand, films from branched polyesters with enhanced OH-functionality by incorporation of e.g. glycerol, have good solvent resistance, excellent impact resistance and high hardness. Provided that isosorbide of high purity is used, these coatings are transparent and colorless. This, in combination with their excellent mechanical properties, makes them very promising materials for coating applications. Due to the high attainable T_g values, these renewable polyesters can even be used in powder coating formulations. Accelerated weathering experiments have shown that isosorbide-based coating systems appear to have similar weathering resistance as commercially available terephthalic acid-based formulations.

References

(1) Kapilow, L.; Puglisi, J. S.; Cheng, C.-W. F. (UCB S.A.). US5097006, 1992.

(2) Freriks, J.; Van Gaalen, R. P. C.; Hitchings, G. J.; Kooijmans, P. G. (Shell Oil Company). US6107442, 2000.

(3) Marsh, S. J. *JCT CoatingsTech* **2005**, *2,* 32.

(4) Van Benthem, R. A. T. M. *Prog. Org. Coat.* **2000**, *40,* 203.

(5) Johansson, M.; Glauser, T.; Jansson, A.; Hult, A.; Malmstrom, E.; Claesson, H. *Prog. Org. Coat.* **2003**, *48,* 194.

(6) Moens, L.; Buysens, K.; Maetens, D. (UCB, S.A.). WO0017279, 2000.

(7) Witte, F. M.; Goemans, C. D.; Van der Linde, R.; Stanssens, D. A. *Prog. Org. Coat.* **1997**, *32,* 241.

(8) Misev, T. A.; Linde, R. v. d. *Prog. Org. Coat.* **1998**, *34,* 160.

(9) Boon, H. W.; Forschner, T. C.; Gwyn, D. E.; Smith, O. W.; Thames, S. F. (Shell Internationale Research Maatschappij B.V.). WO0224823, 2002.

(10) Storbeck, R.; Ballauff, M. *J. Appl. Polym. Sci.* **1996**, *59,* 1199.

(11) Brandenburg, C. J.; Hayes, R. A. (Du Pont de Nemours). US2003204029, 2003.

(12) Thiem, J.; Luders, H. *Polym. Bull.* **1984**, *11,* 365.

(13) Beldi, M.; Medimagh, R.; Chatti, S.; Margue, S.; Prim, D.; Loupy, A.; Delolme, F. *Eur. Polym. J.* **2007**, *43,* 3415.

(14) Caouthar, A.; Roger, P.; Tessier, M.; Chatti, S.; Blais, J. C.; Bortolussi, M. *Eur. Polym. J.* **2007**, *43,* 220.

(15) Kricheldorf, H. R.; Chatti, S.; Schwarz, G.; Kruger, R. P. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41,* 3414.

(16) Kricheldorf, H. R. *J.M.S. - Rev. Macromol. Chem. Phys.* **1997**, *C37,* 599.

(17) Okada, M.; Okada, Y.; Aoi, K. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33,* 2813.
(18) Cognet-Georjon, E.; Mechin, F.; Pascault, J.-P. *Macromol. Chem. Phys.* **1996**, *197,* 3593.
(19) Storbeck, R.; Ballauff, M. *Polymer* **1993**, *34,* 5003.
(20) Braun, D.; Bergmann, M. *Journal fur praktische Chemie* **1992**, *334,* 298.
(21) Majdoub, M.; Loupy, A.; Fleche, G. *Eur. Polym. J.* **1994**, *30,* 1431.
(22) Salzburg, H.; Hajek, M. (Bayer AG). US4564645, 1986.
(23) Bengs, H.; Schoenfeld, A.; Boehm, G.; Weis, S.; Joachim, C. (Celanese Ventures GmbH). US6342300, 2002.
(24) Morrison, J. G. (Martin-Marietta Corporation). US3041300, 1962.
(25) (Courtaulds Limited). NL6405497, 1964.
(26) Atlas (Atlas Chemical Industries). US1130936, 1966.
(27) Kricheldorf, H. R.; Krawinkel, T.; Gerken, A.; Schuhmacher, P. (BASF Aktiengesellschaft). US6291629, 2001.
(28) Khanarian, G.; Charbonneau, L. F.; Kitchens, C.; Shen, S. S. (HNA Holdings, Inc.). US5958581, 1999.
(29) Vijayendran, B. R.; King, J. L.; Mitchell, K. P.; Clingerman, M. C.; Cafmeyer, J. T. WO2006/102279, 2006.
(30) Kricheldorf, H. R.; Berghahn, M.; Probst, N.; Gurau, M.; Schwarz, G. *React. Funct. Pol.* **1996**, *30,* 173.
(31) Kricheldorf, H. R.; Gomourachvili, Z. *Macromol. Chem. Phys.* **1997**, *198,* 3149.
(32) Kricheldorf, H. R.; Wulff, D. F. *Polymer* **1998**, *39,* 6145.
(33) Okada, M.; Okada, Y.; Tao, A.; Aoi, K. *J. Appl. Polym. Sci.* **1996**, *62,* 2257.
(34) Okada, M.; Tachikawa, K.; Aoi, K. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35,* 2729.
(35) Okada, M.; Tachikawa, K.; Aoi, K. *J. Appl. Polym. Sci.* **1999**, *74,* 3342.
(36) Okada, M.; Tsunoda, K.; Tachikawa, K.; Aoi, K. *J. Appl. Polym. Sci.* **2000**, *77,* 338.
(37) Storbeck, R.; Rehahn, M.; Ballauff, M. *Makromol. Chem.* **1993**, *194,* 53.
(38) Schwarz, G.; Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34,* 603.
(39) Liu, M. O.; Lin, H.-F.; Yang, M.-C.; Lai, M.-J.; Chang, C.-C.; Feng, M.-C.; Shiao, P.-L.; Chen, I.-M. *Polym. Degrad. Stab.* **2006**, *91,* 1443.
(40) Hannon, M. J.; Rhum, D.; Wissbrun, K. F. *J. Coat. Tech.* **1976**, *48,* 42.
(41) Franck, A., *DMA to improve powder coatings*. 2007, TA Instruments.
(42) Carroccio, S.; Rizzarelli, P.; Puglisi, C. *Rapid Commun. Mass Spectrom.* **2000**, *14,* 1513.
(43) Salhi, S.; Tessier, M.; Blais, J.-C.; El Gharbi, R.; Fradet, A. *e-Polymers* **2005**, *43,* 1.
(44) Williams, J. B.; Gusev, A. I.; Hercules, D. M. *Macromolecules* **1997**, *30,* 3781.
(45) Szeja, W. *J. Chem. Soc., Chem. Commun.* **1981**, *5,* 215.
(46) Fleche, G.; Huchette, M. *Starch* **1986**, *38,* 26.
(47) Brimacombe, J. S.; Foster, A. B.; Stacey, M.; Whiffen, D. H. *Tetrahedron* **1958**, *4,* 351.
(48) Cecutti, C.; Mouloungui, Z.; Gaset, A. *Bioresour. Technol.* **1998**, *66,* 63.
(49) Alicata, R.; Montaudo, G.; Puglisi, C.; Samperi, F. *Rapid Commun. Mass Spectrom.* **2002**, *16,* 248.
(50) Fox, T. G. J.; Flory, P. J. *J. Appl. Phys.* **1950**, *21,* 581.
(51) Devaux, J.; Godard, P.; Mercier, J. P. *Polym. Eng. Sci.* **1982**, *22,* 229.
(52) Smith, W. A.; Barlow, J. W.; Paul, D. R. *J. Appl. Polym. Sci.* **1981**, *26,* 4233.
(53) Otton, J.; Ratton, S. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26,* 2183.
(54) Marks, M. J.; Munjal, S.; Namhata, S.; Scott, D. C.; Bosscher, F.; De Letter, J. A.; Klumperman, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38,* 560.

(55) Cowie, J. M. G.; Henshall, S. A. E. *Eur. Polym. J.* **1976**, *12,* 215.
(56) Pelzer, H. *Rep. Prog. Phys.* **1939**, *6,* 330.
(57) Flory, P. J. *Chem. Rev.* **1944**, *35,* 51.
(58) Higginbottom, H. P.; Bowers, G. R.; Grande, J. S.; Hill, L. W. *Prog. Org. Coat.* **1992**, *20,* 301.
(59) Seidel, C.; Kulicke, W.-M.; Hess, C.; Hartmann, B.; Lechner, M. D.; Lazik, W. *Starch* **2001**, *53,* 305.
(60) Maetens, D. *Prog. Org. Coat.* **2007**, *58,* 172.
(61) Day, M.; Wiles, D. M. *J. Appl. Polym. Sci.* **1972**, *16,* 175.
(62) Skaja, A. D.; Fernando, D.; Croll, S. G. *JCT Research* **2006**, *3,* 41.
(63) Mast, A. P.; Gijsman, P. *Verfkroniek* **1999**, *72,* 11.

The results described in this chapter were published in two separate papers:

1) Noordover, B. A. J.; Van Staalduinen, V. G.; Duchateau, R.; Koning, C. E.; Van Benthem, R. A. T. M.; Mak, M.; Heise, A.; Frissen, A. E.; Van Haveren, J. *Biomacromolecules* **2006,** *7*, 3406.
2) Van Haveren, J.; Oostveen, E. A.; Micciché, F.; Noordover, B. A. J.; Koning, C. E.; Van Benthem, R. A. T. M.; Frissen, A. E.; Weijnen, J. G. J. *J. Coat. Technol. Res.* **2007**, *4*, 177.

3

Hydroxy-functional polyesters based on isoidide and isomannide

Abstract

The difference in reactivity between the endo- and the exo-oriented hydroxyl groups of 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS) during esterification reactions with succinic acid, a non-activated dicarboxylic acid, was demonstrated. These results confirmed the observations made in Chapter 2 and also indicated that isoidide is probably more reactive in melt polycondensation reactions with, for example, succinic acid. Fully biobased co- and terpolyesters based on 1,4:3,6-dianhydro-L-iditol (isoidide, II) and 1,4:3,6-dianhydro-D-mannitol (isomannide, IM) were prepared, having two exo-oriented or two endo-oriented hydroxyl groups, respectively. It was found that II was indeed more reactive than IS and IM under these polymerization conditions. In addition, it was found that the ether ring of isomannide is susceptible to ring opening at elevated temperatures, leading to branched polymeric structures. Several terpolyesters prepared from isoidide and isomannide were semi-crystalline materials and had molecular weights and thermal properties suitable for thermoset coating applications. Coatings applied from solution as well as by powder coating showed good performance with respect to chemical and mechanical stability.

3.1 Introduction

In the previous chapter, (co)polyesters based on 1,4:3,6-dianhydro-D-glucitol (or isosorbide, IS) and thermoset coatings thereof were discussed. Isosorbide proved to be a very useful biobased monomer for polyester synthesis, since it provides the fully aliphatic polyester backbone with sufficient rigidity to obtain materials with suitable T_gs for, for example, powder coating or toner applications.

One of the observations made in Chapter 2 was the difference in reactivity between the *endo*- and *exo*-oriented hydroxyl groups during melt polycondensation using non-activated dicarboxylic acids. The *endo*-oriented hydroxyl group of IS, connected to C5, is known to be involved in internal hydrogen bonding with the adjacent oxygen atom in the cyclic ether ring.[1,2] Depending on the reaction mechanism and conditions, this hydrogen bonded OH-group is either more or less reactive than the *exo*-oriented OH connected to C2. For example, the reaction of IS with acetic anhydride in pyridine leads mainly to acetylation of the *exo*-oriented hydroxyl group. When adding pyridine hydrochloride, on the other hand, the acetylation of the *endo*-OH is favored.[3] These results were confirmed by reactions of IS with benzoyl chloride in pyridine, leading to preferential esterification of the *endo*-OH. On the other hand, the esterification of the *exo*-OH is favored when the reaction between IS and benzoyl chloride is performed under phase transfer catalysis conditions. Similar dependencies of regioselectivity on the synthetic procedures were observed for alkylations as well as for nitrations of IS.[4-7] In reactions during which the initial stereochemistry of IS is conserved, a preference for conversion of the *exo*-OH seems to exist when steric hindrance is the most important factor.[8] In reactions proceeding via S_N2-type mechanisms, such as the chlorination of IS with thionyl chloride, the conversion of the *endo*-oriented hydroxyl group of IS is favored over the conversion of its *exo*-oriented hydroxyl counterpart. This is partly caused by the fact that displacement of the *exo*-hydroxyl is more sterically hindered.[9] In addition, due to the internal hydrogen bonding of the *endo*-oriented hydroxyl group, the carbon atom to which this hydroxyl group is attached (C5) is more positively charged, favoring nucleophilic attack on this carbon atom.

This chapter will describe co- and terpolyesters based on 1,4:3,6-dianhydro-L-iditol (or isoidide, II) and 1,4:3,6-dianhydro-D-mannitol (or isomannide, IM) to study the effect of the orientation of the 1,4:3,6-dianhydrohexitol OH-groups on the properties of these polyesters. Isoidide has two *exo*-oriented hydroxyl groups, while the OH-groups of isomannide are both *endo*-oriented (see Figure 3-2). These monomers have previously been used to synthesize several types of polymers, such as polyesters[10-17], polyamides[18], polyethers[19] and poly(ether urethanes).[20,21] The polyesterifications described in literature were often performed in solution, and always using activated carboxylic acid species (i.e. acid chloride), optionally in combination with bases such as pyridine. The polymerizations described here, on the other hand, were performed in the melt, using non-activated dicarboxylic acid compounds.

3.2 Experimental section

Materials. Isosorbide (polymer grade, trade name Polysorb® P, 98.5+ %) and isoidide (99.8 %) were obtained as gifts from Roquette Frères. Isomannide (97+ %) was a gift from Agrotechnology and Food Innovations. Succinic acid (SA), 2,3-butanediol (2,3-BD), neopentyl glycol (NPG), trimethylolpropane (TMP), titanium(IV) n-butoxide, 4-dimethylaminopyridine (DMAP) and acetic anhydride were purchased from Acros Organics. Normalized solutions of KOH in methanol, 1,3-propanediol (1,3-PD), glycerol (99.5+ %, GLY), glycerol-^{13}C3 (99 atom% ^{13}C), triglycidyl isocyanurate (TGIC) and dibutyltin dilaurate (DBTDL) were obtained from Aldrich. Chloroform-*d* was obtained from Cambridge Isotope Laboratories, DMSO-d_6 was bought from Campro Scientific. All solvents were purchased from Biosolve. Irganox HP2921, a mixture of phenolic and phosphonic anti-oxidants, was a gift from Ciba Specialty Chemicals. Isophorone diisocyanate-based, *ε*-caprolactam blocked, polyisocyanate (trade name: Vestagon B1530) was a gift from Degussa GmbH. Hexamethylene diisocyanate-based polyisocyanate (trade name: Desmodur N3600) and its corresponding *ε*-caprolactam blocked polyisocyanate (trade name: Desmodur BL3272) were gifts from Bayer AG. Flow agent Resiflow PV5 was purchased from Worlée Chemie, benzoin was obtained from DSM Special Products. All chemicals were used as received.

Model reaction: isosorbide with succinic acid. Isosorbide (22.67 g, 155 mmol) and succinic acid (36.64 g, 310 mmol) were weighed into a 250 mL round bottom three-neck flask. The reactor was fitted with a short vigreux column. Before the reaction, the vessel was brought under an inert argon atmosphere by repeated vacuum/argon cycles. During the reaction, the system was left open under a slight argon purge. While stirring, the mixture was heated to 180 ºC using an oil bath. At $t = 0$, at which the reaction mixture became a clear melt, titanium(IV) n-butoxide (0.02 mol% relative to isosorbide), dissolved in toluene, was added to the melt. The reaction was continued during 320 minutes at 180 ºC, samples were taken at regular intervals for ^{1}H NMR analysis.

Polymerization of renewable monomers to form copolyesters. A typical polymerization was carried out according to the following procedure, described for poly(isoidide succinate). Succinic acid (8.22 g, 70 mmol), isoidide (11.60 g, 79 mmol) and Irganox HP2921 (82 mg, 1 wt% relative to succinic acid) were weighed into a 100 mL round bottom flask. The reactor was fitted with a vigreux column and a Dean-Stark type condenser to collect the condensation product. During the first part of the synthesis, the setup was continuously flushed with inert gas to limit oxidation and to facilitate transport of water vapor. While stirring, the mixture was heated to 150 ºC using a heating mantel. Titanium(IV) n-butoxide (0.02 mol% relative to succinic acid), dissolved in toluene, was added to the melt. Subsequently, the reaction temperature was increased stepwise. The maximum reaction temperature was 220 ºC. After 3.5 hours, vacuum processing was started at 210 - 220 ºC, with typical pressures ranging from 1 – 5 mbar. Vacuum was applied for 2.5 hours, after which the polymer was discharged from the reactor. Yield: 15.2 g (88.7 %).

Solvent casting and curing of hydroxy-functional polyesters. Hydroxy-functional polyesters were cured using conventional polyisocyanate curing agents: (1) an ε-caprolactam blocked trimer of isophorone diisocyanate (trade name: Vestagon B1530, NCO equivalent weight = 275 g/mol), (2) a trimer of hexamethylene diisocyanate (trade name: Desmodur N3600, NCO equivalent weight = 183 g/mol) and (3) an ε-caprolactam blocked trimer of hexamethylene diisocyanate (trade name: Desmodur BL3272, NCO equivalent weight = 410 g/mol).
Ad 1 & 3: A solution of 0.3 – 0.5 g of polyester, 1.05 molar equivalent of the cross-linker (calculated from the OH-value, determined by titration) and 0.5 wt% (relative to solid resin) of dibutyltin dilaurate in 1 mL N-methyl-2-pyrrolidone (NMP) was prepared. Subsequently, a wet film of approximately 250 μm thickness was applied onto an aluminum panel, using a doctor blade. The film was left to dry at room temperature followed by curing at 200 ºC during 30 minutes under nitrogen, resulting in films having thicknesses between 30 and 100 μm. Ad 2: A solution of 0.3 – 0.5 g of polyester in 0.7 mL of NMP was prepared, as well as a separate solution of Desmodur N3600 (1.05 molar equivalent, calculated from titration data) in 0.3 mL of NMP. The two solutions were mixed and applied directly to the aluminum substrate as a wet film with a thickness of 250 μm. After drying at room temperature, the film was cured at 180 ºC under N_2 during 20 minutes. Coatings were also applied through a powder coating process, which typically proceeds as follows: a polyester resin was co-extruded with the curing agents in a 1 to 1 ratio at approximately 100 ºC, using a twin-screw mini-extruder. In addition, 1.5 wt% flow agent (Resiflow PV5, Worlée) and 0.75 wt% degassing agent (benzoin) were added to the formulation. The obtained extrudate was ground to particles smaller than 90 μm and powder coated onto an aluminum gradient panel using corona spraying, followed by curing in a gradient oven at temperatures ranging from 100 to 250 ºC.

Measurements. SEC analysis in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was carried out using a set-up equipped with a Shimadzu LC-10AD pump and a WATERS 2414 differential refractive index detector (at 35 ºC). Injections were done by a MIDAS auto-injector, the injection volume being 50 μL. PSS (2× PFG-lin-XL, 7 μm, 8×300 mm, 40 °C) columns were used. The eluent flow rate was 1.0

mL/min. Calibration curves were obtained using PMMA standards. Data acquisition and processing were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer, chloroform-*d* was used as the solvent (unless stated otherwise). Glass transition and melting temperatures were determined by DSC measurements, carried out with a DSC Q100 from TA Instruments. Curing of powder coating formulations was also followed by DSC, using a Perkin Elmer DSC Pyris 1 device, calibrated using indium and tin. The measurements were carried out at a heating/cooling rate of 10 ºC/min unless stated otherwise. Data acquisition was carried out using Pyris 7 software. MALDI-ToF-MS measurements were performed on a Voyager DE-STR from Applied Biosystems. Calibrations were carried out with poly(ethylene oxide) standards for the lower mass range and polystyrene standards for the higher mass range. The mass accuracy was better than 0.2 Dalton, the mass resolution was approximately m/z 12,000. DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as matrix. Potassium trifluoroacetate (Aldrich, >99 %) was used as cationization agent. Solutions of the matrix (40 mg/mL), potassium trifluoroacetate (5 mg/mL) and the polyester sample (1 mg/mL) in THF were premixed in a ratio of 5:1:5. The mixture was subsequently hand-spotted on the target and left to dry. Spectra were recorded in reflector mode at positive polarity. Potentiometric titrations were carried out using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The carboxylic acid functionality was measured by titration with a normalized 0.1 N methanolic KOH solution. The acid value (*AV*) is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize 1 g of polymer resin. Polyester hydroxyl end-groups were acetylated in solution (NMP) with acetic anhydride at room temperature (4-dimethylaminopyridine was used as catalyst), followed by titration of the resulting acetic acid with a normalized 0.5 N methanolic KOH solution. Blank measurements were necessary to obtain the hydroxyl values. The hydroxyl value (*OHV*) is the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of material. All titrations were carried out in duplo. Dynamic Mechanical Analysis (DMA) was carried out using a TA Instruments AR1000-N Rheolyst rheometer, having a parallel plate geometry. Samples were prepared by compression molding (at 400 bar) of powder paint formulations at room temperature. Solid, opaque disks of approximately 500 μm thick were obtained. Temperature as well as time sweeps were performed, using the following parameter settings: temperature range = 70 - 250 ºC, temperature ramp rate = 2 ºC/min, strain = 1 %, frequency = 1 Hz (= 6.283 rad/s). Data acquisition was done with Rheology Advantage Instrument Control software, data analysis with Rheology Advantage Data Analysis software. Cross-linking and coating performance at room temperature were evaluated using several characterization methods: acetone rub test (Solvent resistance test: the sample is rubbed with a cloth drenched in acetone. If no damage is visible after more than 150 rubs, the coating has good acetone resistance), rapid deformation test (Reverse impact test, ASTM D 2794) and pendulum damping test (ASTM D 4366, to determine König hardness). The thicknesses of the obtained coatings were measured using a magnetic induction coating thickness measuring device (Twin-Check by List-Magnetik GmbH).

DFT calculations. Standard computational methods based on the density functional theory have been employed using the Spartan program.[22] The functional used is the three-parameter exchange functional of Becke together with the correlation functional of Lee, Yang, and Parr (B3LYP).[23,24] For H, O, Si and Ti the basis set used is the Pople style basis set 6-31G[25] with diffuse (+) s and p functions added on the heavy atoms and polarization function (d, p), adding one d function on the heavy atoms and one p function on the hydrogens (6-31+G-(d,p)).[26,27] The geometries of all the model compounds have been fully optimized using analytical gradient techniques at the B3LYP level of theory previously cited. No symmetry constraints have been introduced. The convergence criteria used in these calculations are 10^{-6} hatrees for the energy, 4.5×10^{-4} hartrees/bohr for the gradient, and 1.8×10^{-3} Å for the Cartesian coordinates.

3.3 Results and discussion

3.3.1 The reactivity of the OH-groups of isosorbide in melt esterification reactions

In general, the 1,4:3,6-dianhydrohexitols IS, IM and II are less reactive in polycondensation reactions than diols having primary OH-groups, such as 1,3-propanediol and neopentyl glycol. In Chapter 2 of this thesis, this difference in reactivity was observed for IS-based terpolyesters. In addition, we showed that the hydroxyl end-groups of these polyesters are predominantly of the *endo*-oriented type. This indicates that the *exo*-oriented OH-group of isosorbide (IS) is more reactive in melt polycondensations. Apparently, the steric hindrance of the OH-group connected to C5 restricts its esterification under these reaction conditions.

To visualize the difference in reactivity between the two OH-groups of IS, we performed a model reaction between one molar equivalent of IS and two molar equivalents of succinic acid (SA), catalyzed by $Ti(OBu)_4$. This reaction was performed at 180 ºC under a slight inert gas flux. The conversions of both OH-groups were followed in time with ^1H NMR spectroscopy (Figure 3-1).

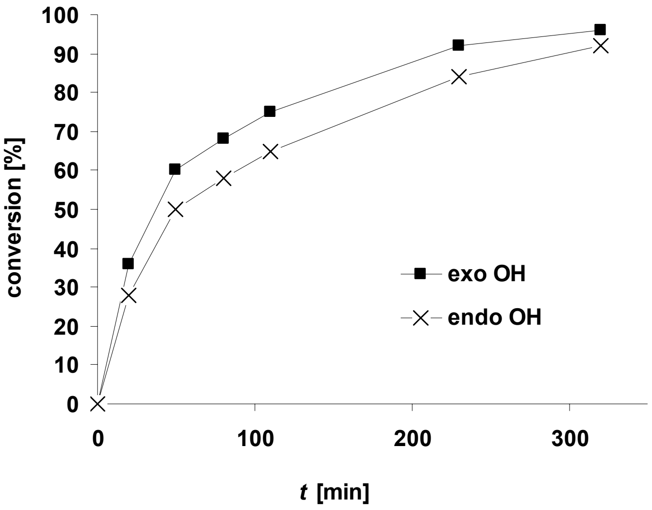


Figure 3-1. Conversions of the *exo*- (■) and *endo*-oriented (×) OH-groups of IS during esterification with succinic acid. Ratio IS: SA = 1:2, T = 180 ºC. Data were obtained from ^{1}H NMR spectra, measured in DMSO-d_6.

It is clear that the *exo*-oriented hydroxyl group of IS reacts more rapidly with SA under these reaction conditions. Conversions of this OH are up to 10 % higher during the first 4 hours of the reaction. When conversion proceeds past 80 %, it seems that the difference in conversion decreases. After 320 minutes of reaction, the difference in conversion between the *exo*- and the *endo*-OH is approximately 5 %. Similar values were found for poly(isosorbide succinate), synthesized from a monomer feed ratio of SA:IS = 1:1.14, after vacuum processing. For this particular polyester (Table 3-1, entry **1**), this relatively small difference in conversion between the *exo*- and the *endo*-oriented OH-groups results in a 60:40 ratio of *endo*:*exo* OH-groups at the polyester chain ends (see Chapter 2).

Based on these observations, it was anticipated that polycondensation of II to form polyesters might proceed more rapidly due to the fact that this DAH isomer has two *exo*-oriented hydroxyl groups that are less sterically hindered and incapable of forming intramolecular hydrogen bonds.[28] On the other hand, IM has two *endo*-oriented OH-groups, possibly leading to less efficient polymerization in the melt. The three different 1,4:3,6-dianhydrohexitols are depicted in Figure 3-2.

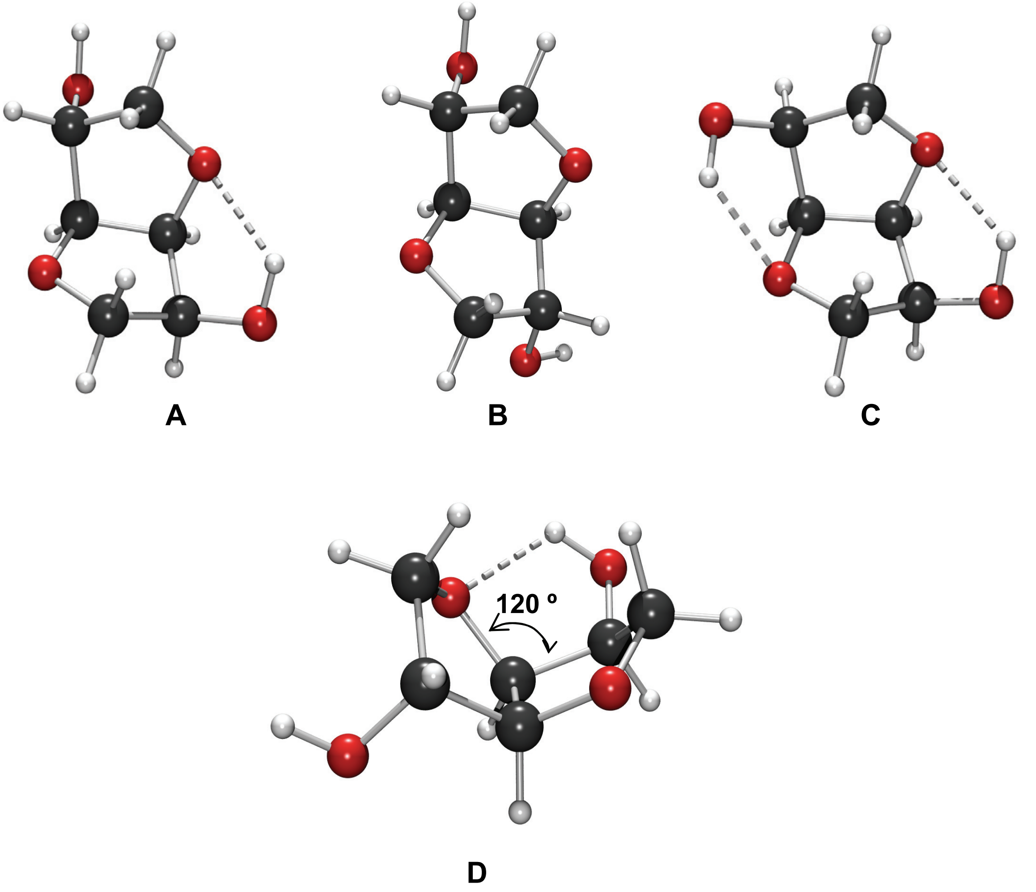


Figure 3-2. (**A**) 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS), (**B**) 1,4:3,6-dianhydro-L-iditol (isoidide, II) and (**C**) 1,4:3,6-dianhydro-D-mannitol (isomannide, IM). Intramolecular hydrogen bonding is indicated by dashed bonds. Structure **D** (isosorbide) demonstrates the angle of 120 º between the two fused furan rings. *These images were obtained through DFT calculations (see Experimental section).*

3.3.2 Poly(isoidide succinate) and poly(isomannide succinate)

Polycondensation reactions between SA and II or IM were performed following the same procedure. The most important properties of these copolyesters are listed in Table 3-1. For comparison reasons, the isosorbide-based polyester **1** is entered in the table as well. The molecular weight data reported in this chapter were obtained by SEC in HFIP using poly(methyl methacrylate) (PMMA) standards, instead of in THF using polystyrene (PS) standards. This is due to the limited solubility of the semi-crystalline isoidide and isomannide-based polyesters in THF. Using a different SEC set-up and different calibration leads to differences in the determined molecular weight for a certain polyester sample. For example, polyester **1** in Table 3-1 is the same sample as polyester **1b** in Chapter 2. In the previous chapter, we reported the following data for this polymer, determined using PS calibration: $\overline{M}_n$ = 2400 g/mol, *PDI* = 1.8 (Table 2-1), while the following data are determined by SEC using PMMA calibration: $\overline{M}_n$ = 3000 g/mol, *PDI* = 2.0. It is clear that in this thesis, we will only compare molecular weight (distribution) data of different polymer samples if they are obtained using the same SEC set-up and, thus, the same calibration. In general, it should be emphasized that SEC data give approximations of the molecular weights of these polyesters, rather than absolute values. Obviously, this is partly due to the differences in chemical structures between these 1,4:3,6-dianhydrohexitol-based polyester and PS or PMMA. In addition, since the materials discussed here have moderate molecular weights, their end-groups may have an important influence on the hydrodynamic volume and, thus, on the molecular weight determined by SEC. Titration and NMR data may afford additional information of the chain lengths of these polymers, as illustrated in Chapter 2, § 2.3.1.

Table 3-1. Properties of poly(1,4:3,6-dianhydrohexitol succinate)s synthesized in the melt.

entry	feed [1] composition	composition (NMR)	T_g [2] [ºC]	T_m [3] [ºC]	$\overline{M}_n$ [4] [g/mol]	$\overline{M}_w$ [4] [g/mol]	*PDI* [4]
1	SA/IS [1:1.14]	SA/IS [1:1.11]	56.5	-	3000	6000	2.0
2a	SA/II [1:1.12]	SA/II [1:1.08]	73.4	175.4	3900	8500	2.2
2b	SA/II [1:1.14]	SA/II [1:1.1]	63.9	177.7	3100	6600	2.2
3	SA/IM [1:1.12]	SA/IM [1:1.0]	46.0	147.5	*2400* [5]	*5200*	*2.2*

[1] SA = succinic acid, IS = isosorbide, II = isoidide and IM = isomannide.
[2] Determined at a heating/cooling rate of 10 ºC/min from the second heating curve of the DSC thermogram.
[3] Determined from the second heating curve at a heating rate of 10 ºC/min, after cooling at 2 ºC/min.
[4] Determined by SEC in HFIP, using PMMA standards.
[5] This sample was only partially soluble in HFIP, used as the eluent for the SEC measurements.

Some striking differences between the three poly(DAH succinate)s are observed. First of all, the degrees of discoloration of these transparent glassy polymers differ considerably. While the isoidide-based polyesters are colorless, the isosorbide-based materials are pale yellow and the isomannide-based polymers are yellow. This is probably partly due to the higher purity of the isoidide (99.8 %) compared to the purity of the isosorbide (98.5+ %) and the isomannide (97+ %) used in this study, although the thermal stability of the different isomers might also play a role (*vide infra*). The molecular weight as well as the T_g of the isoidide-based polyester **2a** appear to be significantly higher than of poly(isosorbide succinate) (**1**) and poly(isomannide succinate) (**3**), which were prepared under the same conditions. This seems to confirm the earlier observation that the *exo*-hydroxyl groups of these 1,4:3,6-dianhydrohexitols are more reactive in melt polymerizations with dicarboxylic acids. During the sample preparation for SEC, however, it was noted that polyester **3** did not fully dissolve in HFIP. Therefore, the SEC data given for this polymer only apply to the soluble part of the polymer. The partial insolubility of this IM-based polyester might indicate that, to a certain extent, cross-linking had occurred. A similar observation, made during the melt polycondensation of IM with terephthaloyl dichloride at 180 ºC, was mentioned by Thiem and coworkers.[16] Under the same conditions, IS and II proved to be stable. In general, these two 1,4:3,6-dianhydrohexitols have been reported to have better thermal stability than IM, which might be due to the destabilization of the anhydro ether rings by *endo*-oriented OH-groups.[2,10,19] On the other hand, IM is reported to be sufficiently stable when polycondensations are performed in solution up to 230 ºC, even if hydrochloric acid is present.[13] It seems that IM is not sufficiently thermally stable when polymerized at high temperatures in the melt, especially when strong acids are present. This probably partly explains the stronger discoloration observed during the IM-containing polymerizations and the partial insolubility of the resulting polyesters.

Ring-opening of the ether rings in isomannide

When studying the MALDI-ToF-MS spectra of the poly(DAH succinate)s **1**, **2a/b** and **3**, further evidence for the limited thermal stability of IM is found.

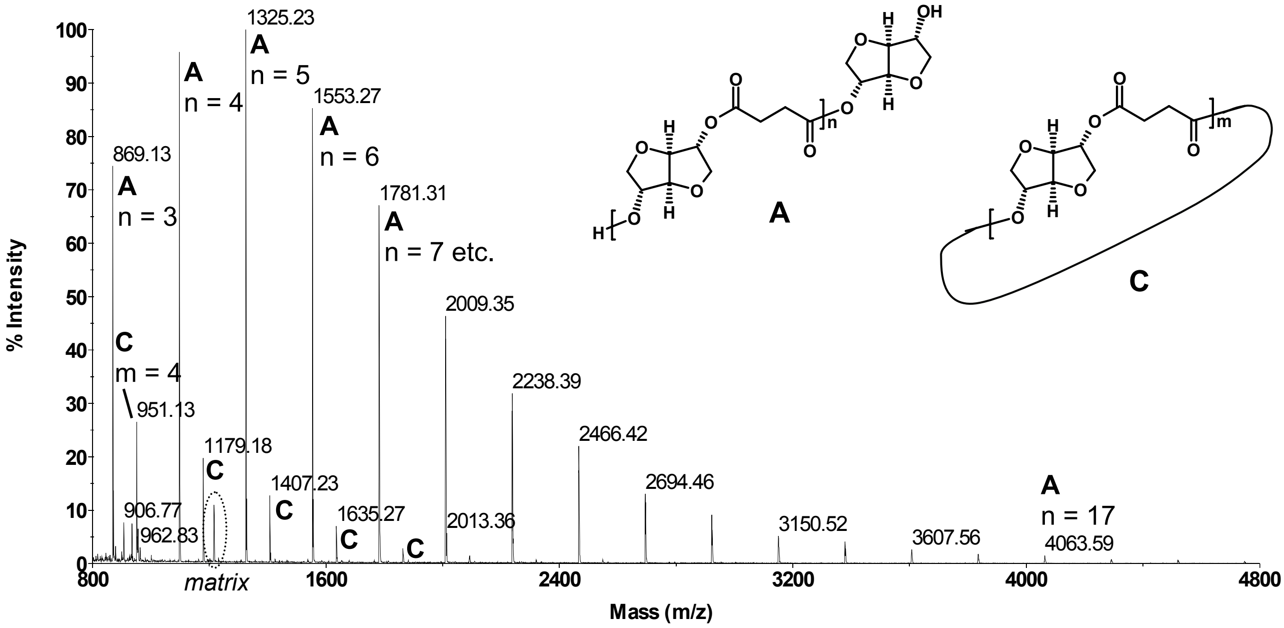


Figure 3-3. MALDI-ToF-MS spectrum of poly(isoidide succinate), entry **2b** in Table 3-1.

The spectra of polyesters **1b** and **2a/b** are quite similar. In Figure 3-3, the spectrum of polyester **2b** is given. Signals attributed to linear chains (having two isoidide end-groups, **A**) as well as cyclic polyester (**C**) species are observed, at intervals of 228 Da, the mass of the repeating unit of this polymer. In the MALDI-spectrum of polyester **1b** (not shown), also some low intensity signals corresponding to linear chains with one hydroxyl and one carboxylic acid end-group can be identified. Such chains were not observed in the MALDI spectra of polymers **2a** and **2b**. For polyester **3**, besides the linear peaks **A** and some very low intensity signals for cyclic chains **B**, the spectrum of the soluble fraction of the polyester shows some additional species (Figure 3-4, signals **G**). These signals appear at a mass difference of +18 Da with respect to the signals attributed to the linear hydroxy-functional chains **A**. This might indicate that some of the ether rings present in isomannide were opened. It is known that the DAH ether rings can be ring-opened using either strong electrophiles such as iodotrimethylsilane or through acetolysis (i.e. acidolysis) in the presence of a strong acid catalyst at elevated temperatures.[29-31] It might be that an acidolysis-type of ring-opening of the cyclic ether of IM has occurred at high temperature, leading to branching of the polyester chain (Scheme 3-1). This might explain the formation of partially cross-linked, and therefore insoluble, polymers.

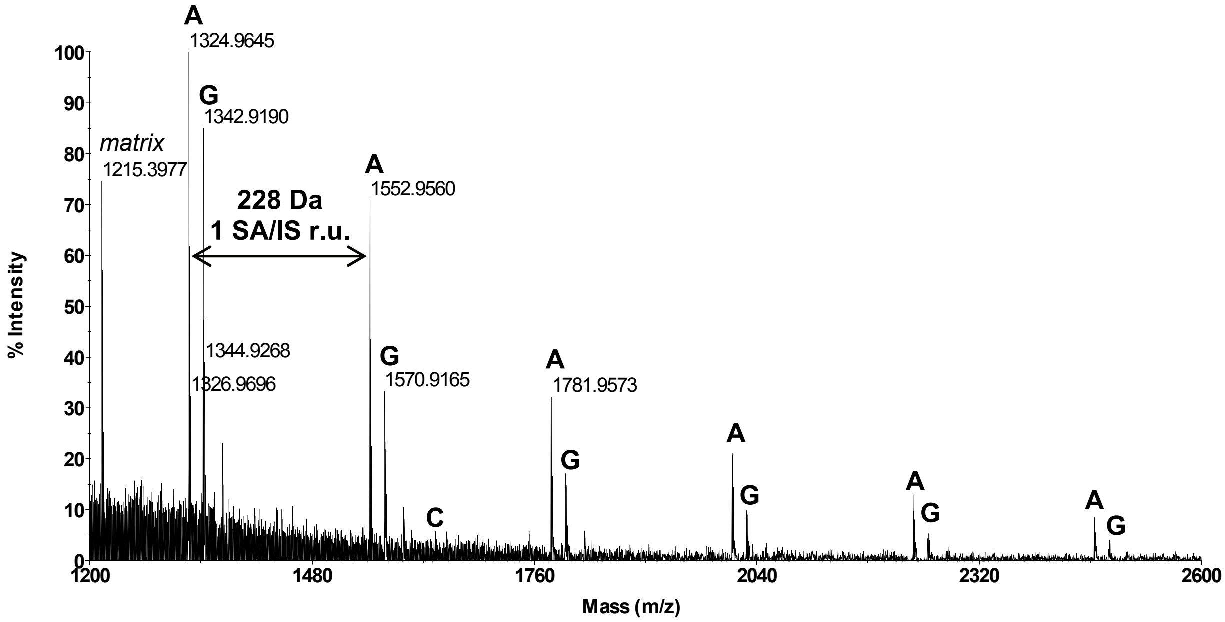
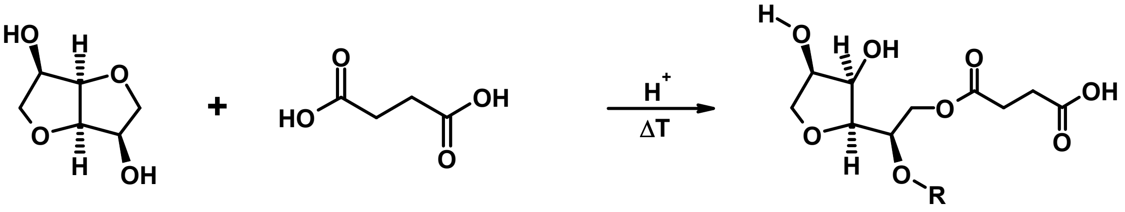


Figure 3-4. Section of the MALDI-ToF-MS spectrum of poly(isomannide succinate), entry **3** in Table 3-1. The following species can be observed: (**A**) linear chains with two OH end-groups; (**C**) cyclic chains; (**G**) branched chains (due to ring-opening of one of the ether rings of an isomannide-residue) with four OH end-groups.



Scheme 3-1. Acidolysis of the cyclic ether of an isomannide residue by a succinic acid-moiety during polyesterification performed at elevated temperature, leading to the (branched) species **C** (Figure 3-4). R is either a polyester chain fragment or a proton.

The proposed structures of the acidolyzed products in Scheme 3-1 exactly match the masses detected with MALDI-ToF-MS. This ring-opening reaction proceeds via a S_N2-type mechanism and this type of displacement reactions are known to proceed efficiently for *endo*-oriented OH-groups, while similar reactions involving *exo*-oriented OH-groups are sterically hindered.[9] However, products allegedly formed through ring-opening of an anhydro ether ring were only observed in isomannide-based polyesters, while isosorbide also has an *endo*-oriented OH-group. Apparently, there are additional factors causing this type of ring-opening to occur exclusively with isomannide. It was assumed that the *endo*-orientation of both hydroxyl functionalities plays a crucial role. The following hypothesis was formulated, proposing a concerted mechanism in which, simultaneously, two intramolecular H-bonds exist within an isosorbide/succinic acid monoester (see Figure 3-5).

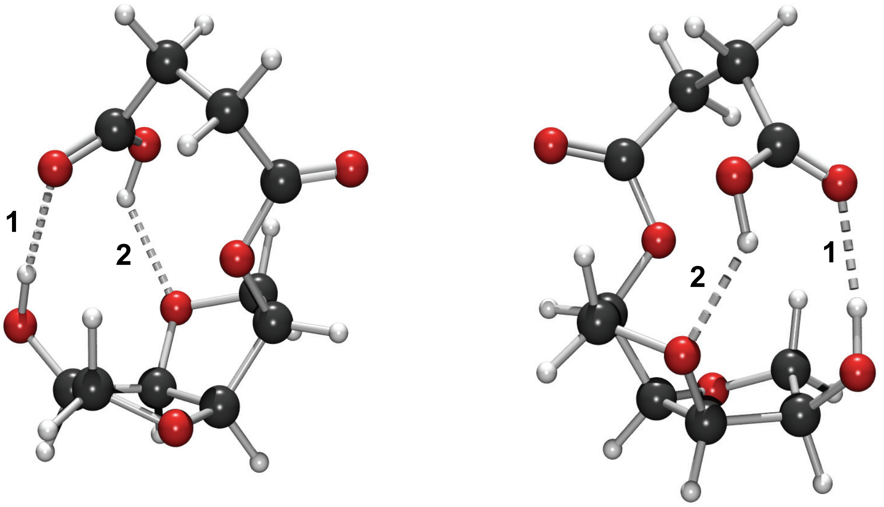
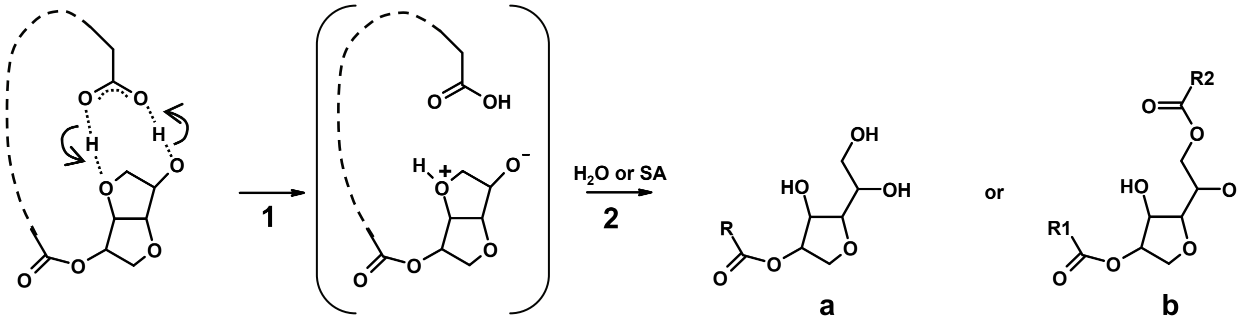


Figure 3-5. Two projections of the double hydrogen-bonding in a succinic acid/isosorbide monoester between (**1**) the double bonded oxygen of the SA residue with the *endo*-oriented OH-group of IM and (**2**) the ether oxygen atom of IM with the OH-group of the SA residue. *These images were obtained through DFT-calculations (see Experimental section).*

Upon esterification of one of the two OH-groups of isomannide with succinic acid, two hydrogen bonds can be formed: one between the unreacted OH-group of isomannide and the double-bonded carbonyl oxygen atom of the succinic acid residue (Figure 3-5, **1**) and one between the OH-group of the unreacted carboxylic acid group of the succinic acid residue and the ether oxygen atom of the five-membered ring of isomannide (Figure 3-5, **2**). Subsequently, the ether oxygen atom may be protonated by succinic acid, while the proton of the H-bonded OH-group of isomannide is transferred to the carbonyl oxygen of the succinic acid residue (Scheme 3-2, step **1**).



Scheme 3-2. Hypothetical mechanism of the ring opening of an isomannide-residue, due to the nucleophilic attack of water or a carboxylic acid (in this case, succinic acid, SA) on a zwitterionic intermediate. *N.B. for clarity reasons, the succinic acid residue is represented in an extended fashion, by the dashed line (see Figure 3-5)*

Thus, formally, a zwitterionic intermediate is formed, which can lead to opening of the anhydro ring through nucleophilic attack by water or a carboxylic acid. In the presence of water (which is formed through the initial esterification of isomannide with succinic acid), a ring-opened structure may result, having one primary and one secondary OH-group (Scheme 3-2, structure **a**). These OH-groups are obviously susceptible towards further esterification, leading to branched or potentially even cross-linked structures. By direct attack of a carboxylic acid, an ester linkage as well as a hydroxyl group will be formed (Scheme 3-2, structure **b**) Interestingly, the proposed mechanism can only occur during the first reaction between an isomannide and a succinic acid molecule, since it requires one unreacted *endo*-oriented OH-group of isomannide and one unreacted carboxylic acid functionality to obtain the double hydrogen-bonded structure. This probably explains the exclusive ring-opening of isomannide, while the ether rings of isosorbide remain intact. In the case of isosorbide, the unreacted OH-group would point in the wrong direction, preventing hydrogen-bond formation with the carbonyl oxygen of the succinic acid residue.

Although the proposed reaction scheme (Scheme 3-2) affords polyester chains with a higher number of hydroxyl end-groups and, thus, an enhanced average functionality of the polyester resin, this reaction is considered to be detrimental to the performance of the resulting coating system. Apart from the branched structures, this side-reaction also seems to lead to cross-linked structures, as evidenced by the partial insolubility of this polyester.

Semi-crystallinity of isoidide- and isomannide-based polyesters

Another interesting feature of the II and IM based polyesters is that they are semi-crystalline materials, in contrast to the amorphous polyesters based on isosorbide. This was also observed by other groups. For poly(isomannide succinate), prepared from IM and succinyl dichloride in the melt at 180 ºC, a $\overline{M}_n$ of 10,000 g/mol (PDI = 1.7), a T_m of 175 ºC and a T_g of 75 ºC were reported.[12,32] Interestingly, no mention was made of the instability of IM under these reaction conditions. IM and II-based polyesters prepared using sebacoyl chloride as the activated dicarboxylic acid were also reported to be semi-crystalline and, in addition, these materials proved to be less susceptible to degradation by enzymes than IS-based polyesters, which was claimed to be due to steric hindrance (in the case of IM-based polyesters) as well as to the semi-crystalline character of these polyesters.[17] Also in semi-aromatic polyesters prepared from IS, II and IM combined with 2,3-diethoxyterephthaloyl dichloride, semi-crystallinity was only observed for the II- and the IM-based polymers.[10]

The melting temperatures of polyesters **2a/b** and **3** could not be determined from the second heating curve of the DSC thermogram after cooling at 10 ºC/min, since these materials seem to crystallize only slowly from the melt. Similar observations were made for poly(1,4:3,6-dianhydrohexitol terephthalate)s.[33] In general, crystallization of these polyesters occurs more easily from solution. When cooling at a lower rate (i.e. 2 ºC/min), on the other hand, broad crystallization exotherms and clear melting peaks were observed, also in the second heating curve (measured at a heating rate of 10 ºC/min). For example, the thermograms of polyester **2b** have a broad exothermic crystallization peak in the first heating curve (between 100 and 140 ºC), the second heating curve (between 100 and 160 ºC, Figure 3-6, **A**) and the cooling curve (from 140 ºC down to the T_g at approximately 64 ºC). The crystallization exotherms in both heating curves are almost directly followed by relatively sharp melting endotherms, having a maximum at 177.7 ºC in the second heating curve. Plot **B** in Figure 3-6 is the second heating curve of polyester **3**, demonstrating that this material is also a semi-crystalline polymer with a melting trajectory between 130 and 160 ºC (peak maximum = 147.5 ºC). No clear crystallization exotherms are observed in this case. At this lower cooling rate of 2 ºC/min, the determined value for the T_g of polyester **3** deviates slightly from the value presented in Table 3-1, determined at 10 ºC/min.

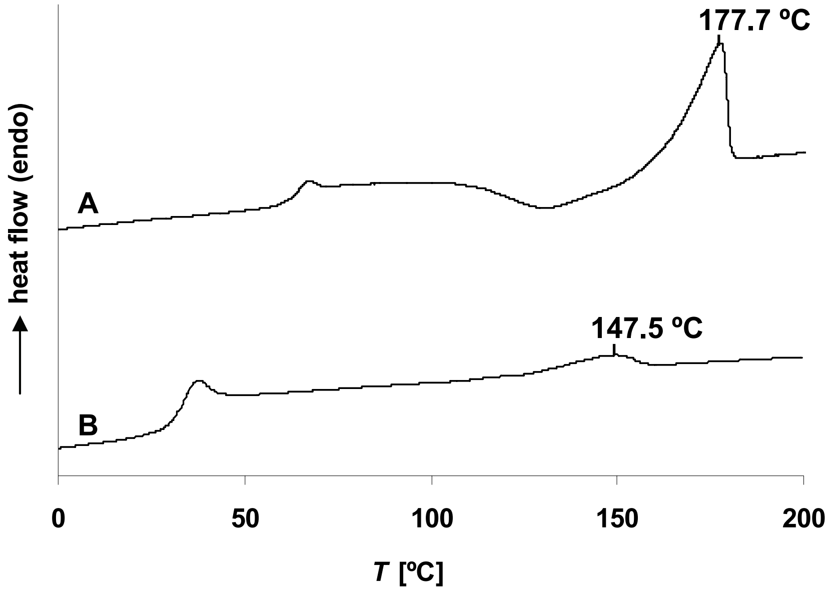


Figure 3-6. Second heating curves of the DSC thermograms of polyesters **2b** (**A**) and **3** (**B**), measured at a cooling rate of 10 ºC/min after cooling at 2 ºC/min.

In powder coating applications, the resins are mostly amorphous polyester glasses. Even though most of these polymers are usually capable of crystallizing to some extent, they are processed in such as way that crystallization does not have time to occur. This is done to prevent high melting material from being formed, since this might give problems with reduced flow during coating application. The DAH-based polymers presented in this chapter are also semi-crystalline, but crystallization from the melt is relatively slow and, often, T_m is considerably lower than T_{cure}, so no problems are expected during powder coating application.

The copolyesters based on isoidide and isomannide, described in this paragraph, are semi-crystalline polymers, in contrast to the amorphous isosorbide-based materials. The differences in reactivity between the two types of hydroxyl-groups of isosorbide seem to be confirmed by the reactivities of isoidide and isomannide in melt polycondensations with dicarboxylic acids. While isoidide and isosorbide appear to be stable under the applied reaction conditions, the ether rings of isomannide are susceptible to ring-opening at high temperatures.

3.3.3 Linear and branched terpolyesters based on isoidide and isomannide

In order to extend the comparison between IS-based polymers and those synthesized using isoidide (II) and isomannide (IM), terpolyesters were prepared by introducing several comonomers (Table 3-2). These polycondensations were carried out following a fixed synthetic procedure, with respect to reaction time and temperature.

Table 3-2. Terpolyesters based on isoidide and isomannide.

entry	**feed composition**	**composition (NMR)**	T_g **[ºC]**	T_m [2] **[ºC]**	$\overline{M}_n$ [3] **[g/mol]**	$\overline{M}_w$ [3] **[g/mol]**	***PDI*** [3]
			isoidide-based terpolyesters				
4	SA/II/2,3-BD [1:0.92:0.23]	SA/II/2,3-BD [1:0.89:0.14]	57.9	151.3	6700	13600	2.0
5	SA/II/1,3-PD [1:0.92:0.23]	SA/II/1,3-PD [1:0.82:0.23]	43.7	136.9	5900	12000	2.0
6a	SA/II/GLY [1:1.08:0.06]	SA/II/GLY [1:0.98:0.06]	63.4	164.8	6200	21500	3.4
6b [4]	SA/II/GLY [1:1.08:0.08]	SA/II/GLY [1:0.98:0.06]	42.4	~145 [5]	2200	4800	2.2
7	SA/II/TMP [1:1.1:0.1]	SA/II/TMP [1:1.03:0.1]	39.8	n/a [5]	5200	17800	3.4
			isomannide-based terpolyesters				
8	SA/IM/2,3-BD [1:0.82:0.24]	SA/IM/2,3-BD [1:0.86:0.2]	59.3	119.4	2300	8000	3.3
9	SA/IM/GLY [1:1.08:0.08]	SA/IM/GLY [1:0.98:0.06]	45.1	140.7	4200	15400	3.7

[1] SA = succinic acid, II = isoidide and IM = isomannide, 2,3-BD = 2,3-butanediol, 1,3-PD = 1,3-propanediol, GLY = glycerol, TMP = trimethylolpropane.

[2] The melting temperatures were determined from the second heating curve of the DSC experiments (after cooling at 2 ºC/min), except for entries **4** and **6a** of which the T_ms were determined from the first heating curve.

[3] Determined using SEC in HFIP, using PMMA standards.

[4] Resin **6b** was prepared on a 350 g scale.

[5] Faint, broad transitions were observed.

Terpolyesters based on II were colorless to pale yellow materials, while IM-based terpolyesters were yellow to light brown. The isomannide-based terpolyester **8** was only partially soluble in THF, $CDCl_3$ and HFIP. Also, the *PDI* of the soluble part of entry **8** is rather high for a linear polyester, which also suggests branching or cross-linking. This was confirmed by the MALDI-ToF-MS spectrum of entry **8**, which shows signals at masses attributed to chains containing ring-opened IM-moieties, as was already observed for poly(isomannide succinate). These peaks are absent in the MALDI-spectra of the corresponding IS- and II-based terpolyesters.

In general, the molecular weights of the II-based polymers are significantly higher than those of the soluble parts of the IM-based materials with a similar composition (e.g. compare resins **4** and **8** or **6a** and **9**). From the ratio in which the different monomers are built-in into the polyesters **4** and **5**, it appears that II is less reactive than 1,3-PD (as expected), but more reactive than 2,3-BD. Isomannide also appears to be built-in into the polyester chain more efficiently than 2,3-butanediol. The terpolyesters **4-9**, including the branched materials, are semi-crystalline, judging from the melting peaks observed during the first and in most cases also the second heating curves of their respective DSC thermograms. The melting temperatures of the crystalline fractions of these materials were found to decrease upon the decrease of the isoidide or isomannide content. The T_gs of all the materials presented in Table 3-2 are in the right range for powder coating application. To illustrate the effect of adding a trifunctional monomer, such as the biobased triol glycerol, the MALDI-ToF-MS spectrum of resin **6b** is shown in Figure 3-7. In addition, the titration data, given in Table 3-3, show the relatively high hydroxy-values (*OHV*) of these branched polyesters.

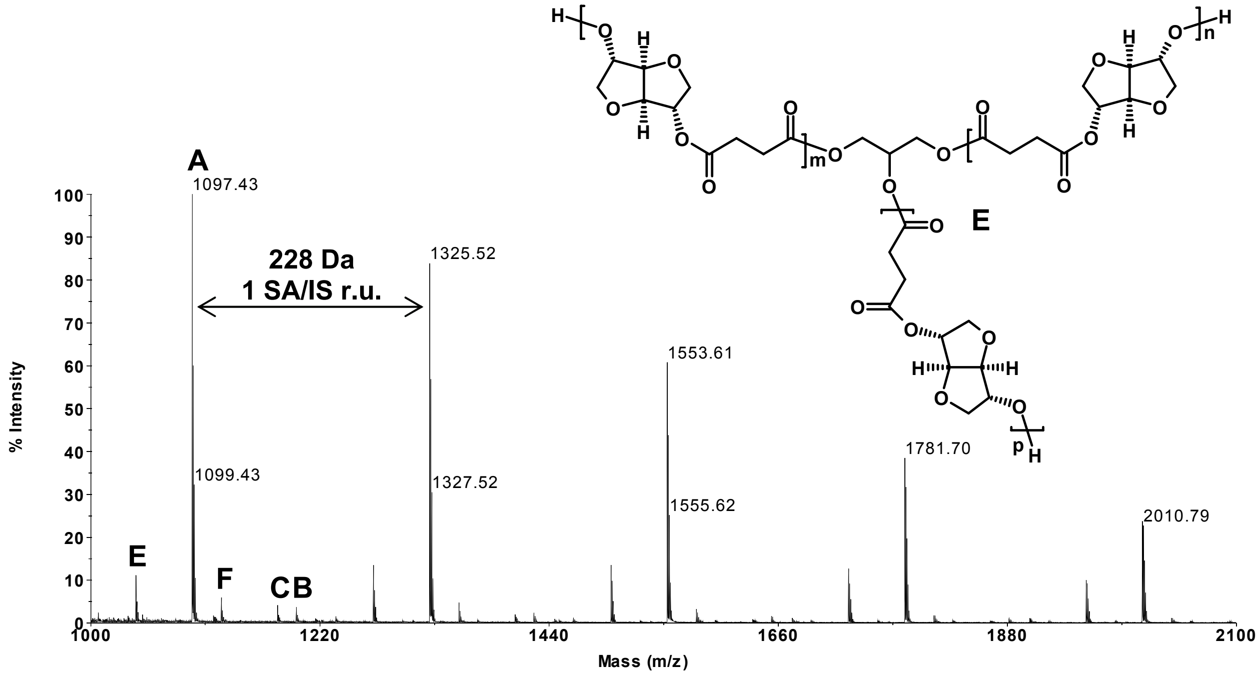


Figure 3-7. Section of the MALDI-ToF-MS spectrum of terpolyester **6b**, a poly(isoidide-*co*-glyceride succinate). The following species can be distinguished: (**A**) linear chains with two hydroxyl end-groups; (**B**) linear chains with one hydroxyl and one carboxylic acid end-group; (**C**) cyclic chains; (**E**) branched chains with three hydroxyl end-groups, containing one glyceride residue (see inset scheme); (**F**) cyclic chains containing one glyceride residue, with one hydroxyl end-group.

According to Figure 3-7, polyester **6b** contains linear as well as branched chains, having two or three hydroxyl end-groups, respectively. The intensities of the peaks in this MALDI-spectrum do not give quantitative information concerning their relative amounts.[34]

3.3.4 Curing and coating properties

Formulations and properties of solvent-cast coatings

Coating formulations were prepared using the conventional polyisocyanate curing agents mentioned in Chapter 2 (Scheme 2-4) of this thesis. Due to the limited availability of isomannide and isoidide, these coatings were all applied from NMP solution, requiring less material than powder coating application. The amount of cross-linker added to the polyester resin was calculated on the basis of the OH-values determined by titration and a slight molar excess of cross-linker (0.05) was used. Only one formulation, based on poly(isoidide-*co*-glyceride succinate) **6b**, was evaluated as a powder coating resin. The coatings described here are hard (they have König hardnesses of around 200 seconds) and their average film-thicknesses are approximately 40 +/- 4 μm.

Table 3-3. Coatings based on hydroxy-functional isoidide- and isomannide-based polyesters.

film	resin	*OHV / AV* [mg KOH/g]	curing agent [1]	T_{cure} [ºC]	t_{cure} [min]	coating T_g [ºC]	acetone [2] resistance	impact test [2] [1 kg, 100 cm]
isoidide-based poly(ester urethane) networks								
F1	4	30.8 / 6.0	I	200	30	65.5	-	-
F2	4	30.8 / 6.0	II	180	20	59.4	+/-	+/-
F3	5	59.2 / 4.6	II	180	20	45.5	+	+
F4	6b	97.2 / 7.8	I	200	30	69.5	+	-
F5	6b	97.2 / 7.8	II	180	20	75.8	+	+
F6	7	104 / 5.0	I	200	30	64.9	+/-	-
F7	7	104 / 5.0	II	180	20	57.8	+	+
F8	7	104 / 5.0	III	200	20	n.d.	+	+
isomannide-based poly(ester urethane) networks								
F9	8	28.6 / 10.2	II	180	20	n.d.	-	-
F10	9	68.4 / 9.4	I	200	30	n.d.	+/-	-
F11	9	68.4 / 9.4	II	180	20	n.d.	+/-	-

[1] **I** = caprolactam-blocked IPDI-based polyisocyanate, **II** = HMDI-based polyisocyanate, **III** = caprolactam-blocked HMDI-based polyisocyanate (see Scheme 2-4). Curing reactions using blocked polyisocyanates were catalyzed with dibutyltin dilaurate.

[2] + = good, +/- = moderate, - = poor.

The appearance of coatings based on isoidide was better than of those based on isomannide, with respect to color. All coatings were clear and transparent, but the isomannide-based films are more strongly discolored. Upon evaporation of the solvent (NMP) at room temperature, some of the resins crystallized from solution, leading to opaque films before curing. At curing temperature, the films became transparent and stayed transparent due to the formation of a cured network, preventing crystallization upon cooling of the cured system. The relatively low melting crystalline domains present in these terpolyesters may be useful in the sense that the powder paint might be processed and stored as a semi-crystalline material, leading to a better storage stability. During the coating application, the crystalline domains will melt (i.e. $T_{cure} > T_m$) and flow out without negative effects on film formation. As expected, the T_gs of the formed poly(ester urethane) networks are higher than the T_gs of their respective base resins. The increase in T_g during curing is significantly larger for the branched polyesters **6b** and **7** (ΔT_g between 18 and 33 ºC) than for the linear polyesters **4** and **5** (ΔT_g between 1.5 and 7.6 ºC), which is caused by the significantly higher polyurethane content and a more efficient build-up of the polymeric network when curing branched resins. Especially the presence of the rigid IPDI-based curing agent **I** leads to a strong increase in T_g. The linear resins perform less well than the branched materials (as was also observed for IS-based poly(ester urethane)s in Chapter 2), with one exception, coating **F3**. In general, it was observed that resins containing 1,3-PD instead of 2,3-BD perform better. This is thought to be due to the higher reactivity of the former diol, leading to a higher conversion and better functionalization as well as an enhanced average reactivity of the hydroxyl end-groups of the polyesters containing 1,3-PD. As was already noticed for isosorbide-based systems, curing with the IPDI-based curing agent **I** does not yield coatings with good properties, especially with respect to mechanical performance. In the isoidide-based formulation **F4**, however, it seems to perform slightly better than in the comparable isomannide-based systems **F10**. This may indicate that the reaction between the bulky isocyanate moiety and the sterically hindered *endo*-oriented OH-groups of isomannide proceeds with more difficulty compared to the same curing reaction with the *exo*-oriented OH-groups of isoidide. On the other hand, these results may also suggest that the isomannide-based system is intrinsically more brittle than its isoidide-based counterpart. In general, coatings from isomannide-containing polyesters are not sufficiently stable, with respect to solvent contact and mechanical deformation. This may be partly caused by the relatively high acid values of the polyesters **8** and **9**, causing less efficient network formation.

Thermal properties of II-based powder paints and coating performance

Resin **6b** was formulated for powder coating application. This powder paint **F12** had the following composition: resin **6b**, curing agent **I** (1 molar equivalent of NCO relative to the amount of OH-groups), dibutyltin dilaurate (1 wt%), benzoin (0.75 wt%, degassing agent) and Resiflow PV5 (1.5 wt%, acrylic resin, used as flow agent). Figure 3-8 shows the plots of the shear modulus (*G'*) and the temperature (*T*) versus time (*t*) for formulations **F12**. A conspicuous feature in Figure 3-8 is the large increase of the shear modulus between 100 and 120 ºC (or: 15 and 25 minutes) and its subsequent decrease between 120 and 150 ºC. This increase is probably the result of the partial recrystallization (and subsequent melting) of the isoidide-based polyester resin upon slow heating (the heating rate during these experiments was 2 ºC/min). To verify this hypothesis, DSC measurements were performed to determine the thermal transitions of the resin **6b** as well as the formulation **F12**. In the thermogram of resin **6b,** a small endotherm was observed between 138 and 150 ºC (peak maximum 144.6 ºC, see Table 3-2), indicating the melting of a crystalline phase. The DSC heating curve of **F12** (Figure 3-9) also clearly shows an endothermic phenomenon, between 110 and 135 ºC (peak maximum 127.6 ºC). The fact that this melting range is somewhat lower for this powder paint formulation than for resin **6b** is caused by the presence of curing agent and the other additives, acting as plasticizers and hampering the crystallization process to some extent. These additives also obviously cause the significantly lower T_g of **F12** (T_g = 29.2 ºC) compared to **6b** (T_g = 42.4 ºC). In addition to the melting endotherm, a faint crystallization exotherm can be observed between approximately 90 and 115 ºC. These results indicate that the increase of the modulus in Figure 3-8 is indeed caused by crystallization of the polyester resin during slow heating of **F12**.

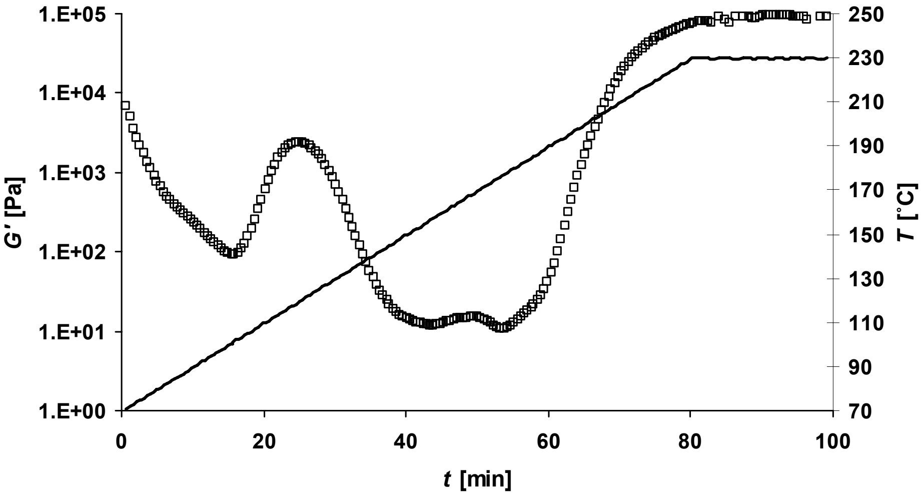


Figure 3-8. Shear modulus G' (□) and temperature T (▬) as functions of time t during isoidide-based poly(ester urethane) network formation, formulation **F12**. The temperature sweep was performed at 2 ºC/min.

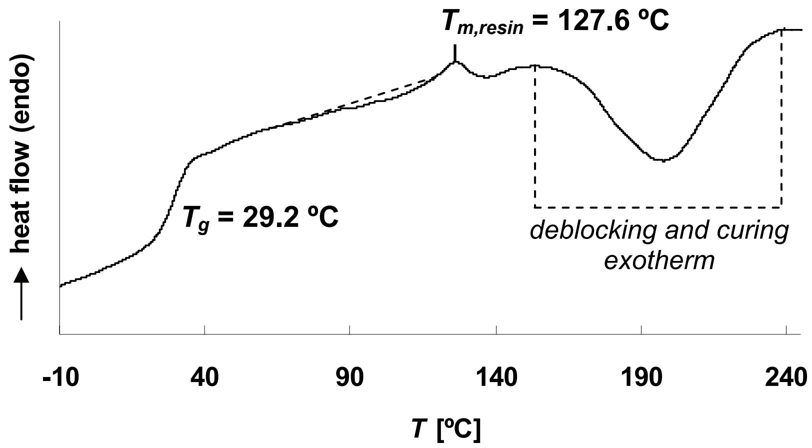


Figure 3-9. DSC thermogram (heating curve) of the curing reaction of formulation **F12**.

Between 145 and 175 °C, a minimum is observed in the shear modulus in Figure 3-8. Above 175 °C, the modulus increases rapidly up to a plateau value of approximately 90 MPa (corresponding to a cross-link density of ν_e = 21.5 mol/m^3). This plateau modulus is significantly higher than the modulus (55 MPa) determined for the isosorbide-based powder paint discussed in Chapter 2 (formulation **F13**). The two resins used for the isosorbide- and the isoidide-based powder formulation have similar molecular weights and the *OHV* of the isosorbide-based polyester is 10 % higher than that of the isoidide-based polymer. The higher plateau modulus of formulation **F12** indicates that a denser network was formed. In other words, the curing reaction appears to be more efficient in the isoidide-based system. This conclusion is supported by the slightly better solvent resistance and significantly better impact resistance of system **F12** compared to its isosorbide-based counterpart. The powder coating obtained by curing **F12** is a glossy, transparent film that is increasingly discolored when cured at temperatures above 180 °C, especially at temperatures higher than 210 °C.

3.4 Conclusions

In this chapter, we have shown the differences in reactivity between the *exo*- and the *endo*-oriented OH-groups of the 1,4:3,6-dianhydrohexitols. In melt polycondensations using dicarboxylic acids, *exo*-oriented hydroxyls are more reactive, which means that co- and terpolyesters based on isoidide can be synthesized at lower reaction temperatures and/or during shorter processing times. In contrast to isosorbide-based polyesters, the polymers prepared using isoidide and isomannide are semi-crystalline materials. Isomannide-based polyesters show considerably more discoloration than isosorbide- and isoidide-based polymers, which is partially due to the lower purity of this monomer and side-reactions occurring during the polymerization. In addition, branching and cross-linking are thought to occur due to the ring-opening of the ether ring(s) of the isomannide-residues present in the polyester chains. Isosorbide and especially isoidide are therefore considered to be more suitable monomers for this type of polymer synthesis than isomannide. Terpolyesters containing isoidide have suitable thermal properties as well as sufficient functionality for thermoset coating applications. Coatings obtained by curing linear as well as branched isoidide-based polyesters are chemically and mechanically resistant.

References

(1) Szeja, W. *J. Chem. Soc., Chem. Commun.* **1981**, *5,* 215.
(2) Fleche, G.; Huchette, M. *Starch* **1986**, *38,* 26.
(3) Buck, K. W.; Duxbury, J. M.; Foster, A. B.; Perry, A. R.; Webber, J. M. *Carbohydr. Res.* **1966**, *2,* 122.
(4) Abenhaim, D.; Loupy, A.; Munnier, L.; Tamion, R.; Marsais, F.; Queguiner, G. *Carbohydr. Res.* **1994**, *261,* 255.
(5) Cecutti, C.; Mouloungui, Z.; Gaset, A. *Bioresour. Technol.* **1998**, *66,* 63.
(6) Brown, C.; Marston, R. W.; Quigley, P. F.; Roberts, S. M. *J. Chem. Soc., Perkin Trans.* **2000**, *1,* 1809.
(7) Le Lem, G.; Boullanger, P.; Descotes, G.; Wimmer, E. *Bull. Soc. Chim. Fr.* **1988**, *3,* 567.
(8) Stoss, P.; Hemmer, R. *Adv. Carbohydr. Chem. Biochem.* **1991**, *49,* 93.
(9) Cope, A. C.; Shen, T. Y. *J. Am. Chem. Soc.* **1956**, *78,* 3177.
(10) Storbeck, R.; Rehahn, M.; Ballauff, M. *Makromol. Chem.* **1993**, *194,* 53.
(11) Storbeck, R.; Ballauff, M. *Polymer* **1993**, *34,* 5003.
(12) Okada, M.; Okada, Y.; Tao, A.; Aoi, K. *J. Appl. Polym. Sci.* **1996**, *62,* 2257.
(13) Kricheldorf, H. R.; Berghahn, M.; Probst, N.; Gurau, M.; Schwarz, G. *React. Funct. Pol.* **1996**, *30,* 173.
(14) Lin, Q.; Pasatta, J.; Long, T. E. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41,* 2512.
(15) Schwarz, G.; Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34,* 603.
(16) Thiem, J.; Luders, H. *Polym. Bull.* **1984**, *11,* 365.
(17) Okada, M.; Tsunoda, K.; Tachikawa, K.; Aoi, K. *J. Appl. Polym. Sci.* **2000**, *77,* 338.
(18) Thiem, J.; Bachmann, F. *Makromol. Chem.* **1991**, *192,* 2163.
(19) Chatti, S.; Bortolussi, M.; Loupy, A.; Blais, J. C.; Bogdal, D.; Roger, P. *J. Appl. Polym. Sci.* **2003**, *90,* 1255.
(20) Beldi, M.; Medimagh, R.; Chatti, S.; Margue, S.; Prim, D.; Loupy, A.; Delolme, F. *Eur. Polym. J.* **2007**, *43,* 3415.
(21) Kricheldorf, H. R. *J.M.S. - Rev. Macromol. Chem. Phys.* **1997**, *C37,* 599.
(22) Parr, R. G.; Yang, W. in *Density functional theory of atoms and molecules* R. G. Parr; W. Yang, Editors. 1989, Oxford Science Publications: Oxford.
(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98,* 5648.
(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37,* 785.

(25) Hehre, W. J.; Radom, L.; Schelyer, P. V. R.; Pople, J. A. *Ab initio molecular orbital theory*: John Wiley & Sons: New York, 1986.

(26) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80,* 3265.

(27) Krisnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72,* 650.

(28) Brimacombe, J. S.; Foster, A. B.; Stacey, M.; Whiffen, D. H. *Tetrahedron* **1958**, *4,* 351.

(29) Ejjiyar, S.; Saluzzo, C.; Amouroux, R.; Massoui, M. *Tetrahedron Lett.* **1997**, *38,* 1575.

(30) Burgey, C. S.; Vollerthun, R.; Fraser-Reid, B. *Tetrahedron Lett.* **1994**, *35,* 2637.

(31) Sakairi, N.; Wang, L.-X.; Kuzuhara, H. *J. Chem. Soc., Perkin Trans.* **1995**, *4,* 437.

(32) Okada, M.; Okada, Y.; Aoi, K. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33,* 2813.

(33) Thiem, J.; Luders, H. *Starch* **1984**, *36,* 170.

(34) Hunt, S. M.; Sheil, M. M. *Eur. Mass Spectr.* **1998**, *4,* 475.

4

Biobased polymers with enhanced functionality by incorporation of citric acid

Abstract

Citric acid (CA) was evaluated as a renewable functionality-enhancing comonomer in polyesters suitable for coating applications. A detailed study on the thermal stability of CA helped to determine the appropriate process conditions for the modification of biobased OH-functional linear polyesters. Model reactions of CA with several primary and secondary alcohols and diols, including 1,4:3,6-dianhydro-D-glucitol (isosorbide), 1,4:3,6-dianhydro-L-iditol (isoidide) and 1,4:3,6-dianhydro-D-mannitol (isomannide), revealed that titanium(IV) n-butoxide-catalyzed esterification reactions involving these compounds proceed at relatively low temperatures, often via anhydride intermediates. The facile anhydride formation from CA at temperatures around CA's melting temperature (T_m = 153 ºC) proved to be crucial in modifying and activating sterically hindered secondary hydroxyl end-groups. OH-functional polyesters were reacted with CA in the melt between 150 and 165 ºC, yielding slightly branched carboxylic acid-functional materials. Only small amounts (2 - 3 % of the total amount of CA) of unsaturated structures, such as aconitic acid species or their anhydrides were formed. The carboxylic acid/epoxy curing reaction of the acid-functional polymers was simulated with a monofunctional glycidyl ether, demonstrating that most of the acid end-groups esterify with this epoxy compound. In addition, the possibility of anhydride formation during curing at the chain ends of the modified polyesters can be beneficial with respect to the cross-link density of the cured system. The curing behaviour of these systems was investigated with DSC and rheological experiments. The CA-modified polyesters were applied as coatings, using several conventional cross-linking agents and different application techniques. The formulations showed rapid curing, resulting in chemically and mechanically stable coatings. These results prove that CA is a very useful biobased monomer for the chemical modification of OH-functional polyesters.

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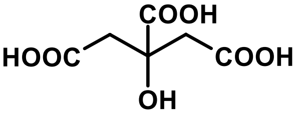
4.1 Introduction

In Chapters 2 and 3 of this thesis, aliphatic OH-functional co- and terpolyesters based on 1,4:3,6-dianhydrohexitols (DAHs) and succinic acid (SA) were described. Said materials have properties that meet the requirements for thermosetting coating systems. In industry, hydroxy-functional as well as carboxylic acid-functional polymers are used to afford cured polymeric coatings. In order to obtain a fully cured network, these polymers are designed to have at least two reactive groups per chain. For hydroxy-functional systems, we have shown that monomers such as glycerol and trimethylolpropane are suitable to increase polyester functionality to sufficient extents. In conventional polyester resins, monomers such as trimellitic anhydride and/or trimethylolpropane are used to synthesize branched carboxylic acid-functional polymers.[1] When trying to synthesize carboxylic acid-functional materials based on isosorbide (IS), some difficulties were encountered. The limited reactivity of the isosorbide end-groups restricts the conversion of polyester chains into carboxylic acid-functionalized polymers. We expected that citric acid (CA, Scheme 4-1), a polyfunctional biobased monomer, might be a useful material to enhance the carboxylic acid functionality of these DAH-based polyesters. As such, CA can be seen as an aliphatic and renewable alternative for trimellitic anhydride.



Scheme 4-1. Chemical structure of citric acid (or: 2-hydroxy-1,2,3-propanetricarboxylic acid).

Citric acid is produced commercially via fermentation of glucose or sucrose, with an approximate annual production of 7 x 10^5 tons.[2] CA has two primary and one tertiary carboxylic acid groups, the latter obviously being less reactive than the primary acid groups. In addition, it contains a sterically hindered tertiary hydroxyl group. This low cost monomer is a solid at room temperature and has a melting temperature of 153 ºC.[3]

CA has been utilized by different authors to esterify or cross-link starch, cellulose fibers or corn fibers.[4-10] Several publications describe the synthesis of biodegradable polyester networks based on CA, in combination with polyol moieties such as glycerol, gluconolactone, sorbitol, linear aliphatic alcohols and poly(ethylene glycol)s.[3,11-15] Reaction temperatures vary, but are usually in the range between 120 and 180 ºC. Acid-functional, water-soluble polyester resins based on citric acid and alkylene oxides (e.g. propylene oxide) have been synthesized at 150 ºC. These polyesters were cured with melamine resins.[16] Low T_g copolyesters of succinic acid and 1,4-butanediol combined with CA, present as a comonomer during the polycondensation carried out at 170 – 200 ºC, were also described.[17]

As opposed to many of the papers described above, we do not aim to use CA itself as a cross-linking agent, but rather as a polyfunctional modifier to transform polyesters with OH-functionalities of moderate reactivity into acid-functional polymers. Ideally, by reacting with only one of its carboxylic acid groups, CA would be introduced at the polyester chains ends. The modification with CA should not lead to cross-linking by itself and the polyester resin should have appropriate flow properties at T_{cure} as well as sufficient functionality to contribute to the network formation upon curing. The remaining two carboxylic acid groups of CA are to react with the curing agent during the final step of the powder coating process, to form the completely cross-linked network. Due to the high polymerization temperatures (up to 230 ºC) and the limited thermal stability of CA, we cannot introduce CA during the initial bulk synthesis of the OH-functional polyester. In addition, solvents are not to be used in the preparation of powder coatings resins, so modification in solution is not an option either.

In this chapter, citric acid is evaluated as a functionality-increasing agent for biobased polyesters. First of all, the thermal stability of CA during polyester modification and curing was assessed. Reactions of CA with several primary alcohols and secondary diols were investigated using NMR- and FTIR-spectroscopy with the aim to gain more insight into the mechanism of the chemical modification of OH-functional polyesters with CA in the melt. In addition, the subsequent curing reaction of the CA-modified polymers with epoxy cross-linkers was studied in detail. Finally, several coating formulations were prepared and evaluated with respect to curing chemistry, rheological behavior as well as chemical and mechanical resistance upon curing of solvent cast and powder coated films.

4.2 Experimental section

Materials. Isosorbide (IS) (polymer grade Polysorb® P, 98.5+ %) and isoidide (II) (99.8 %) were obtained as gifts from Roquette Frères. Isomannide (IM) (97+ %) was a gift from Agrotechnology and Food Innovations. Citric acid (anhydrous, 99+ %), citric acid-1,5-$^{13}C_2$ (99 atom% ^{13}C), citric acid-2,4-$^{13}C_2$ (99 atom% ^{13}C), cis-aconitic anhydride, trimethyl citrate, 1-butanol, *tert*-butyl glycidyl ether, triglycidyl isocyanurate (TGIC) and ethyltriphenylphosphonium bromide were purchased from

Aldrich. Succinic acid and titanium(IV) n-butoxide were bought from Acros Organics. 1,4-butanediol was obtained from Merck. All solvents were purchased from Biosolve. DMSO-d_6 was bought from Campro Scientific. N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide (trade name: Primid XL-552) was obtained as a gift from EMS Chemie, Araldite PT912 (a mixture of triglycidyl trimellitate and diglycidyl terephthalate) was bought from Huntsman. Irganox HP2921, a mixture of phenolic and phosphonic anti-oxidants, was a gift from Ciba Specialty Chemicals. Flow agent Resiflow PV5 was purchased from Worlée Chemie, benzoin was obtained from DSM Special Products. Santowhite (stabilizer) was obtained from Monsanto and TiO_2 was bought from Kronos. All chemicals were used as received.

Reactions of CA with 1-butanol or several diols. CA was reacted with 1-butanol and several diols according to the following procedure, described for isoidide: citric acid (15.93 g, 83 mmol), isoidide (6.06 g, 41 mmol), $Ti(OBu)_4$ (0.02 mol% rel. to isoidide) and Irganox HP2921 (0.16 g) were weighed into a 50 mL three-neck round-bottom flask. The flask was fitted with a Vigreux column and a Dean-Stark type condenser to collect the condensation product. An inert atmosphere was created by repeated vacuum / inert gas flushing cycles. Afterwards, the system was left open under a continuous inert gas flux, avoiding the contact with oxygen. While stirring magnetically, the reaction mixture was heated by means of an oil bath to the required reaction temperature. Reaction times were measured from the moment a clear, homogeneous melt was obtained ($t = 0$). The maximum reaction temperature was 160 ºC.

CA-modification of hydroxy-functional polyesters. Previously synthesized linear OH-functional polyesters (Chapter 2 of this thesis), based on isosorbide and succinic acid, were reacted with CA to obtain polyesters with carboxylic acid end-groups. A typical example was performed as follows: 52.9 g of an OH-functional polymer ($\overline{M}_n$ = 2200 g/mol, acid value = 1.5 mg KOH/g, hydroxyl value = 65.0 mg KOH/g) and 0.1 molar excess of CA (calculated relative to the amount of OH-groups per gram of polyester sample, determined by titration) were charged to the reactor. The temperature was increased slowly up to 170 ºC (T_{max}), leading to a clear melt. After stirring under inert gas flush at atmospheric pressure for 2.5 hours, processing was continued in vacuo (typically between 5 and 10 mbar) for 3 hours. Subsequently, the clear melt was discharged from the reactor and left to cool. For NMR characterization, some experiments were performed on small scale, using the following ^{13}C-labeled CA compounds: citric acid-1,5-$^{13}C_2$ or citric acid-2,4-$^{13}C_2$.

Solvent casting and curing of carboxylic acid-functional polyesters. Carboxylic acid-functional polyesters were cured with triglycidyl isocyanurate (TGIC), N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide or a mixture of diglycidyl terephthalate (60 wt%) and triglycidyl trimellitate (40 wt%).[18,19] Curing from solution proceeds as described in the following example: a solution of 0.3 –

0.5 g of polyester and 1.05 molar equivalent of the cross-linker (calculated from COOH-value, determined by titration) in 1 mL N-methyl-2-pyrrolidone (NMP) was prepared. Subsequently, a wet film of approximately 250 μm thickness was applied onto the aluminum substrate. The film was left to dry at room temperature, followed by curing at 180 ºC during 10 - 20 minutes under nitrogen. Curing reactions involving TGIC were catalyzed by addition of 0.5 wt% (relative to the amount of solid polyester resin) of ethyltriphenylphosphonium bromide. Coatings were also applied through a powder coating process, which typically proceeds as follows: a CA-modified polyester was co-extruded with the curing agents in a 1 to 1 ratio at approximately 90 ºC, using a twin-screw mini-extruder. In addition, 1.5 wt% flow agent (Resiflow PV5, Worlee) and 0.75 wt% degassing agent (benzoin) were added to the formulation. The obtained extrudate was ground to particles smaller than 90 μm and powder coated onto an aluminum gradient panel using corona spraying, followed by curing in a gradient oven at temperatures ranging from 100 to 250 ºC.

Measurements. SEC analysis was carried out using a set-up equipped with a Shimadzu LC-10AD pump and a WATERS 2414 differential refractive index detector (at 35 ºC). Injections were done by a MIDAS auto-injector, the injection volume being 50 μL. PSS (2 × PFG-lin-XL, 7 μm, 8 × 300 mm, 40 °C) columns were used. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was used as eluent at a flow rate of 1.0 mL/min. Calibration curves were obtained using PMMA standards. Data acquisition and processing were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software. ^{1}H NMR and ^{13}C NMR (proton decoupled) spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer, DMSO-d_6 was used as the solvent (unless stated otherwise). Signal assignments of CA anhydride derivatives were partly determined by comparison with the ^{13}C NMR spectrum of *cis*-aconitic anhydride (obtained commercially), which also contains peaks caused by *trans*-aconitic anhydride, due to the spontaneous isomerization of *cis*-aconitic anhydride.[20,21] The thermal stabilities of polymer samples were determined using a Perkin Elmer Pyris 6 TGA apparatus. Approximately 10 mg of polymer was heated from 40 ºC to 700 ºC at a heating rate of 10 ºC/min under a N_2 flow of 20 mL/min. Results were analyzed using Pyris 4.01 software. Glass transition temperatures were determined by DSC measurements, carried out with a DSC Q100 from TA Instruments. Curing of powder coating formulations was also followed by DSC, using a Perkin Elmer DSC Pyris 1 device, calibrated using indium and tin. The measurements were carried out at a heating rate of 10 ºC/min. Data acquisition was carried out using Pyris 7 software. Potentiometric titrations, used to determine acid and hydroxyl values, were carried out as reported in the Experimental section of Chapter 2. Attenuated Total Reflection Fourier-Transform Infrared spectrometry (ATR-FTIR) was performed on a Bio-Rad Excalibur FTS3000MX spectrophotometer. A golden gate set-up was used, equipped with a diamond ATR crystal. The resolution was 4 cm^{-1}. Dynamic Mechanical Analysis (DMA) was carried out using a TA Instruments AR1000-N Rheolyst rheometer, having a parallel plate geometry. Samples were prepared by compression molding (at 400 bar) of powder paint formulations at room temperature. Solid, opaque disks of approximately 500 μm thick were obtained. Temperature as well as time sweeps were performed, using the following parameter settings: temperature range = 70 - 250 ºC, temperature ramp rate = 2 ºC/min., strain = 1 %, frequency = 1 Hz (= 6.283 rad/s). Data acquisition was done with Rheology Advantage Instrument Control software, data analysis with Rheology Advantage Data Analysis software. Cross-linking and coating performance at room temperature were evaluated using several characterization methods: acetone rub test (solvent resistance test: the sample is rubbed with a cloth drenched in acetone. If no damage is visible after more than 150 rubs (i.e. 75 'double rubs'), the coating has good acetone resistance), reverse impact test (a rapid deformation test, performed by dropping a certain weight (in kg) on the back of a coated panel from a certain height (in cm), described in ASTM D 2794) and pendulum damping test (ASTM D 4366, to determine König hardness). The thicknesses of the obtained cured coatings were measured using a magnetic induction coating thickness measuring device (Twin-Check by List-Magnetik GmbH).

4.3 Results and discussion

The polyester resins described in the previous chapters mainly have secondary hydroxyl end-groups, since they are synthesized using an excess of the 1,4:3,6-dianhydrohexitol, relative to the diacid used. In Chapter 2, we have shown that it is not possible to make purely COOH-functional linear polyesters just by adding an excess of succinic acid during resin synthesis. Especially the *endo*-oriented hydroxyl groups of isosorbide and isomannide prove difficult to esterify to high conversions (and low acid concentrations). Only by using activated diacid species, such as succinic anhydride, it might be possible to synthesize polyester chains with predominantly carboxylic acid end-groups. However, the maximum functionality $\overline{F}_n$ obtainable by this method is $\overline{F}_n = 2$.

4.3.1 Thermal stability and reactivity of citric acid

For conventional, non-renewable polyesters, trimellitic anhydride, an aromatic, trifunctional carboxylic acid compound is often used as branching and carboxylic acid functionality enhancing agent. This monomer can be directly added during resin synthesis and can withstand the high temperatures (i.e. temperatures up to 250 ºC) reached during the production process. CA, however, generally cannot be added directly during polycondensation due to its limited thermal stability as CA is prone to dehydration and decarboxylation at elevated temperatures. These side-reactions start to take place at an appreciable rate above 180 ºC. One could think of using trimethyl citrate in the polycondensation or modification reaction, since this compound has a higher thermal stability (analogous to using dimethyl terephthalate in conventional polyester synthesis).[22] However, the aim is to make a polymer with free carboxylic acid groups at the chain end, which will not be obtained when using the trimethyl ester of CA.

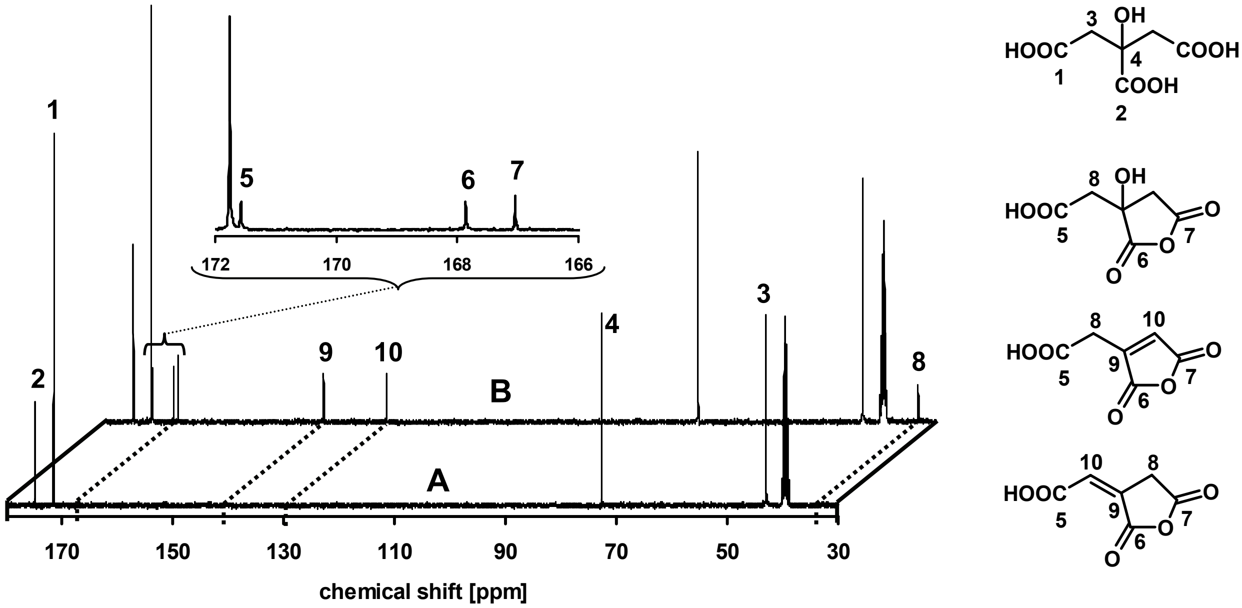
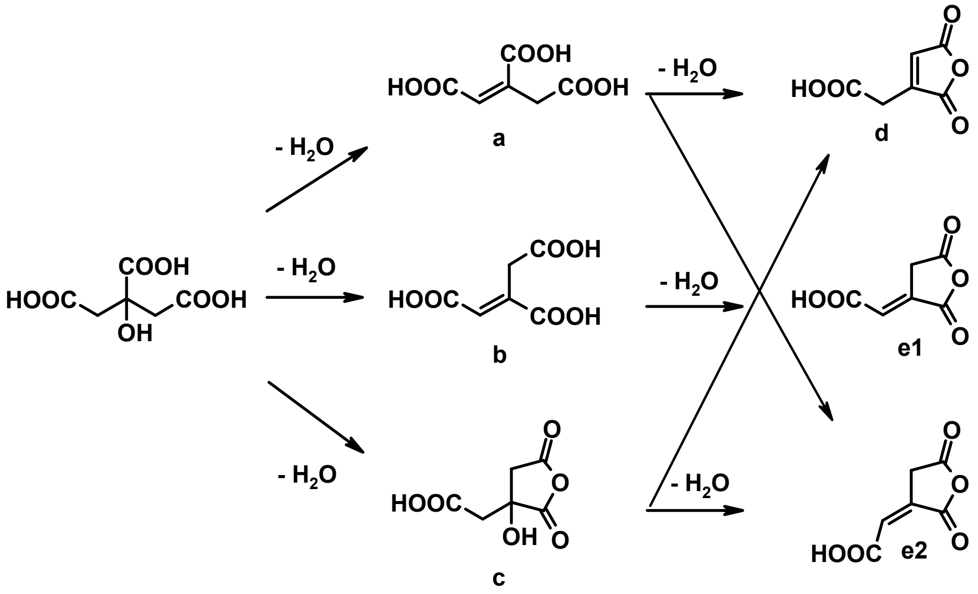


Figure 4-1. ^{13}C NMR spectra of (**A**) citric acid and (**B**) citric acid and degradation products after heat treatment of CA during 2 hrs at 180 °C, including possible structures and peak attributions.

Figure 4-1 shows the ^{13}C NMR spectra of CA before and after a heat treatment of 2 hours at 180 °C in the bulk under a slight argon purge. During this treatment, formation of water as well as of CO_2 (the gas flux was bubbled through an aqueous solution of calcium hydroxide) was observed, suggesting that both dehydration and decarboxylation took place. In the ^{13}C NMR spectrum of the thermal degradation product(s), a new aliphatic carbon signal appears at 33.2 ppm (C8). In addition, peaks at 129.3 ppm (C10) and 140.7 ppm (C9) can be assigned to olefinic carbon atoms. Finally, a signal attributed to carboxylic acid carbonyls is observed at 171.6 ppm (C5) and resonances corresponding to anhydride carbonyls are visible at 167.0 ppm (C7) and 167.9 ppm (C6) (see inset Figure 4-1). The first steps in the thermal degradation of CA are the formation of citric acid anhydride (Scheme 4-2, structure **c**) or the dehydration of the β-hydroxyl group to form *cis*- or *trans*-aconitic acid (**a** and **b**). Subsequently, these compounds can lose a second molecule of water, affording *cis*- or *trans*-aconitic (E/Z configurations) anhydrides (**d** and **e1**/**e2**). For a more extensive degradation scheme, see Appendix A, Scheme A-1.[7,11,23-25]



Scheme 4-2. Initial steps in the thermal degradation of citric acid, with: (**a**) *cis*-aconitic acid, (**b**) *trans*-aconitic acid, (**c**) citric acid anhydride, (**d**) *cis*-aconitic anhydride and (**e1**/**e2**) *trans*-aconitic anhydrides, E/Z configuration.[23,24]

Especially structures **a**, **b, d** and **e** correspond well to the observed signals in Figure 4-1, plot **B**, i.e. the three new carbonyl peaks, the two olefinic signals and the new aliphatic carbon signal. In Figure 4-1, these four structures are displayed with possible peak assignments. Peaks **6** and **7** show shifts which can correspond to carboxylic acids, anhydrides or ester carbonyls. Since only CA was used during the experiment, ester formation could only occur through the reaction of a CA moiety with the tertiary OH of another CA molecule. This is unlikely to occur at an appreciable rate.[26] It is therefore most probable that these signals are caused by acid and/or anhydride species formed from CA by dehydration.

The amounts of *cis*-aconitic acid/anhydride (11 %) and *trans*-aconitic acid/anhydrides (12 %) present in the sample upon thermal degradation were similar, as determined from ^{1}H NMR data. Other identified degradation products such as itaconic acid (~4 %), citraconic acid (~3 %) and 3-hydroxyglutaric acid (~2 %) or the corresponding anhydrides confirmed that decarboxylation had also taken place, but to a lesser extent than dehydration (Appendix A, Figure A-1). It should be noted that the aconitic derivatives, formed through dehydration, all contain three carboxylic acid equivalents (either as the free acid or as an anhydride), while the other degradation products formed through decarboxylation have two acid equivalents per molecule. Hence, partial thermal degradation of CA will only result in a somewhat lower functionality of the final resin (minimum: $\overline{F}_n = 2$), but will never lead to deactivated chains.

Deactivated chains can only be formed if CA degrades even further by losing more than one molecule of CO_2, which is very unlikely to happen at the conditions applied in these systems. To confirm the formation of anhydrides, ATR-FTIR spectra were recorded as a function of time at isothermal heating (170 ºC). In Figure 4-2, the spectra recorded at $t = 0$, $t = 2$ min., $t = 10$ min. and $t = 25$ min. are given.

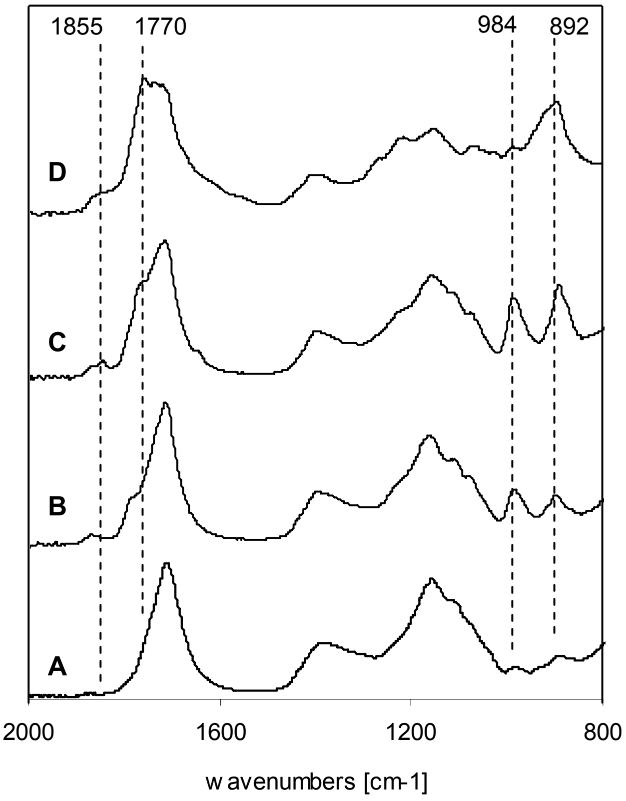
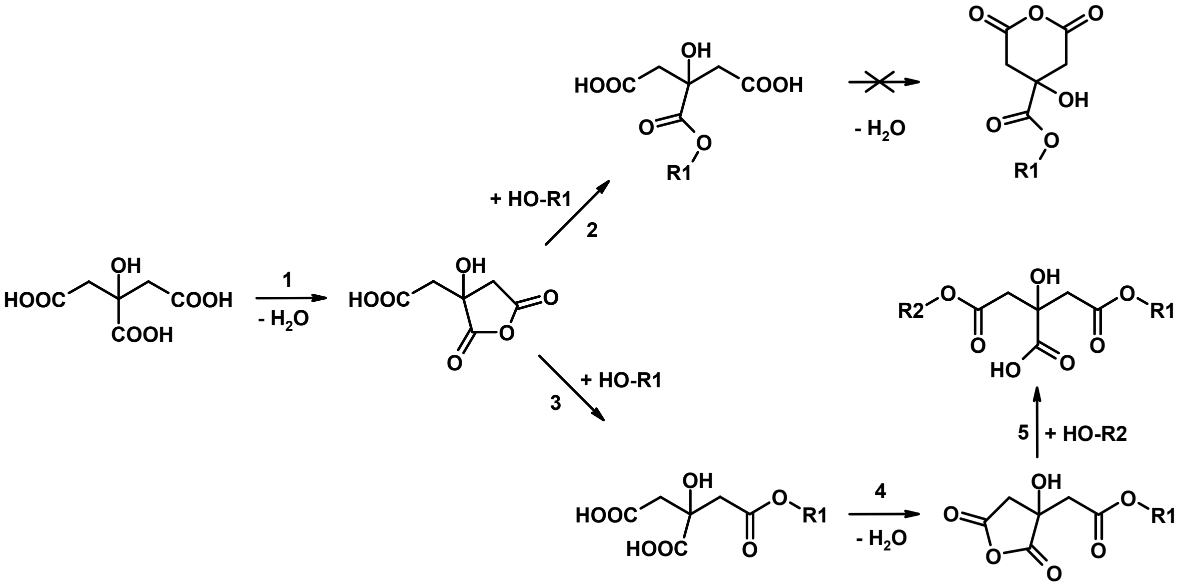


Figure 4-2. FTIR spectra of CA heated isothermally at 170 ºC at (**A**) $t = 0$, (**B**) $t = 2$ min., (**C**) $t = 10$ min. and (**D**) $t = 25$ min.

At $t = 0$ (**A**), there is a strong and relatively sharp absorbance at 1710 cm^{-1}, due to the hydrogen-bonded CA carboxylic acid carbonyls. In time, the peak maximum shifts to 1735 cm^{-1}, attributed to free carboxylic acid carbonyls. Simultaneously, the development of two bands at 1855 and 1770 cm^{-1} is observed, which are characteristic for the symmetric and the asymmetric stretching vibrations of cyclic anhydrides, respectively.[27,28] At the same time, two bands appear at 984 and 892 cm^{-1}, caused by the stretching modes of the C-O-C linkages of the anhydrides. After approximately 25 minutes at 170 ºC, the anhydride band at 1770 cm^{-1} (Figure 4-2, **D**) has become the strongest band in the spectrum, indicating that large amounts of anhydrides had been formed. In addition, broad absorption bands appear between 1650 and 1550 cm^{-1}, which indicates the formation of unsaturated structures. These results support the proposed mechanisms of citric acid anhydride and aconitic anhydride formation (Scheme 4-2).

Although thermal degradation seems detrimental for polymer functionalization, this is not necessarily the case. The anhydrides formed during CA degradation are more reactive than CA itself and react even with deactivated, sterically hindered secondary alcohols. Ironically, the thermal instability of CA facilitates its use at relatively low temperatures: high enough to form reactive anhydrides, but low enough to prevent extensive formation of unsaturated structures by elimination or decarboxylation. CA-derived anhydrides are already formed at temperatures between 140 and 160 ºC. At such temperatures, the SA/IS-based polyester systems under investigation form a melt with sufficiently low viscosity, so that CA can be added and incorporated into the molten polymer without using solvents. In the ideal case, only citric acid anhydride is formed through the dehydration of CA. The formation of this asymmetric cyclic anhydride and its subsequent esterification is shown in Scheme 4-3. The citrate end-group resulting from reaction **3** can again form a cyclic anhydride and react once more with a hydroxyl-terminated polyester chain (reactions **4** and **5**).



Scheme 4-3. Citric acid anhydride formation, followed by its esterification.[7]

The formation of a symmetric 6-membered cyclic anhydride[29] from CA (other than the degradation product glutaconic anhydride, see Appendix A, Scheme A-1, structure **k**) upon heating is not described in literature and we have no indications that a similar compound is formed after esterification of the tertiary carboxylic acid group of CA (Scheme 4-3, reaction **2**). This means that such a 6-membered anhydride is either not formed or very reactive and therefore not observed. If a 6-membered anhydride is not formed after reaction **2** has taken place, subsequent ester formation of the two remaining primary carboxylic acids might be more difficult.[9]

4.3.2 Model reactions of citric acid with 1-butanol and different diols

Reactions of CA with 1-butanol

Since we want to use CA to end-cap linear 1,4:3,6-dianhydrohexitol-based polyesters, it was necessary to determine if the secondary OH-groups of the 1,4:3,6-dianhydrohexitols are sufficiently reactive towards esterification with CA or its anhydrides at temperatures between 150 and 170 ºC. In addition, it was important to establish how readily more than one acid functionality of a single CA moiety would react. If one CA molecule reacts with two or even three polyester hydroxyl end-groups, chain extension, branching or even cross-linking might occur. Model reactions between CA and 1-butanol as well as the diols isosorbide (IS), isoidide (II), isomannide (IM) and 1,4-butanediol (BD) were carried out to monitor ester formation and conversion in time. Due to the volatility of some of the monomers, water could not be actively removed from the reaction mixture by applying vacuum. However, the reactions were performed in open systems under a slight inert gas flux, allowing for some water to evaporate from the reactor. Before elaborating on the differences in reactivity between the several diol compounds, the less complex ^{13}C NMR spectrum of the reaction between 1-butanol and CA will be discussed in more detail.

^{13}C NMR shifts of carbonyls are highly sensitive to even small changes in the molecule and form a very useful probe to monitor anhydride formation, esterification and/or degradation of CA. As already mentioned, CA gives two resonances in the carbonyl region of the ^{13}C NMR spectrum: one assigned to the primary carbonyls at the 1 and 5 positions (Scheme 4-4, No. **1**) and one assigned to the tertiary carbonyl carbon atom (Scheme 4-4, No. **2**). When one of the carboxylic acid groups of CA has been esterified (in this case with the OH-group of 1-butanol), the chemical shifts of the two remaining carboxylic acid carbonyl signals are affected noticeably. The same can be said for the resulting ester carbonyl signals. The various possible carbonyl species depicted in Scheme 4-4 can therefore result in separate signals in the NMR spectrum, as demonstrated in Figure 4-3. The signals are clustered in four groups of either carboxylic acid or ester carbonyl carbon atoms, as already described by others.[12,15]

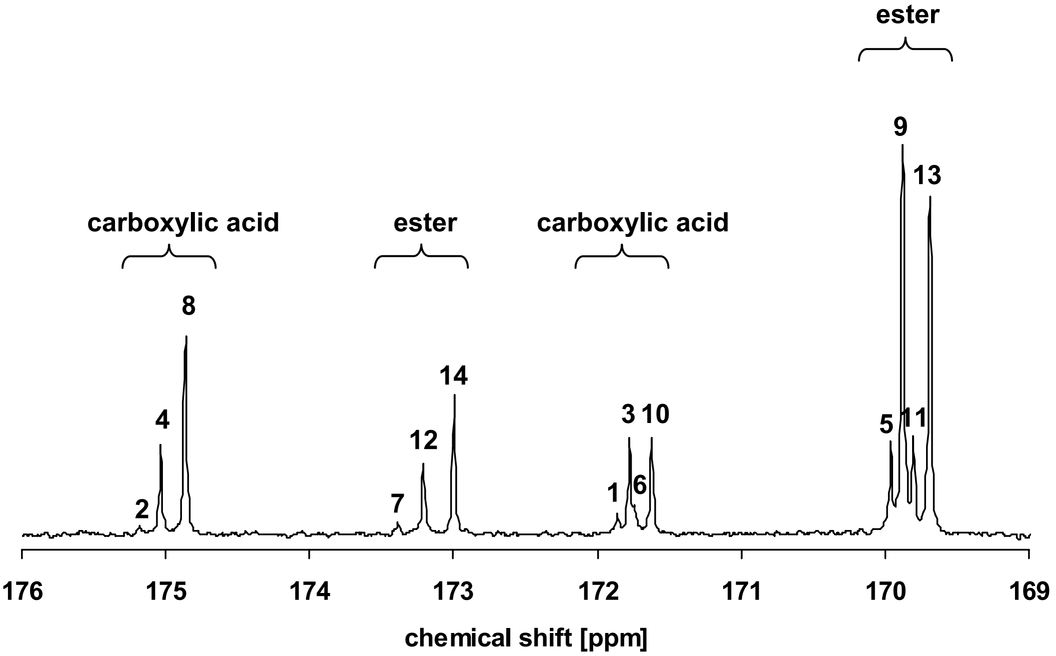
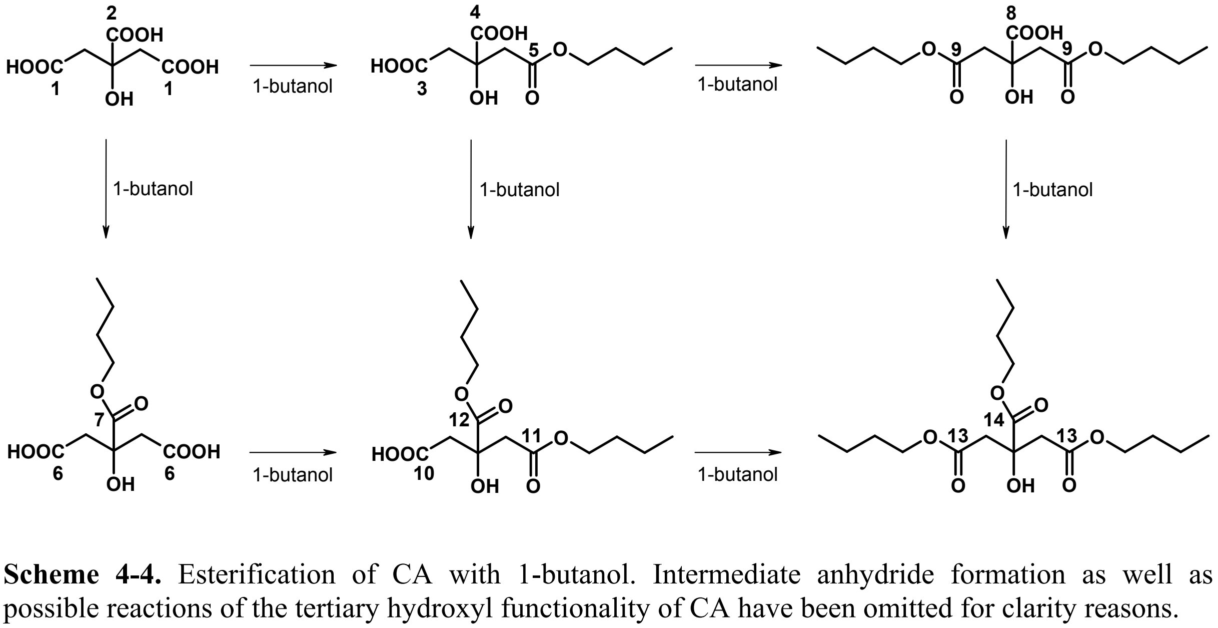


Figure 4-3. Carbonyl region of the ^{13}C NMR spectrum of the product of the reaction between CA and 1-butanol (ratio CA:1-butanol = 1:3, T_{max} = 150 ºC, t = 450 min.). Peak labels refer to the structures in Scheme 4-4.



Scheme 4-4. Esterification of CA with 1-butanol. Intermediate anhydride formation as well as possible reactions of the tertiary hydroxyl functionality of CA have been omitted for clarity reasons.

A three-fold molar excess of 1-butanol (relative to CA, so the overall 1-butanol/COOH molar ratio is 1:1) was added, to make sure that even (part of) the least reactive tertiary acid groups of CA would react. This was necessary to visualize and identify all the 14 different possible carbonyl resonances which might occur in the ^{13}C NMR spectra for the reaction performed (Scheme 4-4 and Figure 4-3). The intensities of the observed signals support the peak assignments. No olefinic signals characteristic for aconitic acids / anhydrides were found, indicating that these species were not formed at 150 ºC. Anhydride signals assigned to citric acid anhydride were absent as well, suggesting that this reactive anhydride species was either not formed, or that it was rapidly converted to esters by reaction with the primary OH-groups of 1-butanol. To investigate whether or not anhydrides are formed at 150 ºC, CA was isothermally heated at this temperature while measuring FTIR spectra as a function of time. Although significantly slower than at 170 ºC, the formation of anhydrides was observed in a similar way as demonstrated before. This experiment also shows that, at 150 ºC, a reaction with water yielding two carboxylic acid groups, could not be the cause of the absence of the CA anhydride signals, since the formation of the anhydride is already more favorable. Therefore, the absence of anhydride peaks in the NMR-spectrum suggests that the reaction of these *in situ* generated anhydrides with 1-butanol is fast and complete. At the same time, the absence of olefinic signals suggests that no or hardly any aconitic derivatives or other unsaturated species are formed at these temperatures. This is beneficial, since this means that loss of functionality does not occur to an appreciable extent. In addition, the absence of UV-labile unsaturated species is advantageous.

Conversion of the carboxylic acid groups was estimated by integration of the clusters of acid and ester peaks. The tertiary acids showed a lower conversion (~43 %) than the primary acid groups (~80 %), which was in line with the expectations. This means that in total approximately 68 % of the carboxylic acid groups have reacted with 1-butanol. From ^{1}H NMR, the conversion of 1-butanol was determined to be 76 %. The slight discrepancy between the determined COOH and OH conversions can be explained by the underestimation of ester formation from the ^{13}C NMR spectrum, caused by the inaccuracy of the integration of such spectra.

Reactions of CA with IS, II and IM

Reactions between CA and several diols were subsequently carried out. To mimic the ratio used to modify a linear polymer chain with two hydroxyl end-groups, the molar ratio CA:diol was 2:1. The reactions were performed following a standard procedure (see the Experimental section) at a maximum temperature of 160 ºC, in order to minimize thermal degradation of CA. Diol conversions were determined from ^{1}H NMR spectra. The results obtained after 170 min at 160 ºC are given in Table 4-1. Conversion values for the differently oriented hydroxyl groups of the 1,4:3,6-dianhydrohexitols are specified as well.

Table 4-1. Conversion values for the OH-groups of IS, II, IM and 1,4-butanediol (BD) after 170 minutes reaction with CA at 160 ºC.

experiment	**feed composition**	**OH-conversion [%]**		**total OH-conv. [%]**
		endo	*exo*	
A	CA:IS 2:1	73	81	77
B	CA:II 2:1	-	84	84
C	CA:IM 2:1	72	-	72
D	CA:BD 2:1	-	-	91

There is a significant difference between the conversions of the *endo* and *exo* hydroxyl groups. After 170 minutes of reaction, the *exo*-oriented OH-functionalities show conversions that are approximately 10 % higher than for their *endo* counterparts. Such differences were also observed in polymerization reactions between the different 1,4:3,6-dianhydrohexitols and succinic acid (see Chapter 3). This means that the (nearly) complete CA-modification of IM- or IS-based polyesters will require longer processing times than the modification of II-based polyesters. Also, from the relatively low conversions we can conclude that vacuum processing is required to actively remove water from the reaction mixture. As expected, the primary OH-groups of 1,4-butanediol react faster than the secondary hydroxyl groups of the 1,4:3,6-dianhydrohexitols, showing a conversion of 91 % after 170 min at 160 ºC.

The carbonyl regions of the ^{13}C NMR spectra of reactions **A** – **D** again encompass four distinct clusters of resonances, attributed to either carboxylic acid or ester carbonyl carbon atoms (Appendix A, Figure A-2). It is clear that the carboxylic acid peaks are more intense than the ester peaks, indicating that significant amounts of free carboxylic acid groups are still present after 170 minutes of reaction. With the ratio carboxylic acid:hydroxyl being 3:1 (i.e. CA:diol = 2:1), the conversion of the carboxylic acid groups was expected to be approximately 33 % at full OH-conversion. The following values for carboxylic acid conversions were estimated from the ^{13}C NMR spectra of the experiments **A** – **D** described in Table 4-1: **A**) 25 %, **B**) 26 %, **C**) 17 % and **D**) 26 %. These values are lower than expected based on the OH-conversion values listed in Table 4-1, which is probably due to the error made when integrating peaks in the ^{13}C NMR spectra, but the conversions are within the right order of magnitude.

Interestingly, signals of citric acid anhydride and/or aconitic acid/anhydride were observed in the ^{13}C NMR and ^{1}H NMR spectra of reactions **A** – **D** (in the presence of diol) after 170 minutes at 160 ºC, corresponding to approximately 3-6 % of the initial amount of CA (determined from the ^{1}H NMR spectra). When heating CA at 180 ºC without adding diol monomers, we observed approximately 22 % of anhydride. The fact that we observe much lower levels of anhydrides when heating CA with diols present, suggests that the anhydride esterifies rapidly. In order to verify this observation, FTIR model experiments were carried out, in which two equivalents of CA were reacted with one equivalent of isoidide, to monitor anhydride levels as well as ester formation and disappearance of OH-groups (Figure 4-4, **I**). Anhydride bands appear at 1855 and 1770 cm^{-1} (symmetric and asymmetric stretching of cyclic anhydride carbonyls) as well as at 981 and 892 cm^{-1} (C-O-C stretching). After having reached a certain level, the amount of anhydrides seems to stay constant. At the same time, the carboxylic acid band shows a shift from 1712 cm^{-1} (H-bonded carboxylic acid carbonyl) to 1734 cm^{-1} (free carboxylic acid carbonyl). The carboxylic acid and the ester carbonyl bands overlap at approximately 1720 cm^{-1}.[28] The esters also give a strong band at 1171 cm^{-1}. However, here there is overlap with the aliphatic ethers present in isoidide. When performing the same experiment with a CA:II ratio of 1:3 (Figure 4-4, **II**), only low levels of anhydride formation are observed and the anhydride absorption bands disappear at high conversion, indicating that the anhydrides have esterified with isoidide. This also becomes clear from the strong increase of the intensity of the ester bands at 1171 and 1720 cm^{-1}.

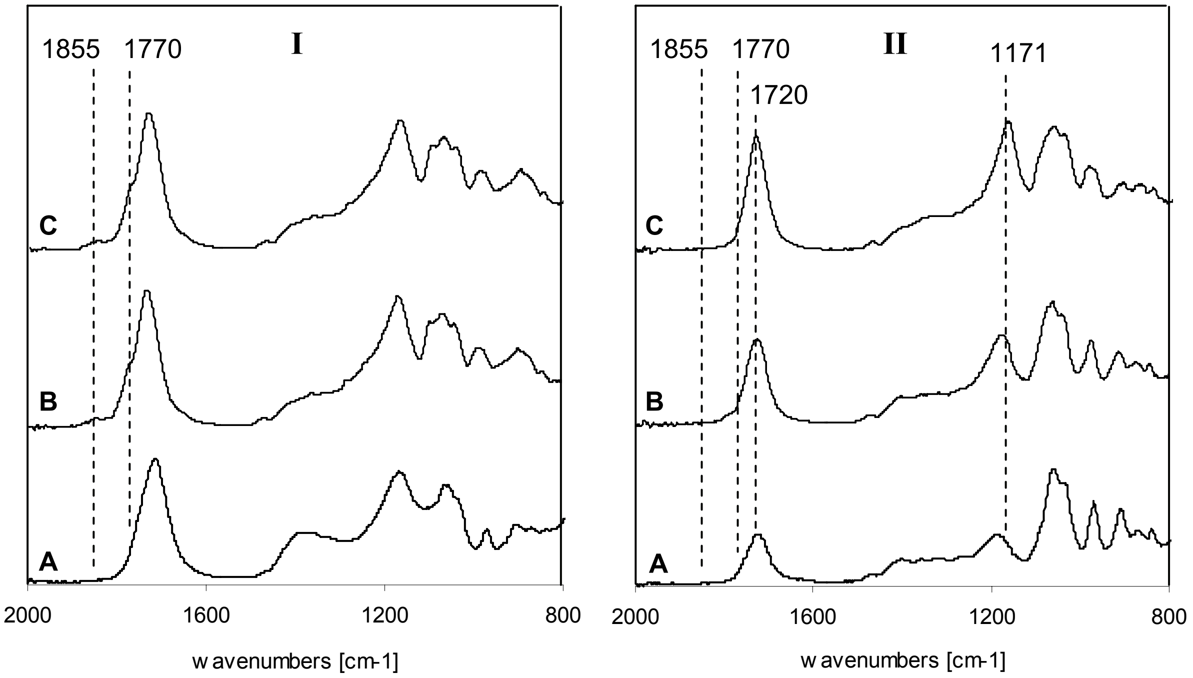
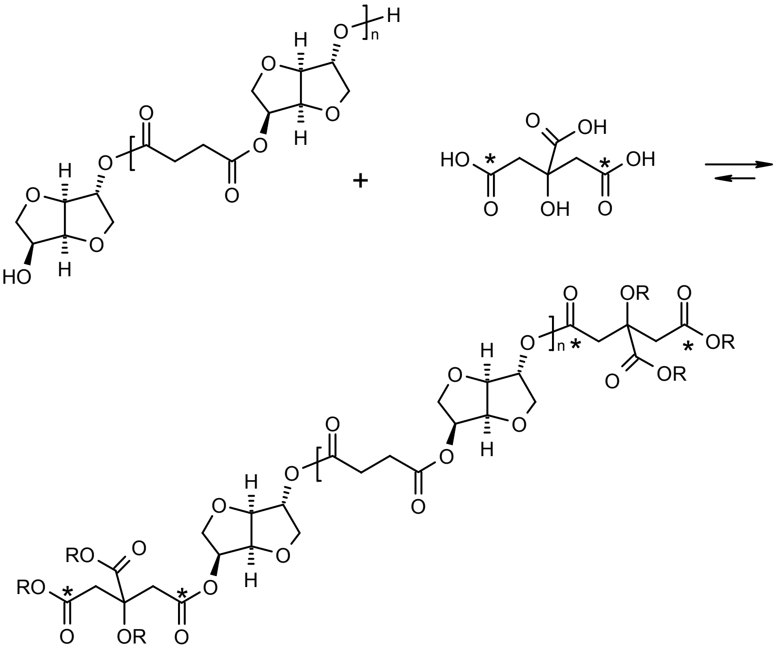


Figure 4-4. FTIR spectra of a mixture of CA and isoidide, heated isothermally at 170 ºC at (**A**) $t = 0$, (**B**) $t = 25$ min., (**C**) $t = 120$ min. Figure **I**: ratio CA:isoidide = 2:1; Figure **II**: ratio CA:isoidide = 1:3.

4.3.3 Citric acid modification of biobased hydroxy-functional polyesters

Since CA should be incorporated into the polyester at relatively low temperatures, linear hydroxy-functional polyesters were first synthesized in the presence of an esterification catalyst at 180 – 230 ºC, followed by a CA-modification step at 150-160 ºC (without further addition of catalyst). For ^{13}C NMR analysis, the OH-functional succinic acid / isosorbide copolyester (entry **1** in Table 4-2) was reacted with ^{13}C-labeled CA (i.e. citric acid-1,5-$^{13}C_2$, referred to as CA-1,5-$^{13}C_2$) (Scheme 4-5). The ratio of OH-groups (determined by titration) to CA-1,5-$^{13}C_2$ was 1:1.1 (i.e. OH:COOH = 1:3.3), which corresponds to approximately 20 wt% of CA-1,5-$^{13}C_2$.



Scheme 4-5. Reaction between OH-functional SA/IS copolyester with citric acid-1,5-$^{13}C_2$. R = H or R = oligo- or polyester if ester interchange occurs. The ^{13}C-labeled carbon atoms are indicated by an asterisk.

During the reaction, samples were taken to monitor the development of molecular weight, polydispersity and conversion of the OH-groups of the polyester resin (^1H NMR) as well as of the carboxylic acid groups of CA (^{13}C NMR). Figure 4-5 shows the SEC data for this reaction.

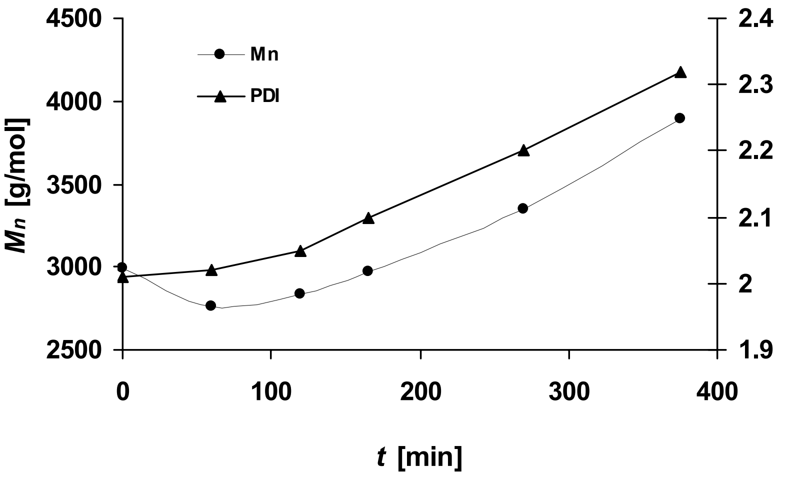


Figure 4-5. $\overline{M}_n$ and polydispersity index (*PDI*) as a function of reaction time for the CA modification of polyester **1** (Table 4-2) with citric acid-1,5-$^{13}C_2$.

In this plot, we can see a slight drop in $\overline{M}_n$ between t = 0 and t = 150 minutes (which corresponds to the atmospheric processing step, see Experimental section), suggesting that, at the beginning of the reaction, polyester chains are broken up through interchange (acidolysis) reactions with CA to some extent. However, when the reaction proceeds under vacuum, the molecular weight is built up again. In addition, the polydispersity index increases from 2.0 to 2.3, implying branching of the polyester by incorporation of CA into the polymer chains. SEC data do not indicate extensive cross-linking of the polymer sample, since the weight average molecular mass of the polyester does not increase exponentially, and the CA-modified polymers remain soluble. In Table 4-2, the characteristics of the initial hydroxy-functional polyester (entry **1**) as well as the modified polymers obtained from entry **1** after two separate CA-modification experiments (entry **2** with CA, entry **3** with CA-1,5-$^{13}C_2$) are summarized.

Table 4-2. Characteristics of initial polyester and of CA-modified polymers.

entry	feed composition	composition (NMR)	T_g [°C]	$\overline{M}_n$ [2] [g/mol]	*PDI*	*AV* [mg KOH/g]	*OHV* [mg KOH/g]
1	SA/IS [1:1.14]	SA/IS [1:1.09]	56.5	3000	2.0	1.5	65.0
2	OH : CA [1:1.1][1]	SA/IS/CA [1:1.11:0.2]	68.7	3500	2.3	108.3	65.2
3	OH : CA-1,5-$^{13}C_2$ [1:1.1][1]	SA/IS/CA-1,5-$^{13}C_2$ [1:1.11:0.19]	64.6	3800	2.3	n.d.[3]	n.d.[3]

[1] The amount of citric acid added to the OH-functional polyester (entry **1**) was based on *OHV* data of these polymers.

[2] All SEC data presented in this chapter were determined by SEC in HFIP, calibrated with PMMA standards.

[3] Not determined, since not enough material was available to carry out titration experiments.

The molecular weights of the polymers listed in Table 4-2 are determined by SEC, making use of PMMA standards. It should be noted that these data give approximations rather than absolute values. Apart from the chemical differences between PMMA and the polymer samples under investigation here, the SEC results can be strongly influenced by the hydrodynamic volume and the type(s) of end-groups of such low molecular weight species. To confirm the order of magnitude of the molecular weight mentioned in Table 4-2, the absolute molecular weight of polyester **2** was determined from SEC measurements, combining light scattering and concentration detection, without using PMMA calibration. The following results were obtained: $\overline{M}_n$ = 3100 g/mol, $\overline{M}_w$ = 6100 g/mol, *PDI* = 2.0.

Functionality of the CA-modified polyester

The ^{1}H NMR spectra of polyesters **1** and **2** show the decrease of isosorbide end-groups upon CA-modification of the OH-functional starting material (Appendix A, Figure A-3). ^{13}C NMR spectroscopy yielded information concerning the reaction between polyester **1** and CA-1,5-$^{13}C_2$. In Scheme 4-6, the various types of carboxylic acids and esters that can be present after this reaction are given. The NMR spectrum (Figure 4-6) is more complex than the spectrum shown in Figure 4-3 due to the different shifts of *endo*- and *exo*-oriented substituents of the isosorbide residue, resulting in an increase of the number of possible signals.

Note that in Figure 4-6, the carboxylic acid and ester carbonyl signals of the unlabeled tertiary carbonyl carbon atoms are not visible due to their low concentrations. The ^{13}C-labeled carbonyl carbon atoms, on the other hand, are clearly visible in the ^{13}C NMR spectrum of the modified polyester. The spectrum contains separate clusters of acid and ester carbonyls. A strong signal is observed at 171.3 ppm in spectrum **A**, caused by the two unreacted labeled carbons of CA-1,5-$^{13}C_2$ (Scheme 4-6, carbonyl **1**). After 170 minutes of reaction (spectrum **B**), peaks are present between 170.8 and 171.3 ppm. These signals result partly from the succinate ester carbonyls of the original SA/IS copolyester. However, they are mainly attributed to the labeled carboxylic acid carbonyls (Scheme 4-6, carbonyls **2** and **3**), which have shifted slightly upon reaction of one (or two) of the other carboxylic acid functionalities.

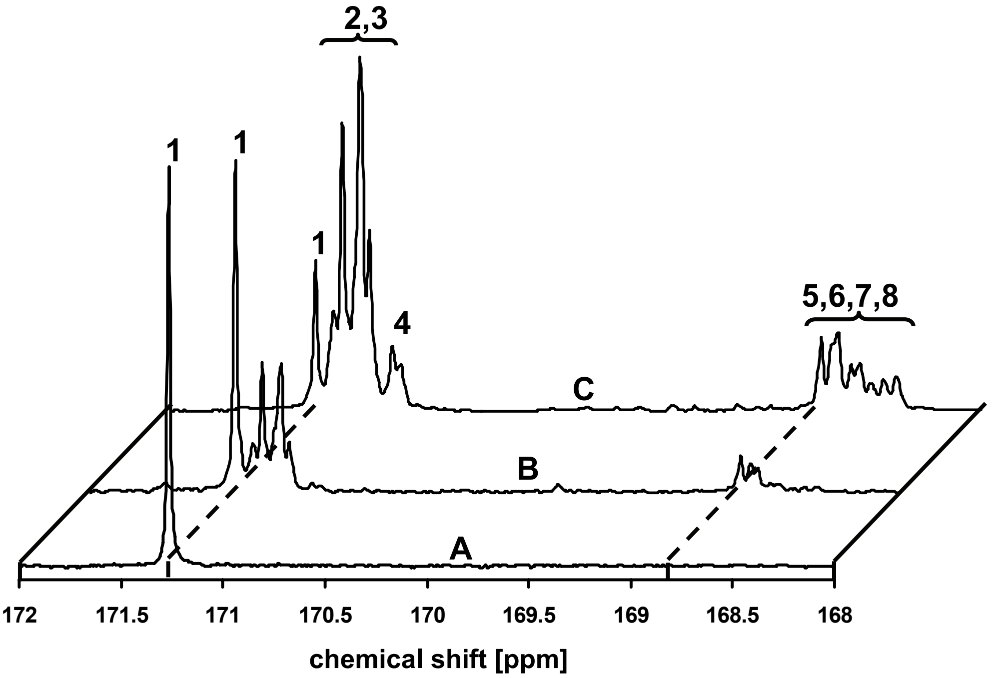
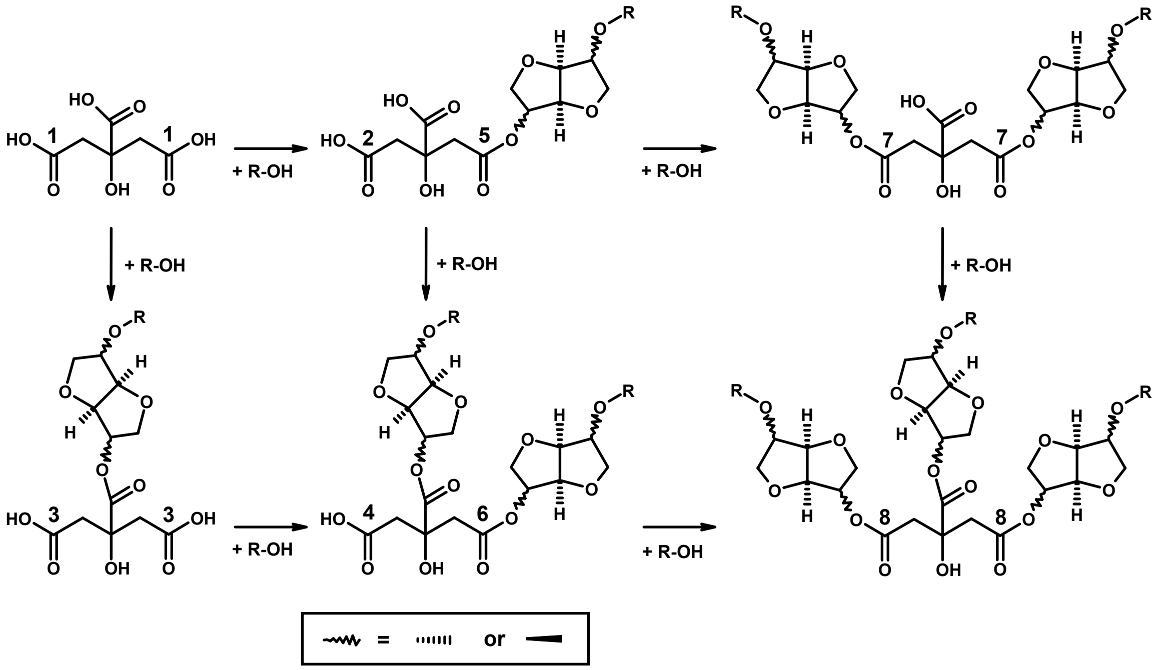


Figure 4-6. Carbonyl region of the ^{13}C NMR spectrum of (**A**) citric acid-1,5-$^{13}C_2$ and of the CA modification of a SA/IS copolyester after (**B**) t = 170 min. and (**C**) t = 375 min. (this particular reaction was performed at T = 155 - 160 °C). *Note: the different spectra are not scaled relative to each other, so they can only be compared qualitatively.*



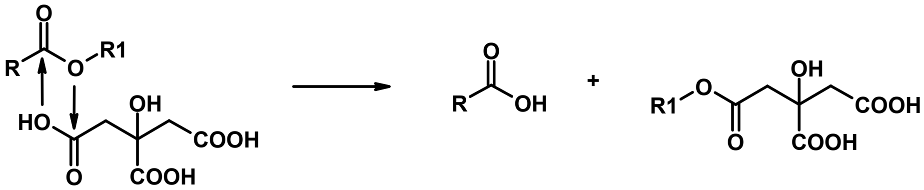
Scheme 4-6. Possible reaction products resulting from CA-modification of a hydroxy-functional polyester. *Note: only the labeled carbonyls are numbered, the tertiary carboxylic acid and ester carbonyls are not visible in the ^{13}C NMR spectrum presented in Figure 4-6.*

As the reaction proceeds, ester signals become visible between 168.4 and 169.1 ppm (Figure 4-6). These signals are significantly lower in intensity than the acid signals. At $t = 170$ min., approximately 50 % of the polyester hydroxyl end-groups have reacted with CA-1,5-$^{13}C_2$, as determined from ^1H NMR spectra. After 375 minutes, high intensity carbonyl signals are visible in the area between 170.8 and 171.3 ppm. All these peaks are attributed to carboxylic acid carbonyls. From the ^1H NMR spectrum of the modified polyester, it appears that the conversion of the polyester hydroxyl end-groups is not complete. To reach full conversion of the OH end-groups, significantly longer reaction times are necessary, since conversion is hampered by the less reactive *endo*-oriented OH groups of isosorbide. After vacuum processing, the conversion of the hydroxyl end-groups of the polyester had increased to 75 %, and the conversion of the carboxylic acid groups of CA was approximately 27 %. The maximum theoretical functionality $\overline{F}_n$ which could be obtained upon modification with CA was $\overline{F}_n = 4$ (at 100 % OH- and 33 % COOH conversion, respectively). On average, the functionality per chain at 75 % OH-conversion is approximately $\overline{F}_n = 3$. When comparing the intensities of signals **2** and **3** (i.e. CA has reacted with only one of its acid functionalities, implying the desired end-capping reaction) with the intensity of signal **4** (i.e. CA has reacted with two of its acid groups, implying chain extension), we can conclude that 80-85 % of the CA has esterified with only one of its carboxylic acid functionalities and is therefore present at the polyester chain end. From these results, it is not possible to give an exact amount of CA molecules that have reacted with two or with all three of their acid groups (implying branching), due to the fact that the ester resonances **5** - **8** show considerable overlap. Based on the integral of signal **4**, we can say that at least 10 % of the CA molecules has reacted with two of their acid groups. Therefore, the remaining 5-10 % of the CA molecules might have reacted with two or with all three acid groups, but this is a rough estimation.

It is important to determine whether the degradation of CA would take place to a significant and possibly detrimental extent during the modification of OH-functional polyesters with CA. Formation of aconitic acids and their anhydrides takes place at a significant rate at temperatures of 180 ºC and above, whereas no unsaturated structures were found when the reaction between CA and 1-butanol was performed at 150 ºC (*vide supra*). To study the formation of unsaturated structures from CA during the modification of a polyester at 150 - 160 ºC, a reaction between citric acid-2,4-$^{13}C_2$ (referred to as CA-2,4-$^{13}C_2$) and an OH-functional linear resin was carried out. The labeled carbon atoms at the 2 and 4 positions were clearly visible in the ^{13}C NMR spectra. If unsaturated structures are formed, signals should appear at a chemical shift between 125 and 145 ppm, as these unsaturated structures would always include one of the labeled carbon atoms. No clear signals were observed in the mentioned region, not even after prolonged heating at 155 ºC, indicating that formation of unsaturated structures did not take place to a significant degree under these conditions (Appendix A, Figure A-4). The ^{1}H NMR spectrum of the same reaction only showed very faint traces of aconitic acid or anhydride. The total amount of degradation products is estimated to be 2-3 % of the original amount of CA-2,4-$^{13}C_2$. It is not expected that these low levels of side products are detrimental to the final properties of the polyester resin. As already mentioned, these degradation products all have at least two acid functionalities. Therefore, if these molecules would react with a hydroxyl end-group of a polymer, this would still lead to a carboxylic acid chain end, which can take part in cross-linking reactions.

Incorporation of citric acid through ester interchange

In order to investigate whether CA can be attached to the polyester chain by means of ester interchange reactions (specifically: acidolysis, Scheme 4-7), an OH-functional polyester was fully end-capped with benzoyl chloride following a procedure described in literature.[30]



Scheme 4-7. Schematic representation of the acidolysis of an ester linkage by citric acid.

After end-capping, no residual OH end-groups were present in the polymer sample as verified by ^{1}H NMR (Appendix A, Figure A-5) and MALDI-ToF-MS. The main signals in the MALDI-ToF-MS spectrum (i.e. the peaks at 1077 d, 1305 d and so on) are separated by 228 Da, the mass of a SA-IS repeating unit, and are attributed to polyester chains end-capped by benzoyl chloride residues at both ends (Figure 4-7, structure **A**). Low intensity peaks can be discerned that correspond to polyester chains with one benzoate end-group and one ethyl ester end-group (Figure 4-7, structure **B**). In the starting poly(isosorbide succinate), low levels of carboxylic acid end-groups (i.e. succinic acid at the chain end) were present. In addition, the solvent (chloroform) used during the modification contained small amounts of ethanol as a stabilizer. The ethyl ester end-groups of structure **B** were therefore most probably formed by esterification of ethanol with a carboxylic acid polyester end-group or through an ester interchange reaction in the presence of the transesterification catalyst $Ti(OBu)_4$. These ethyl ester end-groups do not have a negative influence on the experiments performed with this end-capped material.

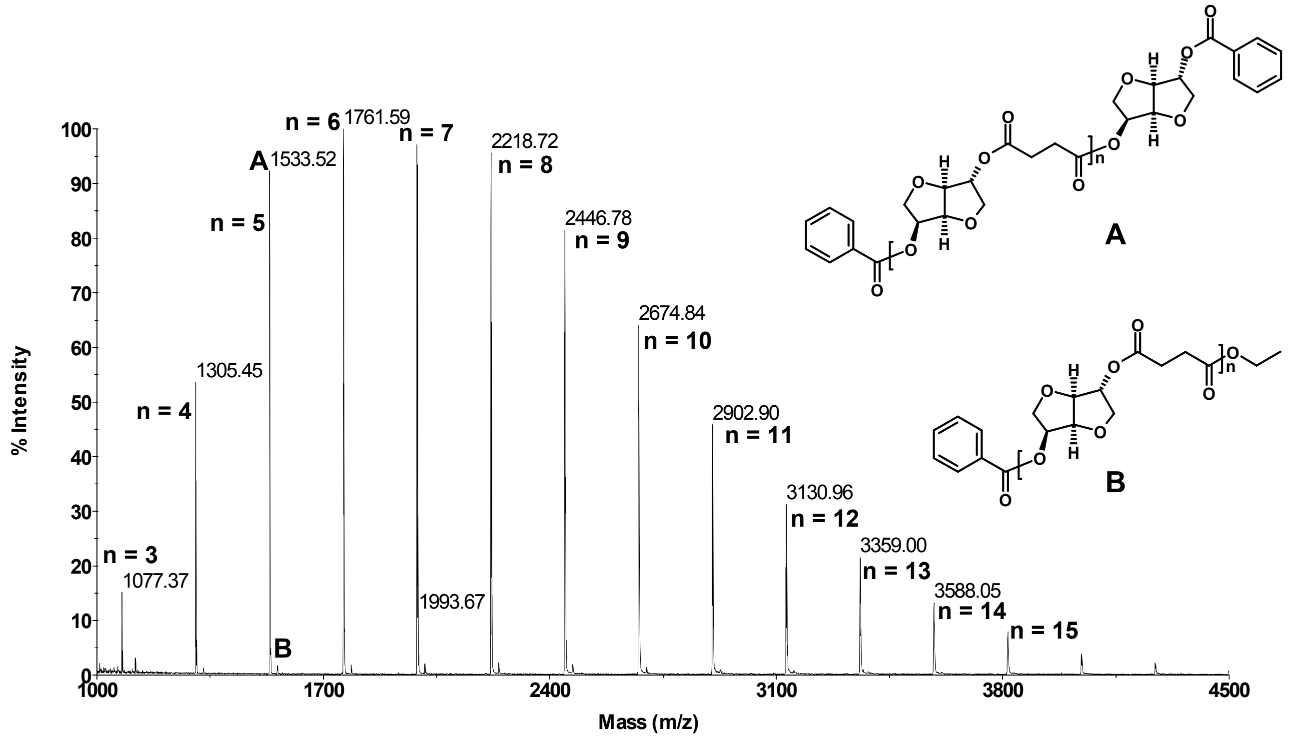


Figure 4-7. MALDI-ToF-MS spectrum of the product of the reaction between an OH-functional poly(isosorbide succinate) and benzoyl chloride.

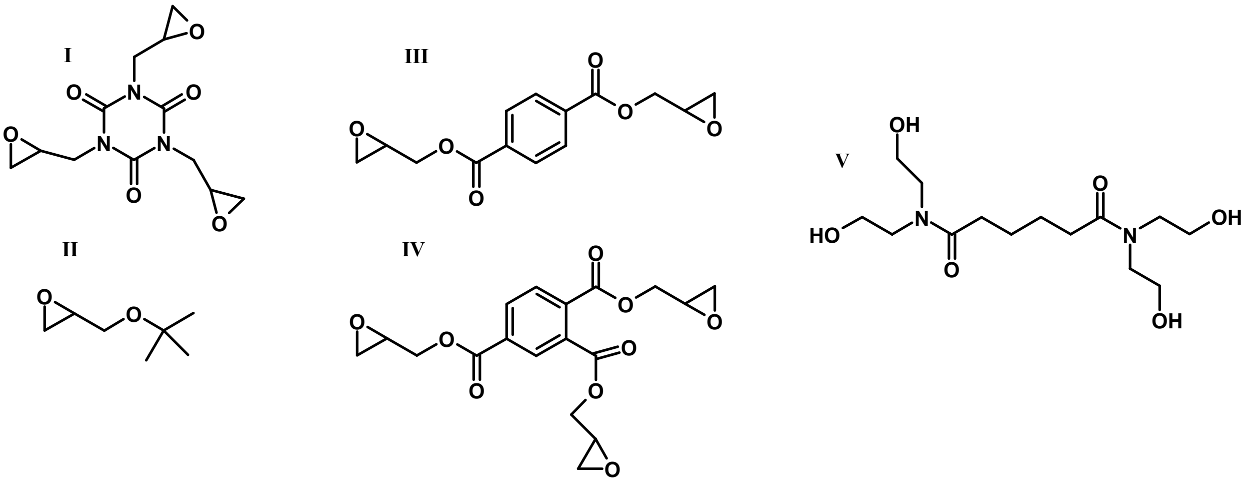
The end-capped polyester ($\overline{M}_n$ = 3300 g/mol, PDI = 1.4, T_g = 59.1 °C) was reacted with CA-1,5-$^{13}C_2$ at 155 °C for 3.5 hours. Since there were no hydroxyl end-groups to be esterified, incorporation of CA-1,5-$^{13}C_2$ could most probably only occur by acidolysis of ester links by the acid groups of CA-1,5-$^{13}C_2$, since the tertiary OH-group of CA-1,5-$^{13}C_2$ is probably not reactive enough to be involved in alcoholysis (i.e. ester interchange) reactions. The ^{1}H NMR spectrum of the resulting polymer was not different from that of the starting material, except the appearance of a new multiplet caused by the presence of CA-1,5-$^{13}C_2$ at 2.95 ppm. In the ^{13}C NMR spectrum (Appendix A, Figure A-6), new signals of higher intensity were present at 169.7 and 171.6 ppm. These peaks were assigned to anhydride species formed by dehydration of CA-1,5-$^{13}C_2$ and amounted to approximately 21 % of the initial amount of CA-1,5-$^{13}C_2$.

Although the spectrum showed no clear CA-1,5-$^{13}C_2$ ester signals (in the area between 168 and 169 ppm), some low intensity carboxylic acid carbonyl signals (between 171.0 and 171.2 ppm) indicated that the labeled CA was built into the polyester chains through acidolysis to some extent (approximately 5 %). These signals could not be caused by unreacted residual

CA-1,5-$^{13}C_2$, since the end-capped polymer was subjected to repeated dissolution/precipitation steps from $CHCl_3$/MeOH, during which residual monomer as well as low molecular weight oligomers were removed. So, the incorporation of CA into the polyester chain through acidolysis proceeds, albeit to a much lower extent than through the normal esterification reaction with hydroxyl end-groups. These results may explain the initial drop in polymer molecular weight during CA-modification, as demonstrated in Figure 4-5.

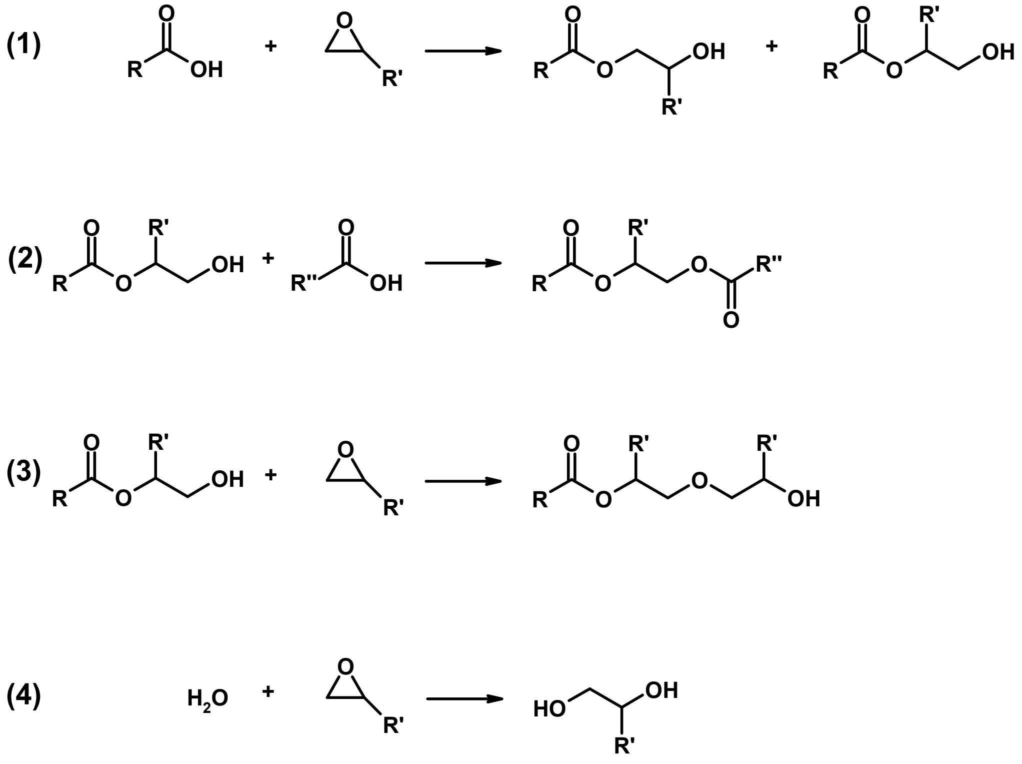
4.3.4 Curing chemistry and model reactions

As was previously determined, the CA-modification of the hydroxyl end-groups of the polyester resin was not complete. However, since acid functionalities of the obtained products were quite high (see Table 4-2), curing experiments were carried out to see if a hydroxyl conversion of ~75 % and a corresponding approximate functionality $\overline{F}_n = 3$ would suffice. In industry, polyesters with carboxylic acid functionality are cured with epoxy- or β-hydroxyalkylamide curing agents. At the moment, triglycidyl isocyanurate (TGIC, Scheme 4-8, structure **I**) is one of the most common epoxy curing agents for acid-functional resins, even though it is classified as a category 2 mutagen.[31] Other commercial epoxy curing agents include mixtures of diglycidyl terephthalate and triglycidyl trimellitate (DGT and TGT, Scheme 4-8, structures **III** and **IV**). An example of a β-hydroxyalkylamide cross-linker is N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide (Scheme 4-8, structure **V**).



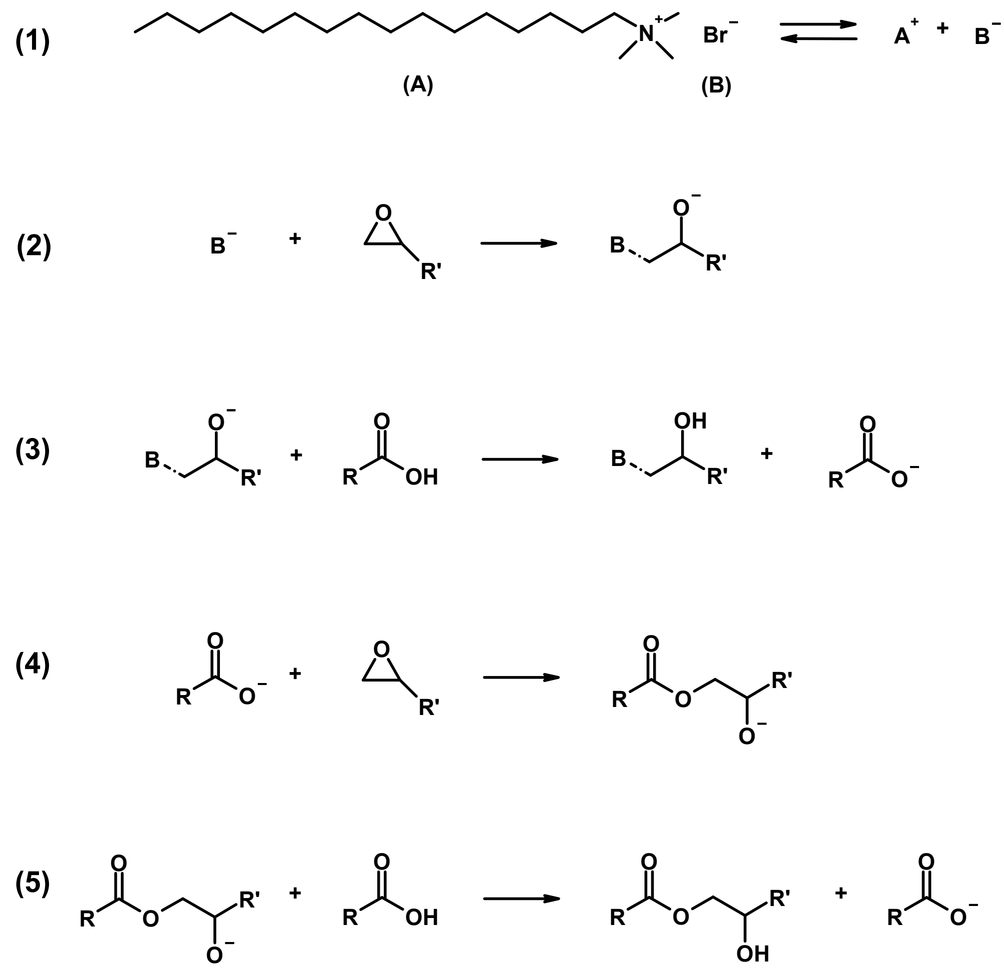
Scheme 4-8. Chemical structures of (**I**) triglycidyl isocyanurate (TGIC), (**II**) *tert*-butyl glycidyl ether (TBGE), (**III**) diglycidyl terephthalate (DGT), (**IV**) triglycidyl trimellitate (TGT) and (**V**) N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide.

Curing of the conventional systems takes place at elevated temperatures (180 – 200 ºC), during approximately 10-15 minutes. Carboxylic acid/epoxy curing can proceed via several types of reactions, depending on reaction conditions and the absence or presence of catalysts. Reactions **1** and **2** (Scheme 4-9) occur at elevated curing temperatures in the absence of an additional catalyst, while reaction **3** only takes place when the curing is catalyzed by strong acids. In fact, reactions **1** and **2** are also acid-catalyzed, meaning that the carboxylic acid end-groups of the polyester resins promote these reactions.[32]



Scheme 4-9. The possible mechanisms for the carboxylic acid/epoxy curing reaction: (**1**) ring opening of the epoxy group by a carboxylic acid; (**2**) esterification of a previously formed hydroxyl group with a carboxylic acid; (**3**) ether formation by reaction of a previously formed hydroxyl group with an epoxide moiety; (**4**) hydrolysis of an epoxide moiety.[1,32,33]

Reactions **1** and **5** in Scheme 4-10 occur when the curing reaction is catalyzed by a quaternary ammonium or phosphonium salt (such as ethyltriphenylphosphonium bromide or hexadecyltrimethylammonium bromide, which are commonly used in industry).



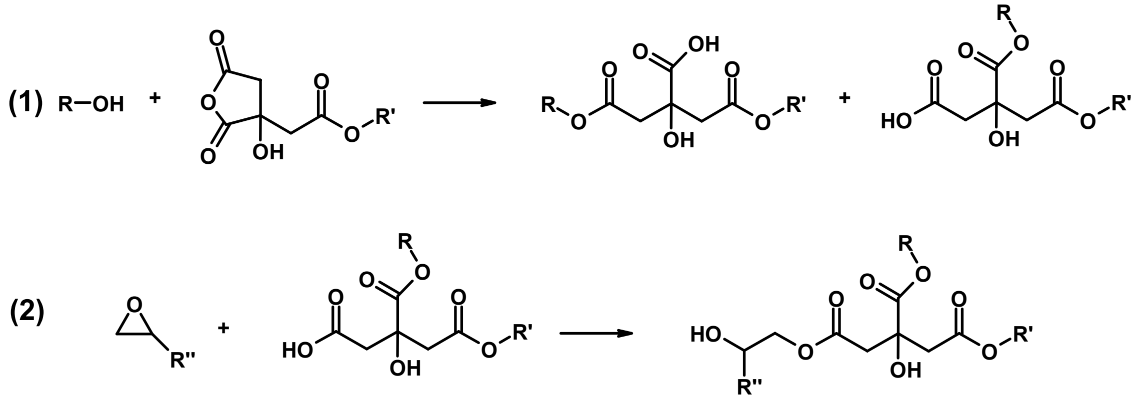
Scheme 4-10. The reaction steps for the carboxylic acid/epoxy curing reaction, catalyzed by a quaternary ammonium salt (here: hexadecyltrimethylammonium bromide): (**1**) dissociation of the quaternary ammonium salt **A**; (**2**) attack on the epoxide by the base **B**; (**3** - **5**) propagation of the reaction via the repeated formation of carboxylate anions.[1]

We studied the reaction of CA end-groups with *tert*-butyl glycidyl ether (TBGE, Scheme 4-8, structure **II**), as a model for epoxy cross-linkers. In this way, we could estimate the extent to which the CA end-groups (i.e. primary and tertiary carboxylic acids) will react with an epoxy curing agent to form a polyester network. Polyester **3** (Table 4-2), synthesized by reacting polyester **1** with CA-1,5-$^{13}C_2$, was selected for the reaction with TBGE. Its labeled CA end-groups are clearly visible in ^{13}C NMR, facilitating the analysis upon reaction with the glycidyl ether. For polyester **3**, the ratio carboxylic acid:ester in the carbonyl region of the ^{13}C NMR spectrum is 73:27. This means that, of all the carboxylic acid groups of CA-1,5-$^{13}C_2$ initially present in the reaction mixture, approximately 27 % had reacted with the hydroxyl end-groups of the starting polyester **1**. The subsequent reaction of polyester **3** with TBGE was performed in solution at 150 ºC at a carboxylic acid:epoxy ratio of approximately 1:1. After

80 minutes of reaction, the ^{13}C NMR spectrum shows a strong decrease in the ratio carboxylic acid:ester, to approximately 15:85. This indicates that an additional 58 % (i.e. 85 – 27 %) of the total amount of carboxylic acid groups had reacted with the glycidyl ether. This corresponds to almost 80 % of the remaining free carboxylic acid groups, present in polyester **3**. With an average chain functionality of $\overline{F}_n = 3$, this extent of conversion is more than sufficient to obtain a well-cured polymer network when using a trifunctional curing agent (in theory, gelation occurs already at 50 % conversion; for calculations see Appendix B). Unfortunately, there is some overlap between the signals caused by the carboxylic acid carbonyls of CA-1,5-$^{13}C_2$ and those caused by the ester carbonyls of the SA/IS copolyester, so the mentioned numbers are estimates.

Curing reactions of anhydride-functional polyesters

Besides the inherent high functionality of the CA-modified polyesters, there is another factor enhancing the curing behavior of these systems. The majority of the CA-modified polyester chains described in this chapter has been shown to have CA moieties at their chain ends. It is therefore possible that, upon heating during curing, anhydride groups are formed at these chain ends, as schematically presented in Scheme 4-3. The curing chemistry should then be, at least partly, considered as an acid anhydride/epoxy system rather than a carboxylic acid/epoxy system. Acid anhydride/epoxy curing systems are known to afford higher reaction rates, higher conversions and higher crosslink densities and to be less sensitive to variations in the stoichiometric balance of the curing formulations.[1] Even if the anhydrides are not actually formed at the polyester chain ends before reaction with the epoxy curing agent, the relatively large amount of carboxylic acid groups present in these CA-modified polymers will probably lead to curing characteristics similar to conventional acid anhydride/epoxy systems. The curing mechanism of such systems is different from the carboxylic acid/epoxy cured formulations and hydroxyl groups present in the polyester resin play an important role (Scheme 4-11).



Scheme 4-11. Exemplary reaction mechanism of a citric acid anhydride polyester end-group with an epoxy curing agent: (**1**) reaction of the anhydride end-group with a hydroxyl compound; (**2**) reaction of the previously formed carboxylic acid end-group with the epoxide.[33]

Residual hydroxyl groups present along the polyester chains can initiate the curing reaction between anhydrides and epoxides by reacting with the anhydride (Scheme 4-11, reaction **1**), forming an ester linkage and a carboxylic acid group. This step is followed by the reaction of the resulting second carboxylic moiety with the epoxide curing agent. In this way, two carboxylic moieties can react to participate in network formation, while only one epoxide equivalent is needed. This also means that, even though the initial CA-modification of the biobased linear hydroxyl-functional polyesters does not proceed to full conversion, the residual hydroxyl end-groups can still contribute to the formation of a fully cured network.

To determine if esters of CA are stable enough to withstand curing cycles at high temperatures, a degradation experiment was performed, in which trimethyl citrate was heated to 180-190 ºC for 2 hours. The trimethyl ester of CA remained colorless and the ^{13}C as well as the ^{1}H NMR spectra, recorded after heating, were identical to those of the starting material. From this experiment, we conclude that a curing cycle of 15 minutes at 180 ºC should not pose a problem with respect to degradation of the polyester. In addition, TGA measurements were performed to investigate the thermal stability of polyester resins **1** and **2** (Table 4-2). The results (Figure 4-8) show that no significant weight loss occurs up to 250 ºC for polymer **1**. For the CA-modified polyester **2**, weight loss is observed to start at approximately 210 ºC. This difference between **1** and **2** is thought to be due to the occurrence of dehydration and/or decarboxylation of the citric acid residues at the polyester chain ends. Still, the thermal stability of the polyesters containing CA is more than sufficient for their application as thermosetting coatings.

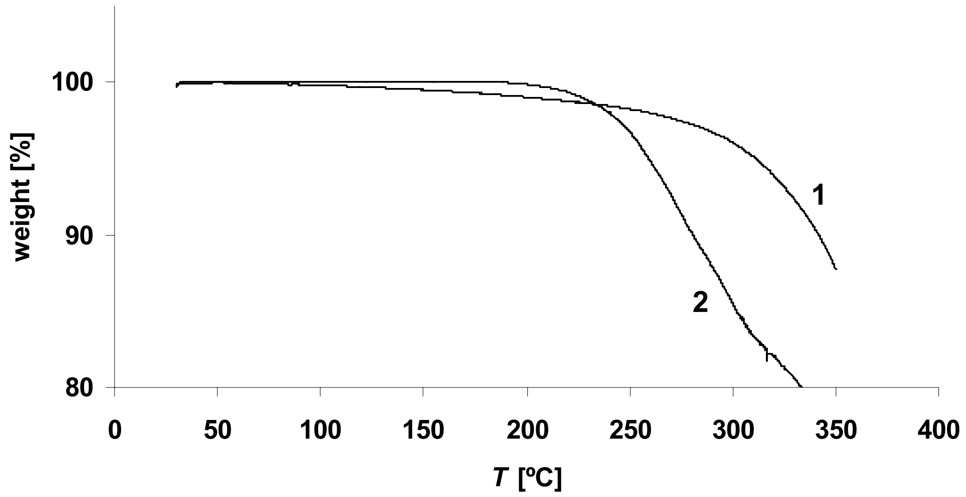


Figure 4-8. Thermogravimetric analysis results of polyesters **1** and **2**. The TGA measurements were performed under a N_2 atmosphere.

4.3.5 Curing of CA-modified polyesters from solution

Several coating formulations were prepared, based on the different CA-modified resins. These polyesters (Table 4-3) were cured with TGIC and N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide (Scheme 4-8, structures **I** and **V**, respectively) and the coatings were applied from NMP solution. Curing reactions involving TGIC were catalyzed by ethyltriphenylphosphonium bromide.

Table 4-3. Properties of CA-modified polyesters used for coating application.

entry	feed composition	composition (NMR)	T_g [°C]	$\overline{M}_n$ [g/mol]	*PDI*	*AV* [mg KOH/g]	*OHV* [mg KOH/g]
2[2]	OH : CA [1] [1:1.1]	SA/IS/CA [1:1.11:0.2]	68.7	3500	2.3	108.3	65.2
4 [3]	SA/IS/CA [1:1.13:0.29]	SA/IS/CA [1:1.09:0.2]	59.0	2200	2.7	101.8	65.2
5a [4]	*SA/IS/1,3-PD* *[1:0.85:0.20]*	*SA/IS/1,3-PD* *[1:0.83:0.25]*	*45.2*	*3600*	*2.2*	*4.7*	*43.9*
5b	OH : CA [1] [1:1.1]	SA/IS/PD/CA [1:0.81:0.21:0.15]	45.2	3400	2.3	81.2	50.5

[1] The amount of citric acid added to the OH-functional polyesters was based on *OHV* data of these initial polyesters.
[2] Synthesized from polyester **1**, see Table 4-2.
[3] Synthesized on 300 g scale. The CA modification was performed directly upon synthesis of the OH-functional precursor, the latter was therefore not isolated or fully characterized.
[4] OH-functional starting polyester from which polyester **5b** was synthesized. 1,3-PD = 1,3-propanediol.

For all the CA-modified polyesters shown in Table 4-3, polydispersity indices higher than 2 are observed. This indicates that side-reactions such as branching take place during the modification. The *OHV* of entry **5b** is significantly higher than of the starting polymer **5a**. This could mean that the reaction between polyester **5a** and citric acid was not carried out to a sufficient extent. The molecular weight and *PDI* only show a slight change, while the T_g is constant, implying that side effects such as branching did not occur as extensively as for polyester **2**. All CA-modified polyesters were amorphous materials, as expected based on the results for OH-functional isosorbide-based polymers discussed in Chapter 2. The properties of the solvent cast coatings are summarized in Table 4-4. Average dry film thicknesses were between 35 and 40 μm for all coatings and all coatings had König hardnesses around 200-220 s (similar to the coatings presented in Chapter 2).

Table 4-4. Coatings based on carboxylic acid-functional polyesters, applied from NMP solution.

film	polyester	curing agent [1]	T_{cure} [°C]	t_{cure} [min]	acetone resistance	impact test [1 kg, 100 cm]
F1	2	I	180	10	+	+
F2	2	V	200	10	+	+/-
F3	4	I	180	20	+	+
F4	4	V	180	20	+	+
F5	5b	I	200	10	+	+/-
F6	5b	V	200	10	+/-	-

[1] See Scheme 4-8.

As displayed in Table 4-4, curing of acid-functional polyesters results in coatings with good to excellent solvent resistance. The impact resistance of **F1** is good, while some slight cracking is observed in **F2**. In general, it was observed that coatings cured with curing agent **I** perform better than those cured with curing agent **V**, with respect to mechanical performance and film appearance. Coatings based on polyester **5b** do not pass impact testing. This is thought to be mainly due to insufficient conversion of the reaction of OH-functional polyesters with citric acid. Further optimization of reaction conditions will probably lead to better results.

From the results presented in this paragraph, it becomes clear that curing of CA-modified polyesters from solution results in coatings with promising characteristics with respect to chemical resistance and mechanical performance. It was therefore interesting to test such systems as powder paints.

4.3.6 Curing of CA-modified polyesters as powder paints

In order to evaluate polyesters with citric acid end-groups as powder coatings resins, the terpolyester poly(isosorbide succinate-*co*-citrate) was synthesized on a larger scale (Table 4-3, entry **4**). The powder paint formulation, application and testing was carried out in the laboratories of DSM Resins (Zwolle, the Netherlands). To determine which curing agent would be suitable for these formulations, gel tests were performed at 200 ºC. The gel tests and coating formulation involved the following cross-linkers: 1) N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide (Scheme 4-8, structure **V**) and 2) a mixture of 60 wt% of diglycidyl terephthalate and 40 wt% of triglycidyl trimellitate (Scheme 4-8, structures **III** and **IV**, respectively). To perform the gel tests, stoichiometric amounts of the curing agents were mixed with the CA-modified resin at 200 ºC. When using the tetrafunctional cross-linker **V**, gelation occurred within 1.5 minutes. In theory, when curing a resin having a functionality $\overline{F}_n = 3$ with a curing agent with a functionality $\overline{F}_n = 4$, gelation occurs at only 41 % conversion (see Appendix B).[34] During curing with curing agent **V** at 200 ºC, the polymer melt displayed foaming. This was caused by the formation of water from this particular curing reaction (Appendix A, Scheme A-2), in combination with the gelation at low conversion. When a gel is formed (at approximately 41 % conversion), the water formed during the remainder of the curing reaction will cause the polymer film to foam. It was concluded that this cross-linker would not be suitable for powder coating formulations in combination with the CA-modified resin, since the rapid curing in combination with the foam formation would lead to a poor coating appearance and performance. The curing reaction of this tetrafunctional cross-linker with a polyester having CA end-groups seems to proceed too rapidly, even though the reactions of β-hydroxyalkylamides with aliphatic carboxylic acids are known to be slower than with aromatic carboxylic acids.[35] The curing reaction between a carboxylic acid-functional polyester and the mixture of glycidyl ethers **III** and **IV** does not produce water, so foaming does not occur in this case. Also, gelation occurred after a slightly longer time of approximately 2 minutes. Therefore, we decided to use this mixture of curing agents DGT and TGT to formulate powder paints. Two formulations were prepared, based on polyester **4**: formulation **F7** is a clear coating without additional catalysts, while formulation **F8** contains the quaternary ammonium salt hexadecyltrimethylammonium bromide, acting as a catalyst, and a titanium dioxide pigment (commonly know as titanium white) (Table 4-5). Due to limited availability of the CA-modified resin **4**, only the basic formulation **F7** and the more elaborate paint **F8** could be prepared. The extrusion of **F7** and **F8** was performed at 80 – 100 °C, leading to pale yellow extrudates.

Table 4-5. Powder paint formulations based on polyester **4**.

F	**polyester** *weight [g]*	**curing agent** *weight [g]*	**catalyst** *weight [g]*	**pigment** *weight [g]*	**additives** [3] *weight [g]*	T_{cure} **[°C]**	t_{cure} **[min]**
7	4	III + IV [1]	-	-	benzoin *0.75*	150-250	15
	100	*26.6*			PV5 *1.5*	*gradient*	
8	4	III + IV [1]	HTABr[2]	TiO_2	benzoin *0.75*	100-200	15
	100	*26.6*	*2*	*50*	PV5 *1.5*	*gradient*	
					stab. *1*		

[1] See Scheme 4-8. The ratio **III** tot **IV** was 60:40 (wt/wt)

[2] HTABr = hexadecyltrimethylammonium bromide.

[3] Benzoin was added as degassing agent; PV5 = Resiflow PV5, a flow agent; stab. = Santowhite stabilizer (4,4'-butylidene-bis(6-*tert*-butyl-*m*-cresol)).

The curing behavior of these formulations was investigated by dynamical mechanical analysis (DMA) using a rheometer with parallel plate geometry. Figure 4-9 shows the plots of the shear modulus (*G'*) and the temperature (*T*) versus time (*t*) for formulations **F7** and **F8**.

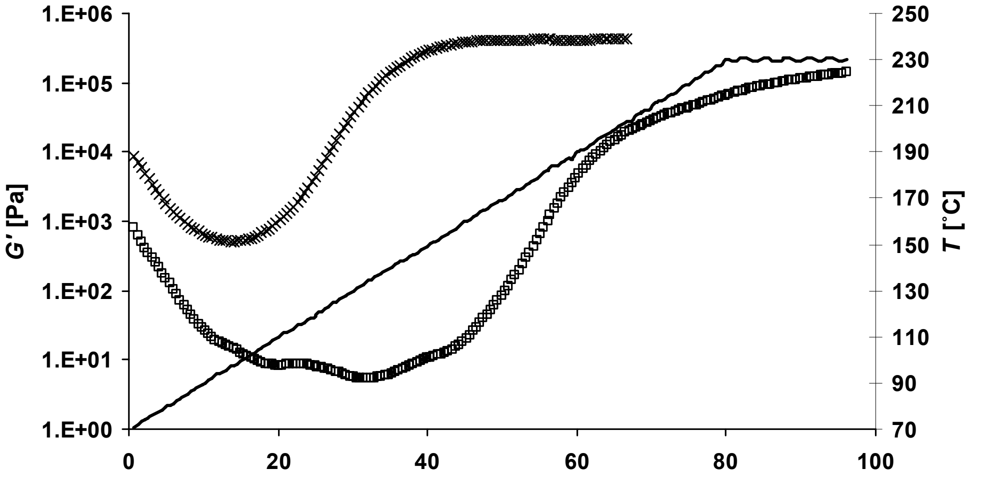


Figure 4-9. Shear modulus *G'* (for formulations **F7** (□) and **F8** (x)) and temperature *T* (—) as functions of time *t* during IS-based polyester network formation. The temperature sweep was performed at 2 °C/min.

At $t = 0$, the modulus of **F8** is significantly higher than that of **F7**, which is mainly caused by the presence of the pigment TiO_2. An increase in the pigment volume concentration (PVC) in powder paints is known to lead to increase in the modulus of the paint, which is also the reason why plateau moduli of pigmented systems should not be used to estimate cross-link density.[36,37] Upon heating formulations **F7** and **F8**, drastically different *G'* curves are obtained. The modulus of **F8** is higher throughout the whole temperature sweep and the onset of curing in the catalyzed, pigmented system occurs at significantly lower temperature (approx. $T = 100$ ºC) than for **F7** (approx. $T = 140$ ºC). At $T = 165$ ºC (and $t = 46$ minutes), the *G'* of **F8** has reached its plateau modulus value of approximately 420 MPa, while the *G'* of **F7** appears not to have even reached its plateau value at $T = 230$ ºC (and $t = 95$ minutes). At this temperature, **F7** has a shear modulus of approximately 140 MPa, corresponding to an estimated cross-link density ν_e of 33.5 mol/m^3 (calculated using Equation 2-3). Note that the cross-link density of system **F7** is significantly higher that the ν_e values determined for the powder paint systems containing isosorbide- and isoidide-based branched polyester resins, as described in Chapter 2 and Chapter 3. This difference might be caused by the fact that, as mentioned earlier on in this chapter, the curing chemistry can be regarded to be an acid anhydride/epoxy system. In other words, the amount of carboxylic acid functionalities at the chain ends of polyester **4** is quite high, leading to a densely cross-linked system.

DSC measurements (Figure 4-10) of the two powder paint formulations revealed that there is a difference in T_g between **F7** ($T_g = 29.8$ ºC) and **F8** ($T_g = 37.1$ ºC), even though the same polyester was used as the binder resin (polyester **4** in Table 4-3). The higher T_g of **F8** is probably due to the presence of TiO_2 in this formulation and similar effects were described in literature.[38] Another reported effect of the addition of TiO_2 to polyester/epoxy systems, is the retardation of the curing reaction.[39,40] Still, rapid curing is observed for the pigmented system **F8** and curing of **F8** occurs faster than of **F7**. The presence of the quaternary ammonium salt as a catalyst for the curing reaction apparently overrules any retardation caused by the pigment.

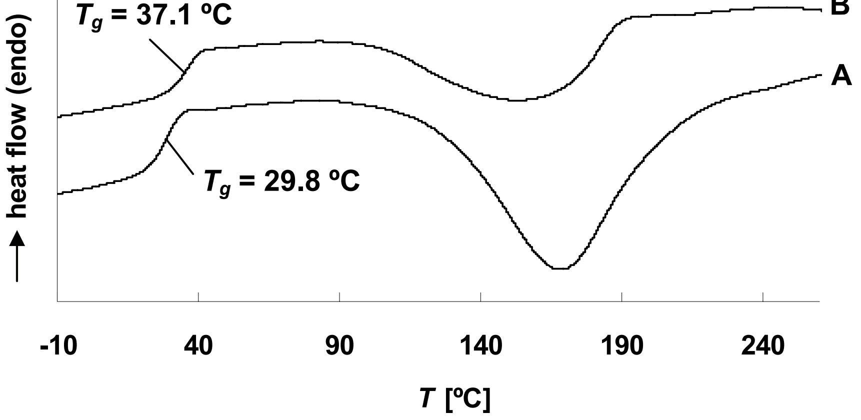


Figure 4-10. Heating curves of the DSC thermograms of powder paints **F7** (curve **A**) and **F8** (curve **B**), measured at 10 ºC/min.

The curing exotherms of the two systems also show considerable differences with respect to the temperatures at which the curing reactions occur. Even though the curing exotherms of both systems seem to start around the same temperature (approximately 90 ºC), it is clear that the curing reaction of system **F8** (curve **B** in Figure 4-10) is completed at significantly lower temperature than of **F7** (200 ºC vs. 240 ºC).

Both systems were applied to aluminum gradient curing panels (Figure 4-11) by powder coating and cured in a gradient oven at temperatures between 150 and 250 ºC (**F7**) or 100 and 200 ºC (**F8**) during 15 minutes. The obtained glossy coatings were tested for solvent and impact resistance at different temperatures. System **F7** had good solvent resistance when cured between 180 and 240 ºC and the coating passed the reverse impact test (performed at 160 pound×inch, equivalent to 184 kg×cm) when cured between 190 and 230 ºC (Figure 4-11, **A**). Above 210 ºC, however, rather strong discoloration of the coating was observed. The pigmented formulation **F8**, containing hexadecyltrimethylammonium bromide to catalyze the curing reaction, was cured in a different temperature range (100 – 200 ºC) than **F7** (150 – 250 ºC), since it was expected that a fully cured network would be obtained at lower temperatures. The solvent resistance of system **F8** was good when cured between 120 and 200 ºC and it was resistant to rapid deformation when cured between 140 and 200 ºC (Figure 4-11, **B**). By the addition of the catalyst and pigment, the performance of system **F8** was enhanced and fully cured coatings could be prepared at approximately 150 ºC after 15 minutes.

Obviously, curing at lower temperature leads to enhanced appearance of the coatings with respect to discoloration. On the other hand, the curing of system **F8** proceeds quite rapidly, which could cause problems with respect to flow and leveling of the coating due to a limited cure-window (see Figure 4-9). Extensive negative effects on flow were not observed, even though some pin-holing occurred.

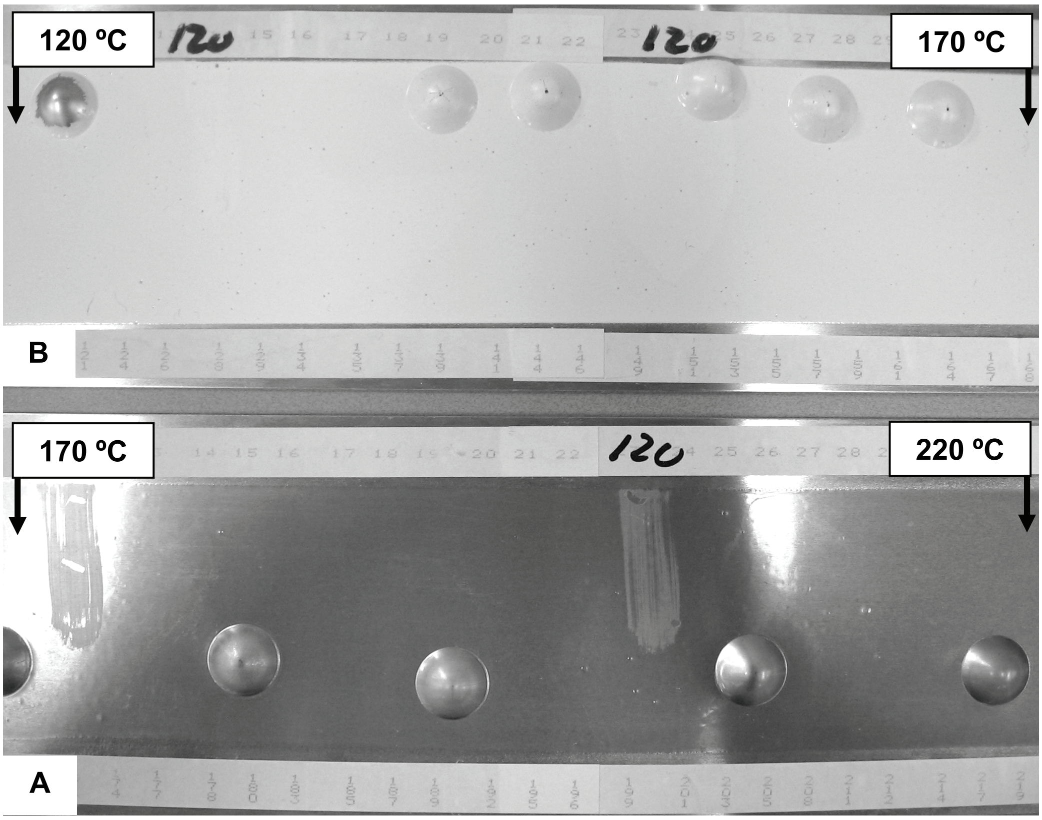


Figure 4-11. Aluminum gradient panels coated with **F7** (**A**, clear coating) and **F8** (**B**, coating pigmented with TiO_2). The curing temperature T_{cure} increases from left to right (indicated by the white textboxes). Hand-written numbers written at the top of the panels (e.g. '120') indicate the number of acetone double rubs performed during solvent resistance testing. *Note: the circular features are dents caused by the reverse impact testing.*

4.4 Conclusions

The feasibility of using citric acid as a functionality-enhancing compound in polyester synthesis was studied. NMR and FTIR studies showed that CA forms a reactive anhydride intermediate above its melting temperature, which seems to react rapidly with hydroxyl end-groups of prefabricated polyester resins to form ester bonds. Actually, the tendency of CA to lose a molecule of water upon heating proves to be highly beneficial as it results in a more reactive anhydride intermediate. Hence, although its thermal stability would suggest otherwise, CA can be applied in polymer modification even in the melt at temperatures up to 160 °C. Model reactions between CA and several mono-and bifunctional alcohol species showed that reaction occurred to a sufficient extent at relatively low temperatures. In addition, it was demonstrated that CA reacts faster with primary OH-groups than with secondary OH-groups, as expected. Interestingly, the model reactions also confirm previous observations that the *exo*-oriented OH-groups present in isosorbide and isoidide are more reactive than their *endo*-oriented counterparts present in isosorbide and isomannide. Linear hydroxy-functional polyesters were modified with CA at moderate temperatures (i.e. between 150 and 160 ºC), yielding slightly branched polymers with high acid functionalities. The presence of carboxylic acid end-groups was confirmed by ^{13}C NMR spectroscopy applied to polyesters modified with ^{13}C-labeled CA. Only low levels of unsaturated structures were formed. Curing of the system was simulated by reaction of the COOH-enriched product with *tert*-butyl glycidyl ether. Also, the rheological behaviour of formulated powder paints was investigated, showing that catalysis of the curing reaction significantly increases the curing rate. Finally, the modified biobased polyesters were cured using several curing agents, leading to chemically and mechanically stable coatings, applied from solvent as well as through powder coating application. Catalyzed systems could be cured at relatively low temperatures, around 150 ºC during 15 minutes. The cross-linking reaction was probably enhanced due to anhydride formation at the polyester chain ends during curing. We can therefore conclude that CA is a very useful monomer for enhancing polyester functionality. CA can be seen as a cheap, aliphatic and biobased alternative for, for example, trimellitic anhydride. The obtained levels of carboxylic acid functionality through modification of hydroxy-functional with the biobased monomer citric acid are clearly more than sufficient for thermosetting coating purposes.

References

(1) Misev, T. A. *Powder coatings - chemistry and technology* 1st ed: John Wiley & Sons: New York, 1991.

(2) Ikram-ul, H.; Ali, S.; Qadeer, M. A.; Iqbal, J. *Bioresour. Technol.* **2004**, *93,* 125.

(3) Pramanick, D.; Ray, T. T. *Polym. Bull.* **1988**, *19,* 365.

(4) Caldwell, C. G. (National Starch Products Inc.). US2461139, 1949.

(5) Wurzburg, O. B. (National Starch and Chemical Corporation). US2935510, 1960.

(6) Klaushofer, H.; Berghofer, E.; Steyrer, W. *Starch* **1978**, *30,* 47.

(7) Wing, R. E. *Ind. Crop. Prod.* **1996**, *5,* 301.

(8) Caulfield, D. F. *Tappi J.* **1994**, *77,* 205.

(9) Yang, C. Q.; Wang, X.; Kang, I.-S. *Text. Res. J.* **1997**, *67,* 334.

(10) Seidel, C.; Kulicke, W.-M.; Hess, C.; Hartmann, B.; Lechner, M. D.; Lazik, W. *Starch* **2001**, *53,* 305.

(11) Doll, K. M.; Shogren, R. L.; Willett, J. L.; Swift, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44,* 4259.

(12) Barroso-Bujans, F.; Martinez, R.; Ortiz, P. *J. Appl. Polym. Sci.* **2003**, *88,* 302.

(13) Yang, J.; Webb, A. R.; Ameer, G. A. *Adv. Mat.* **2004**, *16,* 511.

(14) Yang, J.; Webb, A. R.; Pickerill, S. J.; Hageman, G.; Ameer, G. A. *Biomaterials* **2006**, *27,* 1889.

(15) Ding, T.; Liu, Q.; Shi, R.; Tian, M.; Yang, J.; Zhang, L. *Polym. Degrad. Stab.* **2006**, *91,* 733.

(16) Lamanna, R. A.; Stephens, D. L. (Mobil Oil Corporation). US3956215, 1976.

(17) Mani, R.; Bhattacharya, M.; Leriche, C.; Nie, L.; Bassi, S. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40,* 3232.
(18) Cotting, J.-A.; Gottis, P.-G. (Ciba-Geigy Corporation). US5457168, 1995.
(19) Rickert, C.; Turpin, F.; Francois, J.; Tena, M. (Vantico Inc.). US6437045, 2002.
(20) Remenyi, J.; Balazs, B.; Toth, S.; Falus, A.; Toth, G.; Hudecz, F. *Biochem. Biophys. Res. Commun.* **2003**, *303,* 556.
(21) Zloh, M.; Dinand, E.; Brocchini, S. *Theor. Chem. Acc.* **2003**, *109,* 206.
(22) Jarusek, J. *Chemical Abstracts* **1967**, *66:56,078m,*
(23) Koning, C. E.; Van Duin, M.; Pagnoulle, C.; Jerome, R. *Prog. Pol. Sci.* **1998**, *23,* 707.
(24) Fischer, J. W.; Merwin, L. H.; Nissan, R. A. *Appl. Spectrosc.* **1995**, *49,* 120.
(25) Sessa, D. J.; Wing, R. E. *Ind. Crop. Prod.* **1999**, *10,* 55.
(26) Yao, F.; Bai, Y.; Chen, W.; An, X.; Yao, K.; Sun, P.; Lin, H. *Eur. Polym. J.* **2004**, *40,* 1895.
(27) Mao, Z.; Yang, C. Q. *J. Appl. Polym. Sci.* **2001**, *81,* 2142.
(28) Yang, C. Q.; Wang, X. *J. Appl. Polym. Sci.* **1998**, *70,* 2711.
(29) Repta, A. J.; Higuchi, T. *J. Pharm. Sci.* **1969**, *58,* 1110.
(30) Kollodge, J. S.; Porter, R. S. *Macromolecules* **1995**, *28,* 4089.
(31) HSE. *Revised guidance on control of exposure to TGIC in coating powders*. 2003 [cited 18th of May 2007]; Available from: http://www.hse.gov.uk/press/2003/e03081.htm.
(32) Shechter, L.; Wynstra, J.; Kurkjy, R. P. *Ind. Eng. Chem.* **1957**, *49,* 1107.
(33) Blank, W. J.; He, Z. A.; Picci, M. *J. Coat. Tech.* **2002**, *74,* 33.
(34) Tiemersma-Thoone, G. P. J. M.; Scholtens, B. J. R.; Dusek, K.; Gordon, M. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29,* 463.
(35) Stanssens, D.; Hermanns, R.; Wories, H. *Prog. Org. Coat.* **1993**, *22,* 379.
(36) Perera, D. Y. *Prog. Org. Coat.* **2004**, *50,* 247.
(37) Andrei, D. C.; Keddie, J. L.; Hay, J. N.; Yeates, S. G.; Briscoe, B. J.; Parsonage, D. *J. Coat. Tech.* **2001**, *73,* 65.
(38) Droste, D. H.; DiBenedetto, A. T. *J. Appl. Polym. Sci.* **1969**, *13,* 2149.
(39) Duivenvoorde, F. L.; Laven, J.; Van der Linde, R. *Prog. Org. Coat.* **2002**, *45,* 127.
(40) Higginbottom, H. P.; Bowers, G. R.; Grande, J. S.; Hill, L. W. *Prog. Org. Coat.* **1992**, *20,* 301.

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5

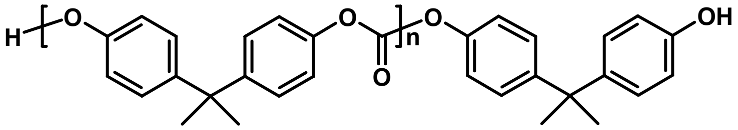
Hydroxy-functional polycarbonates based on the 1,4:3,6-dianhydrohexitols

Abstract

Biobased polycarbonates were synthesized from the three 1,4:3,6-dianhydrohexitols: 1,4:3,6-dianhydro-D-glucitol (isosorbide, IS), 1,4:3,6-dianhydro-L-iditol (isoidide, II) and 1,4:3,6-dianhydro-D-mannitol (isomannide, IM) as the principal diols, using different types of carbonyl sources. The (co)polycarbonates resulting from polycondensation reactions in solution, using phosgene-derivatives as carbonyl sources, consisted of several types of polymer chains with respect to chain topology (e.g. linear or cyclic chains) and end-group structure (e.g. hydroxyl, chloroformate or alkyl chloride end-groups). The introduction of flexible comonomers seemed to increase the amount of cyclic structures in the product mixtures. The transcarbonation of diphenyl carbonate with 1,4:3,6-dianhydrohexitols required high reaction temperatures and led to almost exclusively hydroxy-functional poly(1,4:3,6-dianhydrohexitol carbonate)s. Copolymerizing the 1,4:3,6-dianhydrohexitols with 1,3-propanediol and diphenyl carbonate at high temperature resulted in the partial loss of 1,3-propanediol and is accompanied by ether formation. On the other hand, by melt polycondensation of 1,4:3,6-dianhydrohexitol-based bis(phenyl carbonate) monomers in combination with primary diols and/or triols, the build-in of the comonomers could be achieved in a more controlled way. It was also possible to prepare OH-functional materials with suitable T_g*s and molecular weights. The biobased (co)polycarbonates were cured with conventional polyisocyanate curing agents, resulting in colorless to pale yellow transparent coatings with good mechanical performance and solvent resistance.*

5.1 Introduction

In the previous chapters of this thesis, aliphatic polyesters were described that proved to be suitable for thermoset coating and toner applications. These systems have several advantages, such as straightforward synthesis routes, flexibility in molecular design and good final coating properties. However, we have also found that there is room for improvement in terms of, for example, hydrolytic stability, coating toughness and appearance. We therefore investigated another class of step-growth polymers: polycarbonates. Conventional polycarbonates, such as the well-known poly(bisphenol-A carbonate) (Scheme 5-1), are known for their high toughness, excellent transparency and good solvent resistance. Even though this polymer can be made to crystallize (T_m = 270 ˚C), it is used as an amorphous material.[1] In addition, the carbonate links are more hydrolytically stable than esters.



Scheme 5-1. Chemical structure of poly(bisphenol-A carbonate).

Aromatic polycarbonates, however, are hardly applied in coating applications for several reasons. First of all, the T_gs of such polymers are quite high (approx. 150 ºC), which means that flow of these materials at common curing temperatures is insufficient to get good film formation. A second major disadvantage of such polycarbonates is their poor UV-stability due to their aromatic content. Using coatings prepared from poly(bisphenol-A carbonate) for exterior applications would lead to rapid and severe yellowing of the coating systems.

The ideal solution to these problems would be to design aliphatic polycarbonates of moderate molecular weight, having the right functionality and thermal properties for coating applications. Several types of aliphatic polycarbonates have already been investigated, such as oligo- and polycarbonates based on several linear glycols, materials synthesized by using cyclic carbonate monomers as carbonyl sources and systems based on oxiranes, using CO_2 as the carbonyl source.[2-7] Other aliphatic polycarbonates were based on 1,4-bis(hydroxymethyl) cyclohexane. These materials were applied from solution as coatings, cured with polyisocyanates.[8] Hyperbranched aliphatic polycarbonates having low T_gs have also been described for solvent borne coating applications.[9] Radiation-curable powder coating resins were prepared by ring-opening polymerization of 2,2-dimethyl-1,3-trimethylene carbonate, followed by end-capping with methacrylate moieties.[10] Different (co)polycarbonates based on the 1,4:3,6-dianhydrohexitols (DAH) were also described in literature, but coating applications were not elaborated upon.[11-20]

In this chapter, the synthesis and use of aliphatic polycarbonates are discussed, based on 1,4:3,6-dianhydrohexitols in combination with other diols or polyols having a functionality $\overline{F}_n \geq 2$. Three different polymerization routes were investigated to synthesize linear and/or branched (co)polycarbonates with the required characteristics with respect to molecular weight, T_g and functionality. First of all, polymers were prepared in solution using triphosgene and diphosgene, providing information concerning the effect of the different hydroxyl group orientations (i.e. *endo* or *exo*) on the polymerizations. Melt polycondensations were carried out, using diphenyl carbonate as carbonyl source. Finally, to enhance the control over 1,4:3,6-dianhydrohexitol and comonomer build-in, dialkyl and diaryl carbonate derivatives of the 1,4:3,6-dianhydrohexitols were synthesized, followed by melt polycondensation in the presence of several diols and triols. These synthetic routes were explored to achieve control over molecular weight, T_g and end-group structure. The resulting polycarbonates were subsequently cured with conventional polyisocyanate cross-linking agents and coating properties were assessed.

5.2 Experimental section

Materials. Isosorbide (polymer grade Polysorb® P, 98.5+ %) and isoidide (99.8 %) were obtained as gifts from Roquette Frères. Isomannide (97+ %) was a gift from Agrotechnology and Food Innovations. Diethyl carbonate, 1,3-propanediol (99.6+ %), glycerol (99.5+ %), methyl chloroformate, ethyl chloroformate, phenyl chloroformate, pyridine (anhydrous, 99.8 %), triethylamine (99.5 %), zinc acetate, diphosgene (trichloromethyl chloroformate, 97+ %), *tert*-butyl glycidyl ether, triglycidyl isocyanurate (TGIC), dibutyltin dilaurate as well as normalized solutions of KOH in methanol were purchased from Aldrich. Titanium(IV) n-butoxide, diphenyl carbonate, dimethyl carbonate, trimethylolpropane, 4-dimethylaminopyridine and acetic anhydride were bought from Acros Organics. Triphosgene (bis(trichloromethyl) carbonate, 99+ %) was obtained from Fluka, 1,4-butanediol was puchased from Merck. All solvents were supplied by Biosolve. Chloroform-*d* was obtained from Cambridge Isotope Laboratories, DMSO-d_6 was bought from Campro Scientific. Irganox HP2921, a mixture of phenolic and phosphonic anti-oxidants, was a gift from Ciba Specialty Chemicals. Isophorone diisocyanate-based, ε-caprolactam blocked polyisocyanate (trade name: Vestagon B1530) was a gift from Degussa GmbH. Hexamethylene diisocyanate-based polyisocyanate (trade name: Desmodur N3600) was a gift from Bayer AG. All chemicals were used as received.

Synthesis of (co)polycarbonates using triphosgene. (Co)polycarbonates were synthesized by polycondensation of 1,4:3,6-dianhydrohexitols, possibly in combination with other diol moieties, by phosgenation using triphosgene. The procedure is described for isosorbide in combination with 1,3-propanediol (PD). Isosorbide (1.99 g, 13.6 mmol), triphosgene (3.23 g, 10.9 mmol) and 1,3-propanediol (1.03 g, 13.6 mmol) were weighed into a 250 mL round-bottom flask and subsequently dissolved in a mixture of 1,4-dioxane (20 mL) and dichloromethane (100 mL). Pyridine (8.61 g, 108.9 mmol), diluted with dichloromethane (20 mL) was added dropwise at 0 ºC, while stirring. Subsequently, after 20 hours of stirring at room temperature, the reaction mixture was concentrated to half its original volume (by applying vacuum) and poured into cold methanol (500 mL). The precipitated polycarbonate was isolated by filtration and washed a second time by dissolution/precipitation from dicloromethane/methanol. Upon isolation, the polycarbonate was dried overnight at 40 °C *in vacuo*. Yield: 1.09 g (29 %).

Synthesis of (co)polycarbonates using diphosgene. (Co)polycarbonates were also synthesized by using diphosgene as a carbonyl source. The procedure is described for isoidide in combination with 1,3-propanediol (PD). Isoidide (2.09 g, 14.3 mmol) and 1,3-propanediol (1.09 g, 14.3 mmol) were weighed into a 250 mL round-bottom flask and subsequently dissolved in a mixture of 1,4-dioxane (20 mL) and dichloromethane (80 mL). Subsequently, diphosgene (2.89 g, 14.6 mmol), dissolved in dry dichloromethane (10 mL), was added at once. Pyridine (9.05 g, 114.4 mmol), diluted with dichloromethane (20 mL), was added dropwise at 0 ºC, while stirring. Subsequently, after 6 hours of stirring at room temperature, the reaction mixture was concentrated to half its original volume and poured into cold methanol. The precipitated polycarbonate was filtered from the solution and dried *in vacuo*, overnight. Yield: 0.77 g (20 %).

Synthesis of (co)polycarbonates using diphenyl carbonate. OH-functional (co)polycarbonates were synthesized by polycondensation of the different 1,4:3,6-dianhydrohexitols, possibly in combination with other diol moieties, by transesterification with diphenyl carbonate. A typical melt polymerization was carried out according to the following procedure, described for isoidide. Isoidide (15.31 g, 105 mmol), diphenyl carbonate (20.40 g, 95 mmol), zinc acetate (0.05 mol% relative to DPC) and Irganox HP2921 (0.20 g) were weighed into a 250 mL round-bottom glass flange reactor. The reactor was fitted with a vigreux column and a Dean-Stark type condenser to collect the condensation product (in this case: phenol). During the first part of the synthesis, the setup was continuously flushed with inert gas to limit oxidation and facilitate removal of phenol from the reaction mixture. While stirring, the mixture was heated to 160 ºC using a heating mantle, and a clear melt was obtained. Subsequently, the reaction temperature was increased stepwise up to 245 ºC, to maintain distillation of phenol. After 4 hours, vacuum processing was started at 245 ºC, with typical pressures ranging from 1 – 3 mbar.

Vacuum processing was performed during 2 hours and resulted in a rapid increase in melt viscosity. The polymer was discharged from the reactor and left to cool and solidify. The product is soluble in chloroform, DCM and HFIP, but not in THF. Yield: 17.1 g (95 %).

Synthesis of the dialkyl and diaryl carbonates of isosorbide, isoidide and isomannide. Dialkyl and diaryl carbonates were synthesized based on the three different 1,4:3,6-dianhydrohexitols: isosorbide, isoidide and isomannide. The synthetic procedures were the same for the three isomers and are described here for isoidide.

Isoidide bis(ethyl carbonate) (IIBEC)

Isoidide (5.00 g, 34.2 mmol) and pyridine (8.11 g, 102.5 mmol) were dissolved in 40 mL of dichloromethane (DCM). The flask was placed in an ice-bath. To this solution, ethyl chloroformate (11.13 g, 102.5 mmol) in 30 mL DCM was added dropwise during 2.5 hours, while stirring. The reaction was continued overnight at room temperature. The reaction mixture was then concentrated under reduced pressure and poured into EtOAc (250 mL). The crude product was purified by repeated extraction of the ethyl acetate solution with water. Finally, the purified monomer was obtained as a pale yellow oil by evaporation of the ethyl acetate. Yield: 1.5 g (15 %), purity: 97+ %. *Isosorbide bis(ethyl carbonate) (ISBEC) was prepared following the same procedure. Yield: 18 %, purity: 97 %.*

Isoidide bis(phenyl carbonate)(IIBPC)

Isoidide (15.05 g, 103 mmol) and pyridine (17.96 g, 227 mmol) were dissolved in 200 mL of tetrahydrofuran (THF). Phenyl chloroformate (35.47 g, 227 mmol) was added dropwise during approximately 2 hours at 5-10 ºC, while stirring. The reaction was continued for 4 hours at room temperature. Subsequently, the reaction mixture was poured into demineralized water, affording a white precipitate. This solid was collected on a glass filter (pore size 4) and washed with a 5 wt% aqueous solution of $NaHCO_3$ and several times with water. The crude product was recrystallized from ethyl acetate, collected by filtration over a glass filter (pore size 4) and dried in vacuo at 40 ºC.[16,18] Yield: 26.15 g (65.7 %), purity: 98+ %, mp: 107-109 ºC. *Isosorbide bis(phenyl carbonate) (ISBPC) and isomannide bis(phenyl carbonate) (IMBPC) were prepared following the same procedure. ISBPC: yield: 64.7 %, purity: 98+ %, mp: 151-153 ºC; IMBPC: yield: 79.4 %, purity: 97+ %, mp: 131-132 ºC.*

Synthesis of (co)polycarbonates from 1,4:3,6-dianhydrohexitol bis(phenyl carbonate)s. Several linear and branched OH-functional (co)polycarbonates were synthesized from the bis(phenyl carbonate)s of isosorbide, isoidide and isomannide. A typical melt polymerization was carried out according to the following procedure, described for isosorbide bis(phenyl carbonate) (ISBPC). ISBPC (15.19 g, 39.3 mmol), isosorbide (2.41 g, 16.5 mmol), 1,3-propanediol (2.09 g, 27.5 mmol), trimethylolpropane (0.42 g, 3.1 mmol), zinc acetate (0.05 mol% relative to the amount of ISBPC) and Irganox HP 2921 (0.5 wt% relative to the amount of diols) were weighed into a 250 mL round-bottom glass flange reactor. The reactor was fitted with a Dean-Stark-type condenser to collect the condensation product. During the first part of the synthesis, the setup was continuously flushed with inert gas to limit oxidation and facilitate removal of phenol. While being stirred, the mixture was heated up to 185 °C using a heating mantle. Subsequently, the reaction temperature was increased stepwise to maintain distillation of the formed phenol. The maximum reaction temperature was 210 °C. After 3 h, vacuum processing was started at 205-210 °C, with typical pressures ranging from 1 - 5 mbar. Vacuum was applied until no more phenol was distilled off, after which the viscous polymer melt was discharged from the reactor and left to cool and solidify. The resulting transparent glassy polycarbonate is soluble in, for example, chloroform, dichloromethane (DCM), hexafluoroisopropanol (HFIP) and N-methyl-2-pyrrolidone (NMP), but not in tetrahydrofuran (THF). Yield: 9.31 g (72.8 %).

Synthesis of (co)polycarbonates from isosorbide bis(ethyl carbonate). ISBEC (5.97 g, 20.6 mmol), isosorbide (0.30 g, 2.1 mmol), 1,3-propanediol (1.57 g, 20.6 mmol), phenol (0.39 g, 4.1 mmol), zinc acetate (0.5 mol% relative to the amount of ISBEC) and Irganox HP2921 (78 mg, 1 wt%) were weighed into a 250 mL round-bottom glass flange reactor. The reactor was fitted with a vigreux column and a Dean-Stark type condenser to collect the condensation product (in this case: ethanol). During the first part of the synthesis, the setup was continuously flushed with inert gas to limit oxidation and facilitate the removal of ethanol and phenol from the reaction mixture. While stirring, the mixture was heated to 100 ºC using a heating mantle, and a clear melt was obtained. Subsequently, the reaction temperature was increased slowly up to 210 ºC, to maintain distillation of ethanol. After 5 hours, vacuum processing was started at 210 ºC. Pressures ranged from 1 – 5 mbar, to remove ethanol and phenol. Vacuum processing was continued during 7 hours. The resulting polymer was light brown and transparent. Yield: 2.33 g (41.2 %).

Solvent casting and curing of biobased (co)polycarbonates using conventional cross-linkers. Hydroxy-functional (co)polycarbonates were cured using: (1) a trimer of hexamethylene diisocyanate (NCO equivalent weight = 183 g/mol, trade name: Desmodur N3600) and (2) an ε-caprolactam blocked trimer of isophorone diisocyanate (NCO equivalent weight = 275 g/mol, trade name: Vestagon B1530). Ad 1: A solution of 0.3 – 0.5 g of polycarbonate in 0.8 mL of N-methyl-2-pyrrolidone (NMP) was prepared, as well as a separate solution of Desmodur N3600 (1.05 molar equivalent, calculated from titration data) in 0.2 mL of NMP. The two solutions were mixed and applied directly to the aluminum substrate as a wet film with a thickness of 250 μm, using a doctor blade. After drying at room temperature, the film was cured at 180 ºC under N_2 during 20 minutes. Ad 2: A solution of 0.3 – 0.5 g of polycarbonate, 1.05 molar equivalent of the cross-linker and 0.5 wt% (relative to the amount of polycarbonate used) of dibutyltin dilaurate in 1 mL of NMP was prepared.

Subsequently, a wet film of approximately 250 μm thickness was applied onto an aluminum panel. The film was left to dry at room temperature, followed by curing at 200 ºC during 30 minutes under nitrogen. Both types of curing agents resulted in poly(carbonate urethane) coatings.

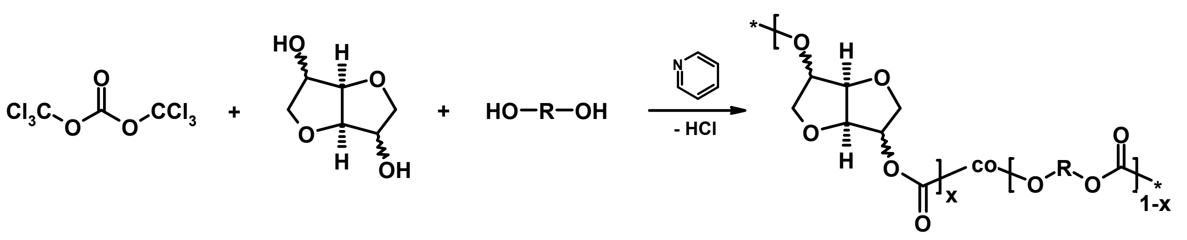
Measurements. SEC analysis was carried out using a set-up equipped with a Shimadzu LC-10AD pump and a WATERS 2414 differential refractive index detector (at 35 ºC). Injections were done by a MIDAS auto-injector, the injection volume being 50 μL. PSS (2× PFG-lin-XL, 7 μm, 8×300 mm, 40 °C) columns were used. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was used as eluent at a flow rate of 1.0 mL/min. Calibration curves were obtained using PMMA standards. Data acquisition and processing were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer, chloroform-*d* was used as the solvent (unless stated otherwise). The thermal stabilities of polymer samples were determined using a Perkin-Elmer Pyris 6 TGA apparatus. Approximately 10 mg of polymer was heated from 40 ºC to 700 ºC at a heating rate of 10 ºC/min under a N_2 flow of 20 mL/min. Results were analyzed using Pyris 4.01 software. DSC measurements were carried out with a DSC Q100 from TA Instruments. MALDI-ToF-MS measurements were performed on a Voyager DE-STR from Applied Biosystems. Calibrations were carried out with poly(ethylene oxide) standards for the lower mass range and polystyrene standards for the higher mass range. The mass accuracy was better than 0.2 Dalton, the mass resolution was approximately m/z 12,000. DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as matrix. Potassium trifluoroacetate (Aldrich, >99 %) was used as cationization agent. Solutions of the matrix (40 mg/mL), potassium trifluoroacetate (5 mg/mL) and the polyester sample (1 mg/mL) in THF were premixed in a ratio of 5:1:5. The mixture was subsequently hand-spotted on the target and left to dry. Spectra were recorded in reflector mode at positive polarity. Potentiometric titrations were carried out using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The hydroxyl end-groups of the polymer samples were acetylated with acetic anhydride at room temperature (4-dimethylaminopyridine was used as catalyst), followed by titration of the resulting acetic acid with normalized 0.5 N methanolic KOH solution. Blank measurements were necessary to obtain the hydroxyl values. The hydroxyl value (*OHV*) is the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of material. All titrations were carried out in duplo. Complex viscosities of polycarbonates were determined as a function of temperature using a TA Instruments AR1000-N Rheolyst rheometer, having a parallel plate geometry. Temperature sweeps were performed, during which the temperature was decreased starting at a maximum temperature of 180 ºC. When the storage modulus G' exceeded 10^6 Pa, the measurements were stopped automatically. The following parameter settings were used: cooling rate = 3 ºC/min., strain = 1 %, frequency = 1 Hz (= 6.283 rad/s). Data points were collected after every cooling step of 3 ºC and an equilibration time of 1 minute. Data acquisition was done with Rheology Advantage Instrument Control software, data analysis with Rheology Advantage Data Analysis software. Cross-linking and coating performance at room temperature were evaluated using the following characterization methods: acetone rub test (solvent resistance test: the sample is rubbed with a cloth drenched in acetone. If no damage is visible after more than 150 rubs, the coating has good acetone resistance) and reverse impact test (a rapid deformation test, performed by dropping a certain weight (in kg) on the back of a coated panel from a certain height (in cm), described in ASTM D 2794). The thicknesses of the obtained coatings were measured using a magnetic induction coating thickness measuring device (Twin-Check by List-Magnetik GmbH).

5.3 Results and discussion

In this paragraph, the synthesis, characterization and properties of (co)polycarbonates based on the renewable 1,4:3,6-dianhydrohexitols (DAHs) are described. Linear as well as branched polycarbonates were prepared following three different synthetic procedures: 1) polymerization of diols and polyols in solution using phosgene derivatives such as tri- and diphosgene as carbonyl sources; 2) melt polycondensation of diols and polyols using diphenyl carbonate as a carbonyl source; 3) melt polycondensation of diols and polyols using DAH-based di(alkyl/aryl carbonate)s as a carbonyl sources.

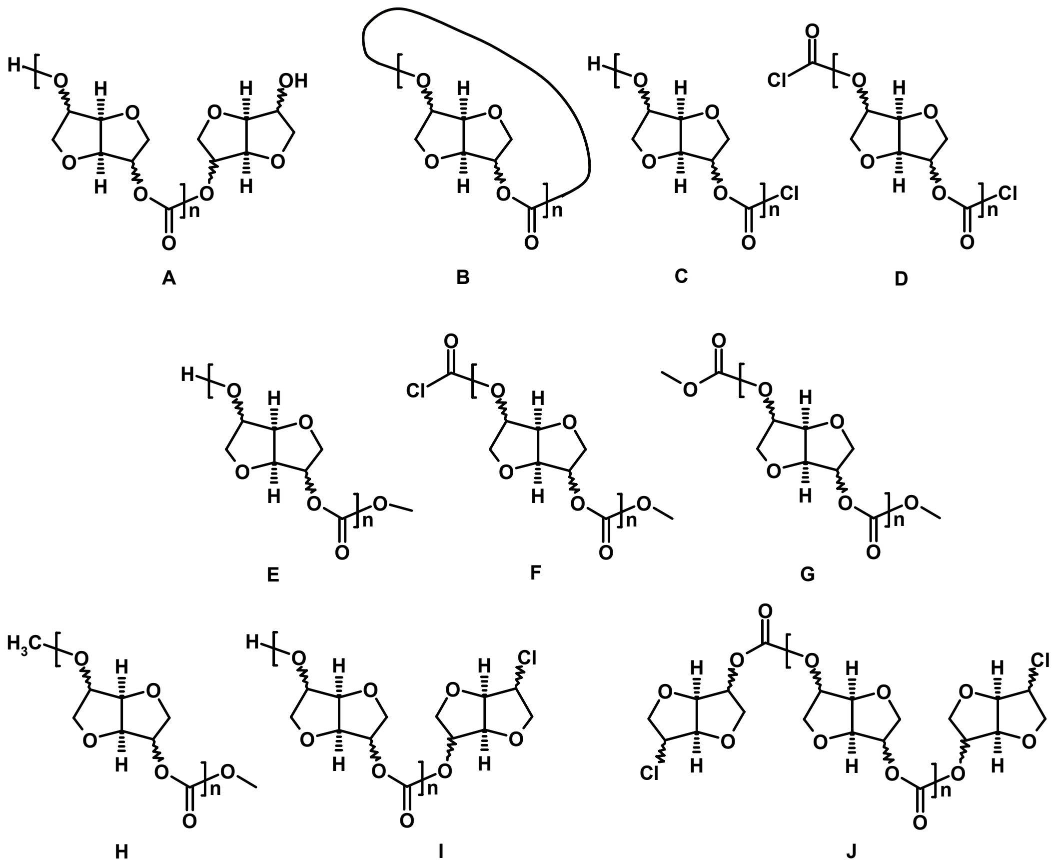
5.3.1 Polycarbonates using tri- and diphosgene as carbonyl sources

In this study, the solid triphosgene (TPh) and the liquid diphosgene (DPh) were used, since these phosgene derivatives are more convenient to manipulate than the gaseous phosgene itself. Under the influence of a base (e.g. pyridine or triethylamine), phosgene is formed *in situ*, reacting with the available OH-functionalities of the diol monomers. A more detailed reaction mechanism of a reaction between TPh and a DAH is depicted in Appendix C, Scheme C-1. Overall, the polycondensation reaction yielding (co)polycarbonates can be summarized as depicted in Scheme 5-2. Several types of polymer end-groups can result from the reaction between diols or polyols and TPh, using pyridine as a catalyst and HCl scavenger.[21,22] The types of end-groups present in a certain polymer sample depend on reaction conditions such as stoichiometry, monomer concentration and TPh concentration as well as on the work-up procedure.



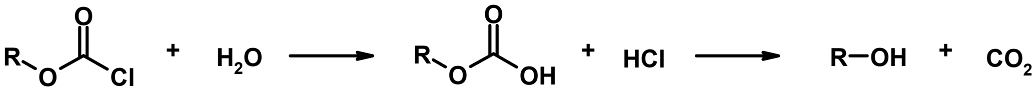
Scheme 5-2. Polycondensation of 1,4:3,6-dianhydrohexitols and, optionally, comonomers (with $0 < x \leq 1$) using triphosgene (TPh) as a carbonyl source.

MALDI-ToF-MS spectra that were obtained for the different polycarbonates, prepared using di- or triphosgene, confirm that several types of polymeric species are formed. In Scheme 5-3, these different species are depicted for 1,4:3,6-dianhydrohexitol-based polycarbonates. Besides the desired structure **A**, having 2 hydroxyl end-groups, also cyclic structures **B** are formed. In addition, several types of linear species can be formed, such as polymer chains having one or two chloroformate-type end-groups (structures **C** and **D**). If the work-up procedure, applied to such chloroformate-terminated species, involves precipitation in methanol, structures such as **F, G** and **H** can be formed.



Scheme 5-3. Potential products of the reaction between a 1,4:3,6-dianhydrohexitol and TPh (products **E**, **F**, **G** and **H** are formed during work-up of the polymers, more specifically during precipitation in methanol).

Precipitation of chloroformate-functional polycarbonates **C**, **D** and **F** in water would yield a carbonic acid ester, formed through hydrolysis. This end-group is not stable and will loose one molecule of CO_2 to form a hydroxyl group (Scheme 5-4).[23,24]



Scheme 5-4. The hydrolysis of chloroformate end-groups, followed by decarboxylation, yielding a hydroxyl end-group.[23]

Finally, structures **I** and **J** can be formed by decarboxylation of the aliphatic chloroformate end-groups of **C**, **D** and **F**, catalyzed by pyridine.[22,25] In the following paragraphs, Scheme 5-3 will be referred to in order to show which end-groups have been identified in the synthesized polycarbonates.

Poly(DAH carbonate)s prepared using triphosgene (TPh) as a carbonyl source

Initially, the DAH homopolycarbonates were prepared by reacting isosorbide (IS), isoidide (II) and isomannide (IM) with TPh. As was described by Chatti et al.[13], IS and IM have different behaviors when used in polycondensation reactions using diphosgene. For example, the MALDI spectra of homopolycarbonates of isosorbide hardly showed signals corresponding to cyclic species, while the MALDI spectrum of copolycarbonates of isosorbide and isomannide showed high intensity signals of cyclic chains. These differences are mainly due to the different orientations of the OH-groups of these monomers. We expected that polycarbonates based on isoidide would contain predominantly linear chains and to examine whether this is indeed the case, we first investigated the three different poly(1,4:3,6-dianhydrohexitol carbonate)s, synthesized following the same procedure. Their properties are given in Table 5-1. All SEC results presented in this chapter are obtained from measurements using HFIP as the eluent, due to poor solubility of these polycarbonates in THF. The T_gs of these polycarbonates seem to depend on their $\overline{M}_n$ values (compare entries **1a** and **1b**) but also on the type of 1,4:3,6-dianhydrohexitol used, when synthesized under these conditions. For example, the T_g of poly(isoidide carbonate) **2** is somewhat lower than the T_g of poly(isosorbide carbonate) **1a**, while these two materials have similar molecular weights and polydispersities. The only difference between entries **1a** and **1b** is the amount of

TPh used to synthesize these polymers. Adding more TPh to, in this case, isosorbide, causes a significant increase of the resulting molecular weight.

Table 5-1. Properties of poly(DAH carbonate)s prepared using TPh as a carbonyl source.

entry [1]	**feed composition**	T_g **[°C]**	$\overline{M}_n$ **[g/mol]**	$\overline{M}_w$ **[g/mol]**	***PDI***	**main types of end-groups** [2]
1a	IS/TPh [1:0.33]	134.8	3500	6100	1.8	**A**, B, H
1b	IS/ TPh [1:0.38]	137.6	5200	10100	1.9	**G**, B
2	II/TPh [1:0.33]	130.9	3200	6200	1.9	**A**, H
3	IM/TPh [1:0.33]	120.9	3400	10700	3.1	**B**, H

[1] Reaction conditions (see Experimental section): addition of pyridine solution to diol/TPh solution at 0 ºC, followed by stirring at room temperature for 20 hrs.

[2] As identified from MALDI-ToF-MS spectra, codes refer to structures depicted in Scheme 5-3. **Bold** codes refer to the main type of signals present in the spectra.

The molecular weight distribution of poly(isomannide carbonate) (entry **3**, Table 5-1) is broader than those of the other two polycarbonates. The broad *PDI* as well as the limited solubility of polymer **3** (this material is only partly soluble in $CHCl_3$) suggest that branching and/or cross-linking might have occurred, possibly through acid catalyzed ring-opening of the anhydro ether ring of IM.[26,27] In other words, the possible branching of poly(isomannide carbonate) might be due to the limited stability of isomannide in the aggressive reaction environment during these polymerizations. Polycarbonates **1a**, **1b** and **2** have *PDI* values below 2 and appear to be fully soluble in $CHCl_3$ as well as in HFIP. In addition, the T_g of polycarbonate **3** is lower than those of polymers **1a** and **2** having similar molecular weights, which might indicate branching as well.[28] Furthermore, sample **3** probably contains more cyclic structures than samples **1a** and **2**, which might also be a factor influencing the observed T_g.

The ^{1}H NMR spectrum of polycarbonate **1a**, depicted in Figure 5-1, shows several resonances, similar to the spectra of isosorbide-based copolyesters shown in Chapter 2. The isosorbide end-groups of polymer **1a** (signals **d** and **e**) can be clearly distinguished in this spectrum, indicating that at least part of the polycarbonate chains has hydroxyl end-groups. Also, two singlets are visible at 3.7 ppm (signal **h**) and at 3.85 ppm (signal **g**, partly overlapping with the group of resonances **f**) which can respectively be attributed to methyl ether and methyl carbonate groups, resulting from the precipitation of the reaction mixture in methanol.

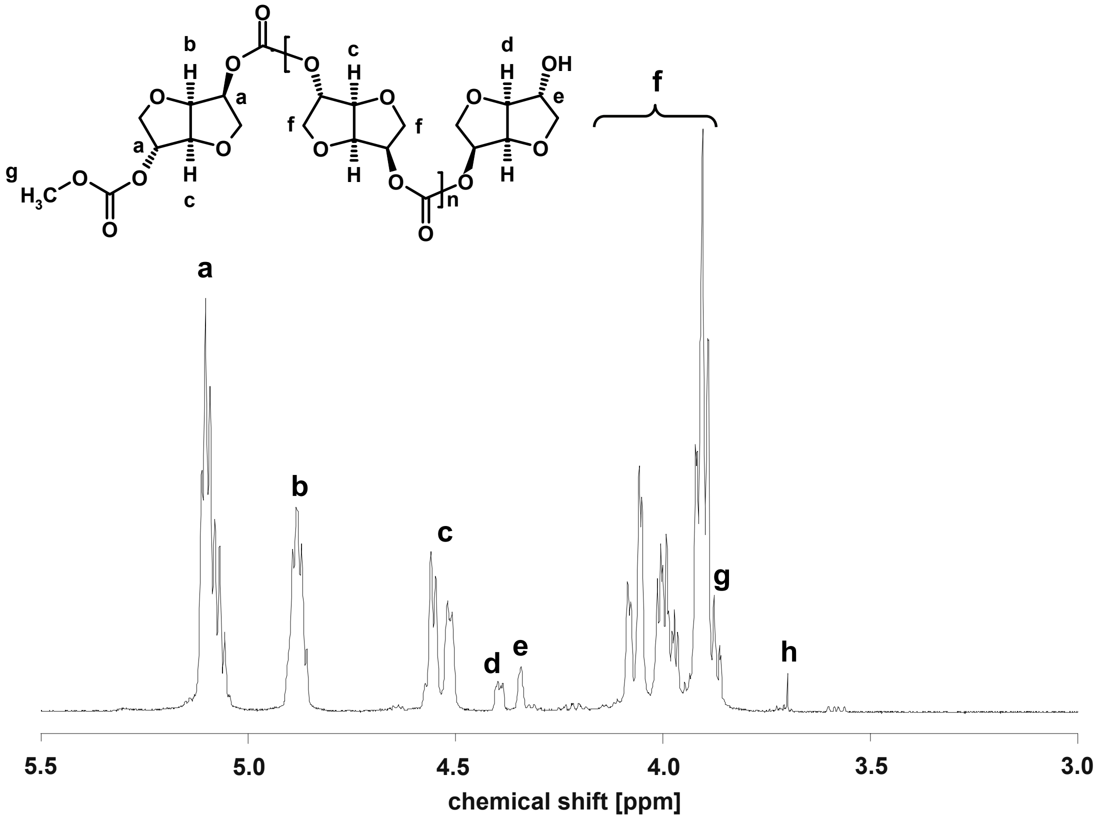


Figure 5-1. ^{1}H NMR spectrum of poly(isosorbide carbonate), polymer **1a**, prepared using TPh as a carbonyl source.

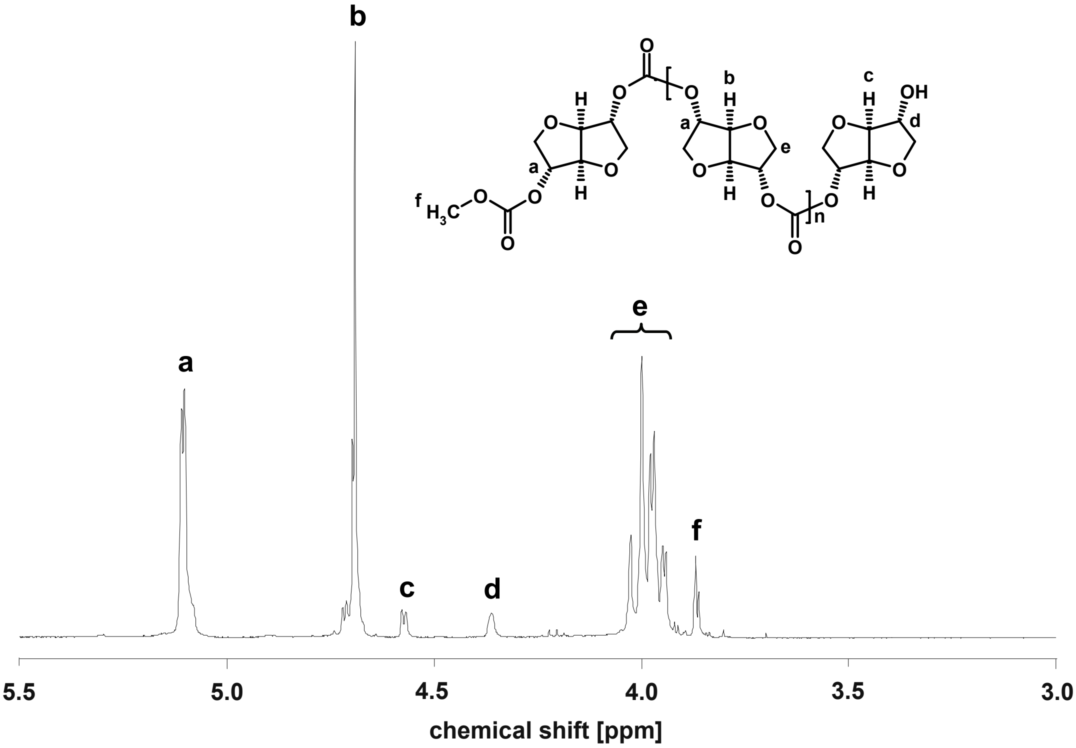


Figure 5-2. ^{1}H NMR spectrum of poly(isoidide carbonate), polymer **2**, prepared using TPh as a carbonyl source.

Contrary to what was observed previously for isosorbide-based polyesters prepared by melt polycondensation (see Chapter 3), it appears that the *endo*-oriented OH-groups of isosorbide have reacted to form carbonate linkages to a higher extent (conversion = 97 %) than the *exo*-oriented hydroxyls (conversion = 88 %), as determined by integration of the signals **b** and **c** (Figure 5-1). This confirms observations described in literature concerning the reactivity of these different types of OH-groups in the presence of, for example, pyridine hydrochloride.[29-31] As becomes clear from Scheme C-1 in Appendix C, the hydroxyl groups of the 1,4:3,6-dianhydrohexitols act as nucleophiles in the reaction with triphosgene. The nucleophilic character of the *endo*-OH (present in isosorbide and isomannide) is enhanced by its internal hydrogen bonding as well as by the presence of pyridine/pyridine hydrochloride.[32] This is probably the main cause for the increased reactivity of these OH-groups relative to that of the *exo*-oriented hydroxyl groups.[33]

End-group structures of homopolycarbonates prepared using TPh

As expected, the ^{1}H NMR spectrum of polymer **1b** does not show clear resonances corresponding to isosorbide moieties at the chain ends due to the excess of TPh (and, thus, phosgene moieties) present during its synthesis. As was already described for polymer **1a**, resonances corresponding to methyl groups were also observed in the spectrum of polymer **1b**. The ^{1}H NMR spectrum of polycarbonate **2** (Figure 5-2) clearly shows hydroxyl end-groups, also indicating at least partial hydroxy-functionality of the resin. Polycarbonate **3** was only partly soluble in $CDCl_3$, which resulted in poor NMR spectra. Still, it was possible to distinguish some isomannide hydroxyl end-groups and resonances corresponding to methyl groups.

The MALDI-ToF-MS spectra of these poly(DAH carbonate)s, synthesized using TPh as a carbonyl source, show signals at the same molecular masses, but the relative intensities of these peaks differ for the different materials. For example, Figure 5-3 shows sections of the MALDI spectra of polymers **1a**, **2** and **3,** in which the ratios of linear versus cyclic chains are different for all three samples. First of all, peaks corresponding to linear chains having two hydroxyl end-groups (signals **A**) are abundant in the spectra of **1a** and **2**, while they only have low intensities in spectrum **3**. On the other hand, spectrum **3** has high intensity peaks attributed to cyclic polycarbonate chains (signals **B**), whereas spectra **1a** and **2** do not show strong signals for this species. Especially the isoidide-based polycarbonate **2** shows very low levels of cyclic species, according to MALDI-ToF-MS.

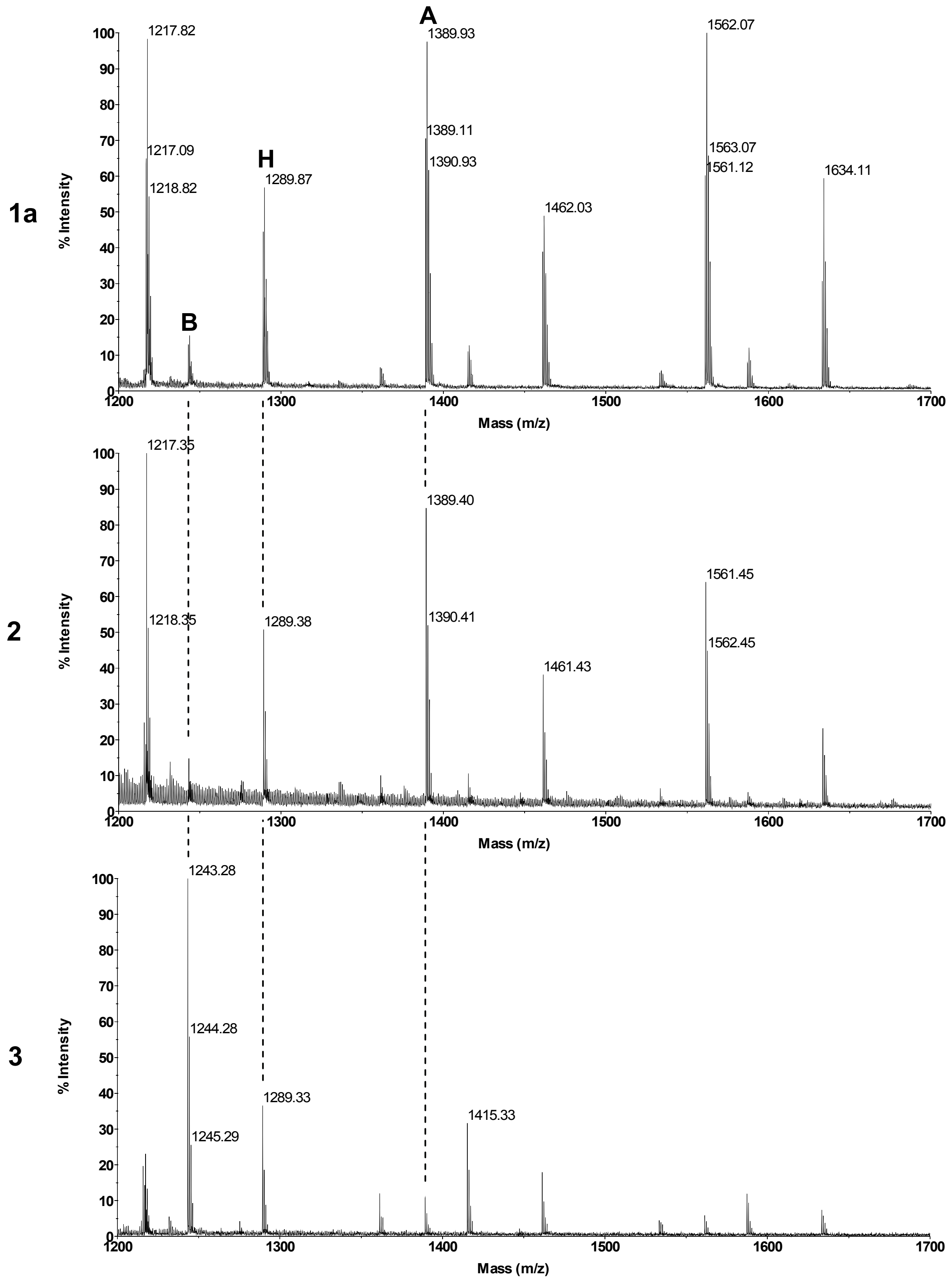
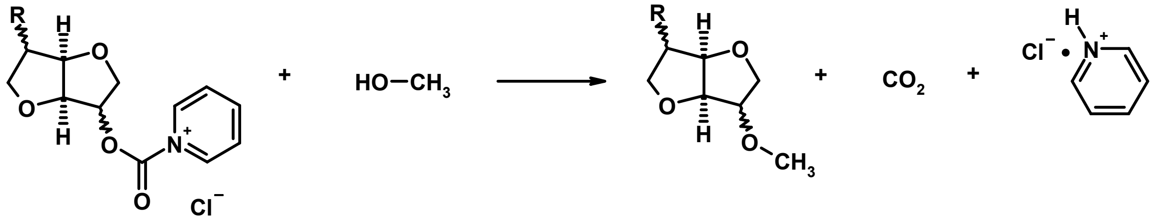


Figure 5-3. Sections of MALDI-ToF-MS spectra of polycarbonates **1a**, **2** and **3**, with (**A**) linear chains with two hydroxyl end-groups, (**B**) cyclic chains and (**H**) linear chains containing one ether linkage and having methyl carbonate or ether end-groups. Codes refer to structures drawn in Scheme 5-3.

Although the quantitative interpretation of the MALDI spectra in terms of relative concentrations of linear and cyclic species is impossible, the trend observed here is as may be expected when considering the orientations of the OH-groups of the different 1,4:3,6-dianhydrohexitols. It was previously found that polymerization of isosorbide in solution, using diphosgene as a carbonyl source, hardly yields cyclic structures. This was thought to be due to the formation of a compact immobile polymer chain, hampering cyclization. When copolymerizing equimolar amounts of isosorbide and isomannide, predominantly cyclic polymer chains were formed. Apparently, the presence of isomannide in the polymer chains disturbs the conformation of the poly(isosorbide carbonate) chains, enhanced its mobility and, thus, its capability to form cyclic structures.[13] Possibly, the conformation of poly(isomannide carbonate) **3** is such that cycle formation is favored. The main difference between isosorbide and isomannide is the orientation of their hydroxyl groups: *endo*/*exo* and *endo*/*endo*, respectively. The observation that polymerization of isoidide, having two *exo*-oriented hydroxyl groups, apparently yields even less cyclic polymer chains than are observed in poly(isosorbide carbonate), may indicate that the *exo*-orientation of the hydroxyl groups of the 1,4:3,6-dianhydrohexitols favors the formation of more extended, less mobile polycarbonate chains and, as a result, leads to reduced cycle formation.

A third type of polycarbonate chains, species **H** (Scheme 5-3), causes peaks of significant intensities in all three MALDI spectra. These signals can be assigned to a linear polycarbonate chain containing one ether linkage. At very low molecular weights (around 800-900 Da), chains with two ether linkages were identified. However, no species with more than two ether linkages were identified. Based on these observations, it seems probable that the ether linkages are present at the chain end as part of the end-group structure of these particular chains. In this case, the end-groups of these chains should be methyl ethers, which are formed during the precipitation of the reaction mixture in methanol during work-up. Presumably, the ether linkages are formed by the reaction of a pyridinium complex, present at the polymer chain end, with methanol, according to Scheme 5-5 (see also Scheme C-1 in Appendix C). The presence of these methyl ether end-groups seems to be confirmed by the presence of a singlet signal at 3.7 ppm in the ^{1}H NMR spectra of polymers **1a**, **1b**, and **2**. Methyl carbonate end-groups caused resonances at slightly higher shifts of approximately 3.85 ppm. The formation of ether linkages through decarboxylation of a carbonate group or through dehydration of two alcohol end-groups[34] seems unlikely in this case, since these types of degradation reactions usually occur at elevated temperatures, while the described materials were synthesized between 0 and 25 ºC.



Scheme 5-5. The formation of a methyl ether end-group through the reaction between a pyridinium complex and methanol during the precipitation of the concentrated polymerization reaction mixture in methanol.

By comparing the MALDI-ToF-MS spectra of entries **1a** and **1b**, it is possible to see the effect of the variation of the amount of TPh in the reaction mixture on the types of chains formed (Appendix C, Figure C-1). From Table 5-1, it already became clear that the molecular weight increased significantly when increasing the amount of TPh. By increasing this amount from 0.33 molar equivalents to 0.38 molar equivalents relative to the amount of DAH, the signals attributed to linear OH-functional chains disappear completely. Cyclic chains cause peaks of significant intensity and the predominant signals correspond to linear chains having two methyl carbonate end-groups (which is supported by the presence of a resonance attributed to methyl carbonate end-groups in the ^{1}H NMR spectrum of polymer **1b**). This can be easily explained by the presence of an excess of phosgene moieties relative to the diol, leading to chloroformate groups at the chain ends, which form methyl carbonates upon precipitation in methanol. Signals corresponding to chains containing ether linkages are observed only at very low intensities.

DAH-based copolycarbonates prepared using triphosgene (TPh) and diphosgene (DPh) as carbonyl sources

After investigating the poly(1,4:3,6-dianhydrohexitol carbonate)s, we proceeded to prepare copolycarbonates to reduce the T_g and to enhance the functionalities of these materials. After all, the T_g of poly(isosorbide carbonate) with a $\overline{M}_n$ of 3500 g/mol is around 135 ºC, which is rather high and approaches the T_g of poly(bisphenol-A carbonate) of 150 ºC. Several linear poly(isosorbide-*co*-propylene carbonate)s were synthesized with different ratios of the monomers isosorbide:1,3-propanediol (1,3-PD) to tune the T_g, using triphosgene (TPh) as a carbonyl source. The maximum functionality that can be obtained for these linear polycarbonates is $\overline{F}_n = 2$, which can in principle be improved by introducing monomers with a functionality higher than two (Table 5-2).

Table 5-2. DAH-based copolycarbonates prepared using TPh as a carbonyl source.

entry [1]	**feed composition** [2]	**composition (NMR)**	T_g **[ºC]**	$\overline{M}_n$ **[g/mol]**	$\overline{M}_w$ **[g/mol]**	***PDI***	**main types of end-groups** [3]
4	IS/1,3-PD/TPh [0.5:0.5:0.33]	IS/1,3-PD [0.49:0.51]	42.9	1300	1900	1.4	**B**, A, E
5	IS/1,3-PD/TPh [0.5:0.5:0.38]	IS/1,3-PD [0.53:0.47]	57.2	1800	2500	1.4	**B**, A
6	IS/1,3-PD/TPh [0.5:0.5:0.40]	IS/1,3-PD [0.50:0.50]	83.0	2600	4200	1.6	**J**, A, B
7	IS/1,3-PD/TPh [0.75:0.25:0.33]	IS/1,3-PD [0.73:0.27]	79.3	1200	1700	1.4	**F**, B, A
8	II/1,3-PD/TPh [0.5:0.5:0.35]	II/1,3-PD [0.47:0.53]	48.1	1800	2300	1.3	**F** , B, A
9	IM/1,3-PD/TPh [0.5:0.5:0.38]	IM/1,3-PD [0.54:0.46]	46.7	1900	3200	1.7	**B**, A, J
10	IS/GLY/TPh [0.91:0.09:0.37]	IS/GLY [0.9:0.1]	109.8	3900	12900	3.3	**G**, B

[1] Reaction conditions (see Experimental section): addition of pyridine solution to diol/TPh solution at 0 ºC, followed by stirring at room temperature for 20 hrs. During the syntheses of entries **4** and **7**, stirring at room temperature was continued only for 6 hrs instead of 20 hrs.

[2] IS = isosorbide, II = isoidide, IM = isomannide, 1,3-PD = 1,3-propanediol, TPh = triphosgene, GLY = glycerol.

[3] As identified from MALDI-ToF-MS spectra, codes refer to structures depicted in Scheme 5-3. **Bold** codes refer to the main type of signals present in the spectra. OH-values were not determined for these polymers, since the amount of available product was insufficient for titration purposes.

The ^{1}H NMR spectra of the poly(isosorbide-*co*-propylene carbonate)s **4**-**7** reveal that the *endo*-oriented hydroxyl group of isosorbide reacts to a higher conversion than its *exo*-oriented counterpart under these reaction conditions, confirming the previously described results for poly(isosorbide carbonate) **1a**. As an example, the ^{1}H NMR spectrum of entry **4** is given in Appendix C, Figure C-2. The molecular weights of most of the copolymers in Table 5-2 are significantly lower than those obtained when synthesizing DAH-based homopolycarbonates using TPh (e.g. entry **1a,** Table 5-1). The grade of 1,3-propanediol used in these reactions has a maximum water content of 0.1 wt%, so this difference in molecular weight might be explained by the increased occurrence of hydrolysis of the reactive phosgene or chloroformate species when 1,3-propanediol is present in the reaction mixtures. On the other hand, the glycerol used to prepare polycarbonate **10** contained a maximum of 0.5 wt% of water and in this case, the obtained molecular weight was similar to the poly(DAH carbonate)s presented in Table 5-1. In addition, the DAHs themselves also contain water due to their hygroscopic nature, even though these monomers were always dried overnight before performing the polymerizations. It is therefore unlikely that the water present in 1,3-propanediol is the sole cause of the reduced molecular weights of polycarbonates **4-7**. Still, it is obvious that monomers containing as little water as possible are preferred in these types of reactions.

For entries **4** and **7**, the molecular weights are particularly low, which is caused by the fact that these two polymerizations were performed following a non-optimized synthetic procedure with a shorter reaction time (6 hrs of stirring at room temperature upon addition of the pyridine solution to the reaction mixture, instead of 20 hrs for the other entries). Subsequently, the reaction conditions were optimized by increasing the amount of TPh relative to the amount of diols, as well as by increasing the duration of the reaction. The ratio diols:triphosgene appears to have a strong influence on the molecular weight of the polymer obtained and it is clear that the $\overline{M}_n$ as well as the T_g increase when increasing the amount of triphosgene in the reaction mixture (compare entries **6** and **7**), as already shown for polycarbonates **1a** and **1b** (Table 5-1). In theory, one triphosgene moiety yields three phosgene equivalents during the polymerization reaction (see Appendix C, Scheme C-1), but in practice some loss of phosgene occurs, which is partly due to the hydrolysis of phosgene/chloroformate species (leading to the formation of an OH-terminated polymer chain, one molecule of CO_2 and one equivalent of HCl) or the decomposition of pyridinium chloroformate complexes during the polymerization, yielding alkyl chloride moieties and CO_2. Therefore, when using a stoichiometric amount of TPh (i.e. diols:TPh = 1:0.33), the molecular weight will be relatively low since phosgene moieties are lost during the reaction. It is necessary to use an excess of triphosgene, so that the ratio phosgene:diols can approach unity, leading to higher molecular weights and T_gs .[23,25] In addition, the pyridine solution was added to a solution of the diols and triphosgene, to prevent an excess of pyridine to exist in the reaction vessel, minimizing decomposition of triphosgene and/or chloroformate groups.[13,21]

The T_gs of polymers containing isosorbide increase with increasing isosorbide content (compare entries **6** and **1a**, for example), as was already demonstrated for 1,4:3,6-dianhydrohexitol-based polyesters (see Chapters 2 and 3). This increase is a result of the increased rigidity of the polymer chains by the rigid bicyclic 1,4:3,6-dianhydrohexitol. Obviously, the considerably higher molecular weight of polycarbonate **1a** compared to those of polymers **4-9** also partly causes the higher T_g of the homopolycarbonate.

End-group structures of copolycarbonates prepared using TPh and DPh

Since we are aiming for polymers with hydroxyl end-groups, it is important to determine which types of end-groups result from these reactions at different ratios diols:TPh. After all, it was previously shown that reactions using triphosgene as a carbonyl source may lead to a range of end-groups other than hydroxyl groups, reducing the amount of end-groups available for network formation during curing. Various types of end-groups (Scheme 5-3) are observed in the MALDI-ToF-MS spectra of polymers **1-10** (Table 5-1 and Table 5-2). From the intensities of their signals it seems that the relative amount of cyclic structures increases when increasing the amount of comonomer. As was mentioned before in this thesis, MALDI-ToF-MS is not a quantitative technique and, for example, the intensity of peaks corresponding to certain species depends strongly on their ionization efficiencies. The MALDI results do show, however, that it is difficult to achieve the proper balance of molecular weight and T_g, while maintaining the desired type of end-group. While the molecular weights and the T_gs of most of the polymers in Table 5-2 are acceptable for the applications at hand, it is clear that the functionality of these resins is the main issue. All these polycarbonates have several types of end-groups, including methyl carbonate groups and alkyl chloride groups. The alkyl chloride end-groups of polymer **6** result from the pyridine-promoted decarboxylation of chloroformate end-groups.[21] A constant factor for these copolycarbonates is that cyclic chains are always present in significant amounts, as was previously observed for other types of DAH-based copolycarbonates prepared using diphosgene as a carbonyl source.[12] It appears that especially samples of isomannide-based copolycarbonates, similar to the homopolycarbonate of isomannide, have significant amounts of cyclic structures (entry **9**). The MALDI spectrum of entry **10** also shows high intensity peaks of cyclic structures, but these rings have a pendant hydroxyl group, since these rings contain one or more trifunctional glycerol moieties, leading to branching. Apparently, appreciable levels of hydroxy-functionality in 1,4:3,6-dianhydrohexitol-based copolycarbonates can only be obtained when using relatively low amounts of TPh relative to the amount of diols (e.g. polycarbonate **4**), but this leads to polymers with rather low molecular weights. A better synthetic method towards hydroxy-functional materials might be to work with higher amounts of triphosgene (e.g. polymer **1b** or **10**) during the polymerization, affording chloroformate end-groups. Subsequent precipitation of the reaction mixture in a large excess of diols or triols will probably lead to enhanced OH-functionality. However, a disadvantage of such a procedure might be the formation of alkyl chloride end-groups (e.g. polymer **7**) or extensive cycle formation (e.g. polymer **9**).

Some experiments were performed using diphosgene (DPh) as a carbonyl source, to investigate whether better control over reaction stoichiometry and the type of end-groups could be obtained. The results in Table 5-3 indicate that these polymers also contain cyclic structures. In addition, the main species observed in the MALDI-ToF-MS spectra of polymers **11-13** appear to have one methyl carbonate and one chloroformate end-groups (type **F**, Scheme 5-3). Apparently, the reaction of the chloroformate end-groups with methanol during the precipitation procedure did not proceed to full conversion.

Table 5-3. Poly(DAH-*co*-propylene carbonate)s prepared using DPh as a carbonyl source.

entry	feed composition	composition (NMR)	T_g [°C]	$\overline{M}_n$ [g/mol]	*PDI*	main types of end-groups [1]
11	IS/1,3-PD/DPh [0.5:0.5:0.51]	IS/1,3-PD [0.49:0.51]	53.5	2300	1.5	**F**, B, A
12	II/1,3-PD/DPh [0.5:0.5:0.51]	II/1,3-PD [0.48:0.52]	47.7	1900	1.3	**F**, B, A
13	IM/1,3-PD/DPh [0.50:0.50:0.51]	IM/1,3-PD [0.50:0.50]	29.0	2200	1.7	**F**, B, A

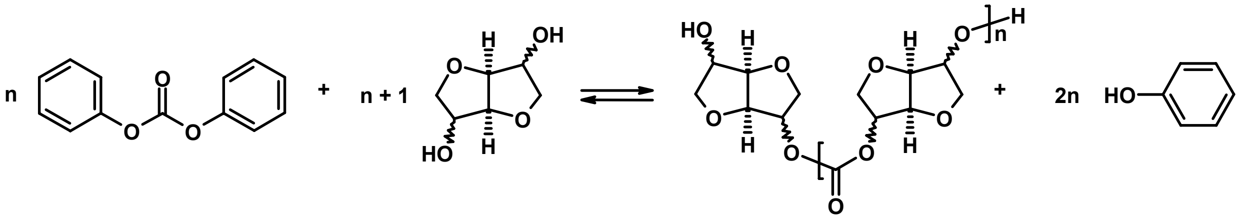
[1] As identified from MALDI-ToF-MS spectra, codes refer to structures depicted in Scheme 5-3. **Bold** codes refer to the main type of signals present in the spectra.

In this paragraph, we have described the synthesis and properties of (co)polycarbonates based on the three 1,4:3,6-dianhydrohexitols using TPh and DPh as carbonyl sources. It has become clear that materials with suitable T_gs and molecular weights can be obtained upon optimization of the reaction conditions. As a result of the synthetic method, these polymers can have a variety of end-groups, many of which are not reactive in curing reactions with, for example, polyisocyanate cross-linkers. Also, cyclic chains are easily formed during these reactions, leading to a further decrease of the average functionality of the polycarbonate resins. Only by improving the control over the various reaction conditions it might be possible to obtain polymers with sufficiently high average functionality to be of use in thermosetting coating formulations. To conclude, we can say that this synthetic procedure does not appear to be the preferred route towards hydroxy-functional polycarbonates.

5.3.2 Polycarbonates using diphenyl carbonate as a carbonyl source

Linear polycarbonates were synthesized from the 1,4:3,6-dianhydrohexitols (DAH) and primary diols by their transcarbonation with diphenyl carbonate. In principle, the polymerization procedures were similar for all these syntheses and the main variables were the maximum reactor temperature and the duration of the reactions. As an example, Scheme

5-6 depicts the reaction between diphenyl carbonate (DPC) and a 1,4:3,6-dianhydrohexitol. This type of reactions can be catalyzed by, for example, zinc acetate, Ti(OBu)$_4$, LiOH·H$_2$O or 4-(dimethylamino)pyridine (DMAP).[35-38]



Scheme 5-6. Synthesis of a poly(DAH carbonate) from DPC and a DAH, through a transcarbonation mechanism.[38]

For the melt polymerizations described in this chapter, zinc acetate was chosen as a catalyst, because of its reported qualities as a transcarbonation catalyst and also because of the fact that it was already used in the synthesis of similar materials.[39,40] In Table 5-4, the properties of some linear polycarbonates, all prepared following the same reaction procedure (Experimental section) are listed.

Table 5-4. Linear copolycarbonates synthesized using DPC as a carbonyl source.

entry [1]	feed composition [2]	composition (NMR)	T_g [ºC]	$\overline{M}_n$ [g/mol]	$\overline{M}_w$ [g/mol]	*PDI*	*OHV* [mg KOH/g]
14	DPC/IS [1:1.1]	-	138.0	3200	7200	2.2	55.0
15	DPC/II [1:1.1]	-	148.2	4600	10300	2.2	34.0
16	DPC/IM [1:1.1]	-	*91* [3]	3700	7500	2.0	n.d.
17	DPC/IS/1,3-PD [1:0.56:0.56]	IS/1,3-PD [0.57:0.43]	48.1	3200	5300	1.7	57.2

[1] Prepared in the melt, T_{max} = 245 ºC.
[2] DPC = diphenyl carbonate, IS = isosorbide, II = isoidide, IM = isomannide, 1,3-PD = 1,3-propanediol
[3] This T_g is an approximate value, since the transition in the DSC thermogram (observed in the first heating curve) was too faint to determine the T_g accurately. No melting transitions were observed.

The polycarbonates **14-17** were synthesized following the same reaction procedure and these materials were transparent, pale yellow to yellow resins. While entries **14**, **15** and **17** were viscous, transparent melts until the end of the synthetic procedure, entry **16** already became an opaque solid during the atmospheric step of the procedure. The polymerization was continued as usual, but it proved impossible to obtain a clear melt again, even when the temperature was increased to 260 ºC for a short while. Possibly, the material has partly crystallized to a high melting solid. In Chapter 3 of this thesis, polyesters based on IM were shown to be semi-crystalline materials. On the other hand, DSC measurements up to 280 ºC resulted in thermograms without clear thermal transitions. Only in the first heating curve of the thermogram, a faint and broad transition was observed between 60 and 145 ºC. Melting phenomena could not be distinguished from the DSC measurements. Polymer **16** appeared to be fully soluble in HFIP (used as a solvent for SEC and MALDI-ToF-MS measurements), but not in $CDCl_3$.

Entry **15**, synthesized from isoidide, has the highest molecular weight, which seems to be in agreement with the observation, made in Chapters 3 and 4, that isoidide is the most reactive 1,4:3,6-dianhydrohexitol in melt polycondensations. The T_gs of entries **14** and **15** are rather high, which might prevent their use as powder coating resins. Entry **17**, a copolycarbonate prepared from isosorbide and 1,3-PD, has a significantly lower T_g and a suitable *OHV* to be cured with polyisocyanate curing agents (see §5.3.5). With ^{1}H NMR spectroscopy, the terminal 1,4:3,6-dianhydrohexitol moieties (and, thus, their hydroxyl end-groups) can be made visible, as shown for entry **15** in Figure 5-4, (i.e. resonances c, d and f). Obviously, other types of polycarbonate chains can result from these melt polycondensations, such as cyclic species and linear chains having phenyl carbonate end-groups, for example (Figure 5-5). Resonances corresponding to cyclic chains cannot be distinguished from those corresponding to linear chains with ^{1}H NMR, whereas phenyl carbonate groups should lead to resonances at chemical shifts between 7 and 8 ppm. However, no such resonances were observed in the ^{1}H NMR spectra of polycarbonates **14** and **15**. Assuming that all the chains in polymer sample **15** are linear and have two hydroxyl end-groups, an estimation of the molecular weight of this polymer can be made from the ^{1}H NMR data. By integration of peak **2** relative to peak **3** in Figure 5-4, the ratio of isoidide residues built into the polymer chain relative to the amount of isoidide moieties at the chain end can be calculated. Since it is assumed that every chain has an isoidide unit at both chain ends, the number of repeating units per chain can be estimated. In the case of polymer **15**, on average a polymer chain has 35 isoidide carbonate repeating units in the main chain and 2 isoidide moieties at the chain ends, suggesting an approximate molecular weight of 6300 g/mol. For polycarbonate **14**, a molecular weight of approximately 4800 g/mol was calculated following the same method. These values are significantly higher than the $\overline{M}_n$ values determined by SEC (Table 5-4), which is due to several factors, including the fact that cyclic chains and chains having end-groups other than isoidide or isosorbide residues are not taken into account in these NMR-based calculations.

End-group structures of polycarbonates prepared using DPC

To investigate the types of end-groups present in the polycarbonates, the MALDI-ToF-MS spectra of these materials were evaluated. Figure 5-5 depicts the MALDI spectrum of poly(isoidide carbonate) (entry **15**).

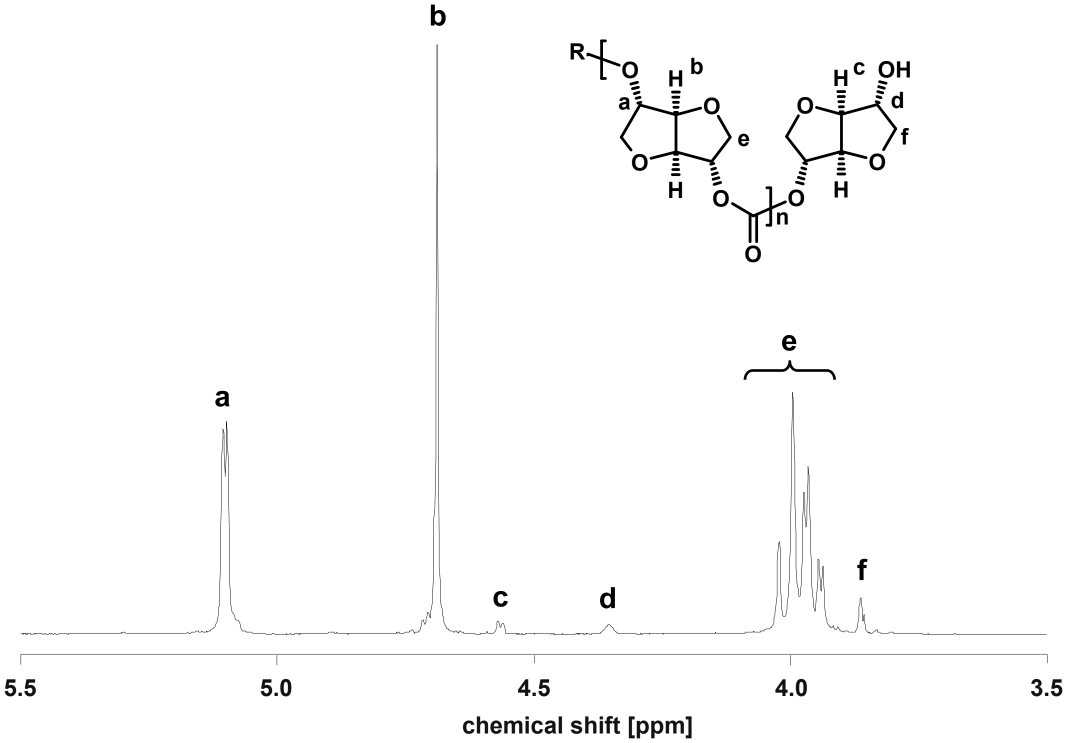


Figure 5-4. ^{1}H NMR spectrum of polycarbonate **15**, poly(isoidide carbonate), where R can be a proton, a carbonic phenyl ester or the other end of the same polycarbonate chain, forming a cyclic chain.

Obviously, the linear species **A**, having two hydroxyl end-groups, cause the main peaks in Figure 5-5, while some peaks of lower intensity corresponding to the expected cyclic species (signals **B**) can be observed as well. The MALDI-spectrum of poly(isosorbide carbonate), entry **14** (see Appendix C, Figure C-3), is quite similar to that of polymer **15**, even though the peaks **B** corresponding to cyclic polycarbonate chains are slightly less pronounced than for polymer **15**. On the other hand, the MALDI-spectrum of poly(isomannide carbonate), entry **16**, is strikingly different. Signals **A** (linear OH-functional peaks) are also the predominant species, but there are hardly any signals of cyclic structures. On the other hand, the spectrum displays strong signals corresponding to linear chains having one or two phenyl carbonate end-groups. This indicates that, even though the same excess of DAH (0.1 molar equivalent relative to the amount of DPC) was used as for entries **14** and **15,** a significantly smaller fraction of the polymer chains is fully OH-functional. In the spectra of polymers **14** and **15**, signals indicating species with phenyl carbonate end-groups were not observed at all. This might be due to the fact that polymer **16** was a solid throughout a large part of the polycondensation reaction, limiting the possibility of mixing of the reactants. Another explanation might be that transcarbonation between DPC and isomannide does not proceed to the same extent as for isosorbide and isoidide.

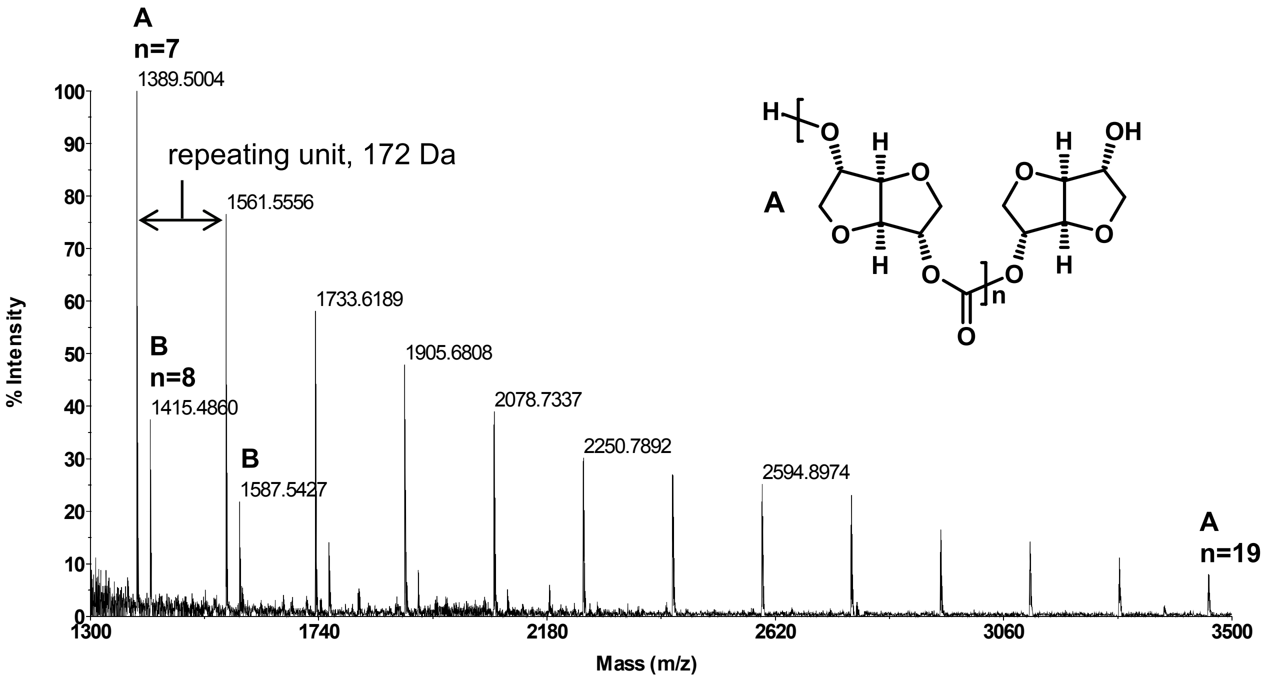


Figure 5-5. MALDI-ToF-MS spectrum of polycarbonate **15**, poly(isoidide carbonate), where species **A** represent linear chains, and species **B** represent cyclic chains.

The lack of cyclic structures in sample **16** shows that the type of polymerization has a very important influence on the properties of the obtained polymer, since solution polycondensation of isomannide using TPh as a carbonyl source (entry **3**, Table 5-1) appeared to give significant amounts of cyclic chains. For poly(isoidide carbonate), the effect of the type of polymerization procedure is also clear since polymer **2** (Table 5-1), prepared in solution using TPh, apparently contains considerably less cyclic structures than polymer **15**, prepared in the melt using DPC. Interestingly, the behavior regarding the formation of linear versus cyclic chains, depending on the reaction procedure (i.e. the phosgene route or the melt transcarbonation route), appears to be opposite for isoidide compared to isomannide. So far, this behavior is not fully understood.

The three poly(DAH carbonate)s described here obviously have too high T_gs for the envisioned application, so flexible diols were added to the polymerizations to decreases T_g. As an example, poly(isosorbide-*co*-propylene carbonate) (entry **17**), is given in Table 5-4. The MALDI-ToF-MS spectrum of this copolycarbonate shows only low intensity peaks for linear polycarbonate chains with two hydroxyl end-groups, while high intensity peaks are present for several species of linear chains with one or two phenyl end-groups. This is striking, since this polymer was synthesized using a significant excess of diols (0.12 mol%) relative to the amount of DPC. The composition of this polycarbonate demonstrates that 1,3-propanediol was partly lost from the reactor, possibly in the form of trimethylene carbonate.[41] This explains that, in the end, an excess of phenol was left, leading to the presence of phenyl end-groups. Another interesting observation is that ether linkages are present in entry **17**. In fact, the main peaks in the MALDI spectrum are all attributed to polycarbonate chains containing at least one ether linkage, which probably means that these chains have lost one (or more) molecules of CO_2 through decarboxylation (Figure 5-6).

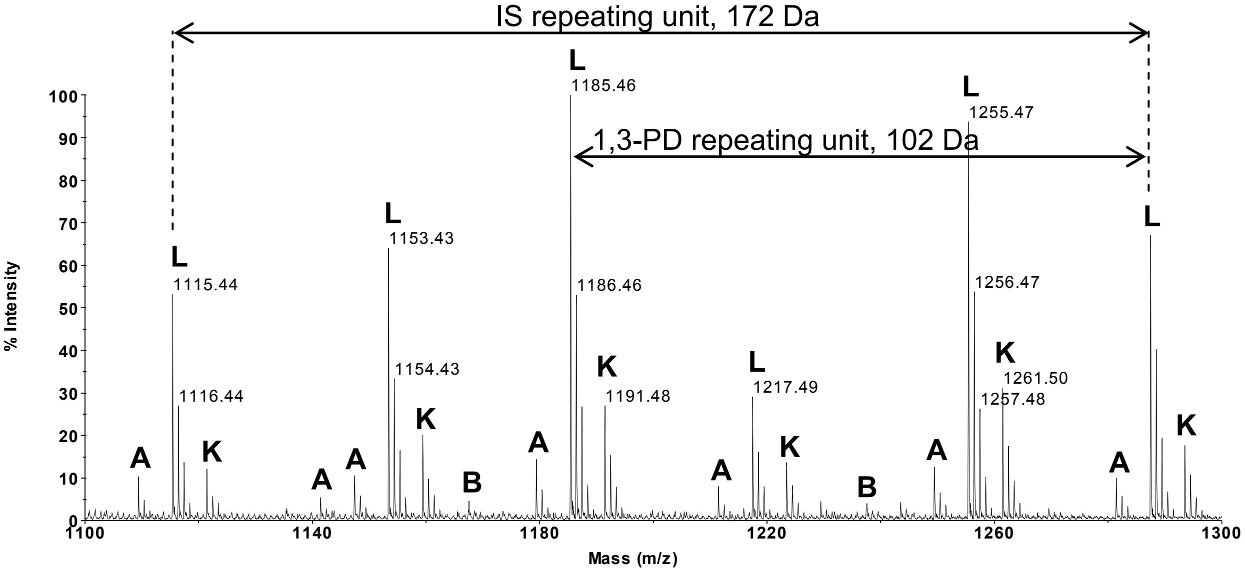


Figure 5-6. Fragment of the MALDI-ToF-MS spectrum of poly(isosorbide-*co*-propylene carbonate) **17**, showing peaks corresponding to the following species: (**A**) linear chains with two hydroxyl end-groups; (**B**) cyclic chains; (**K**) linear chains having one hydroxyl and one phenyl carbonate end-group; (**L**) linear chains containing an ether linkage and having one hydroxyl and one phenyl carbonate end-group.

The presence of ether linkages in the main chain of coating resins is disadvantageous, since they are labile towards UV radiation and might lead to chain scission and, therefore, higher degradation rates of the final coatings. In addition, resin **17** probably does not have enough hydroxyl groups at the chain ends to afford well cured networks upon curing with, for example, a polyisocyanate.

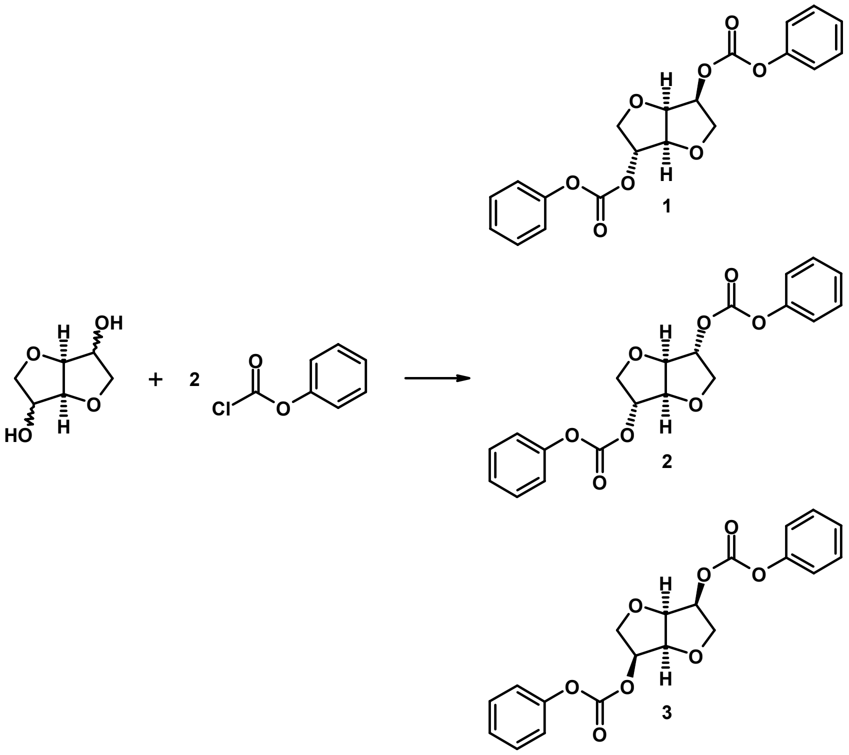
In this paragraph, we have seen that linear, OH-functional poly(DAH carbonate)s can be synthesized from isosorbide and isoidide using DPC as a carbonyl source. When using isomannide, an opaque solid was obtained, which did not appear to melt at temperatures up to 280 ºC (during DSC measurements). A copolycarbonate synthesized from DPC, isosorbide and 1,3-propanediol contained several types of ether linkages, which is not desirable due to the UV instability of such linkages. This synthetic route towards biobased polycarbonates does not seem to be optimal, due to the required high processing temperatures.

5.3.3 Polycarbonates using DAH bis(alkyl/aryl carbonate)s as carbonyl sources

The previous paragraph demonstrated that the synthesis of polycarbonates from DAHs combined with a flexible diol, using DPC as a carbonyl source, led to ether formation and limited build-in of the primary diol, as well as to polymer chains having phenyl carbonate end-groups. Due to the rather high temperatures (up to 250 ºC) at which these reactions were performed, decarboxylation could occur and some of the low molecular weight flexible diol was lost from the reactor. These high temperatures were needed to convert the secondary OH-groups of moderate reactivity of the DAHs to carbonate links and to maintain a polymer melt which could be readily stirred. As was already discussed, the *endo*-oriented hydroxyl groups of the DAHs are less reactive than the *exo*-oriented hydroxyl groups in melt polycondensation reactions, due to steric hindrance and intramolecular interactions. When using dialkyl or diaryl carbonates as carbonyl sources to make polycarbonates via a transesterification mechanism, the moderate reactivity of these secondary OH-groups comes into play. Not only is it necessary to perform the reaction at high temperatures, but one might also expect to obtain blocky polymeric structures if more reactive comonomers, having primary OH-groups, are present in the reaction mixture. In order to control the build-in of the 1,4:3,6-dianhydrohexitols and its comonomers into the polycarbonates and to avoid the formation of blocky polymer structures, highly reactive alkyl and aryl chloroformates were used to convert the different 1,4:3,6-dianhydrohexitols into their respective bis(alkyl/aryl carbonate)s. These carbonate monomers can then be reacted with species containing primary OH-groups, such as flexible alkylene diols, glycerol and trimethylolpropane, a.o, in the presence of a transesterification catalyst (e.g. zinc acetate). At the same time, the reaction temperature can be reduced (as compared to DPC-based polymerizations), limiting ether formation and loss of monomer. It was previously demonstrated that, even at relatively low temperatures, the transcarbonation reaction proceeds efficiently when reacting primary diols with the DAH-based bis(phenyl carbonate)s.[18]

Synthesis of bis(alkyl/aryl carbonate) derivatives from DAHs

A procedure to synthesize the bis(phenyl carbonate)s of isosorbide and isomannide was described in literature.[16,18] We applied this procedure to all three 1,4:3,6-dianhydrohexitol isomers, resulting in the three monomers shown in Scheme 5-7. The purities of the monomers were determined by ^{1}H NMR and were found to be 97+ % for isomannide bis(phenyl carbonate) (IMBPC) and 98+ % for isosorbide bis(phenyl carbonate) (ISBPC) and isoidide bis(phenyl carbonate) (IIBPC).



Scheme 5-7. Synthesis of (**1**) isosorbide bis(phenyl carbonate), (**2**) isoidide bis(phenyl carbonate) and (**3**) isomannide bis(phenyl carbonate), by reacting the 1,4:3,6-dianhydrohexitols with phenyl chloroformate.

The ^{1}H NMR spectrum of IIBPC is characterized by 6 separate (clusters) of resonances, which can be attributed to the different types of protons present in this symmetrical monomer as shown in Figure 5-7. Similar synthetic procedures were developed to synthesize the dimethyl and diethyl carbonate derivatives of the 1,4:3,6-dianhydrohexitols. The purification of these compounds proved to be laborious and resulted in low yields. Especially the purification of the bis(methyl carbonate)s of the DAHs was problematic and, even though isosorbide bis(methyl carbonate) was used as a model compound in a paper by Okada[40], we have not yet been able to find an effective synthetic route towards the pure molecule. On the other hand, isoidide- (Figure 5-8) and isosorbide bis(ethyl carbonate) were synthesized to sufficiently high purities up to approximately 97+ %, albeit at low yields.

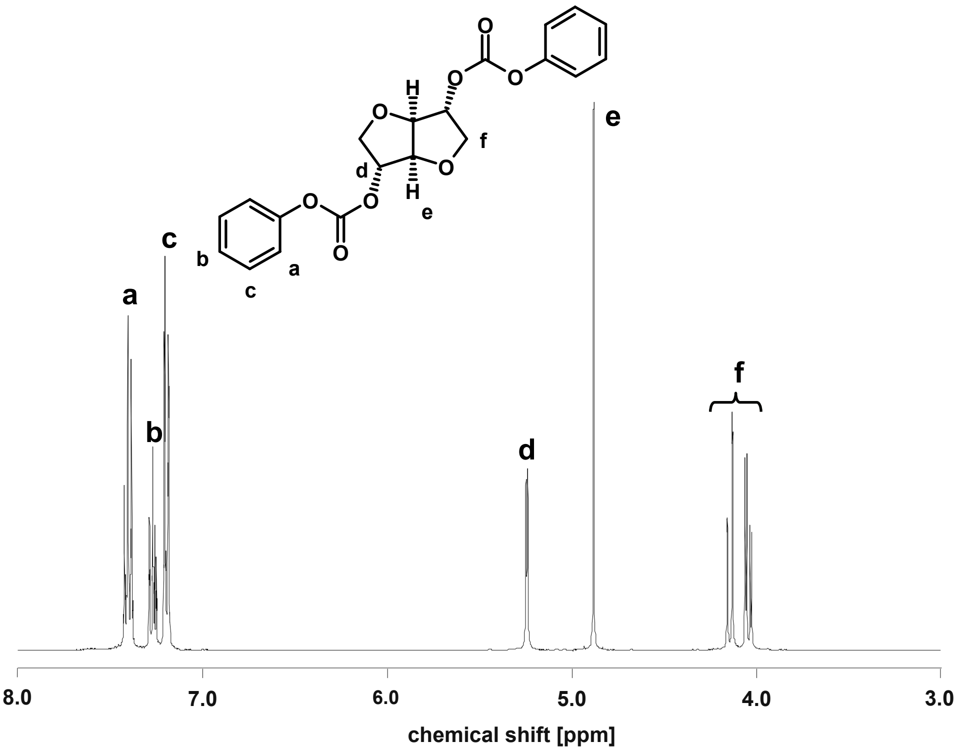


Figure 5-7. ^{1}H NMR spectrum of isoidide bis(phenyl carbonate), recorded in chloroform-*d*.

The impurities in the monomers described here are either the mono-substituted DAH carbonates or some unreacted DAH monomer, both of which will not severely influence the subsequent polycondensation reaction with primary or secondary diols and/or polyols. The bis(alkyl/aryl carbonate) monomers described in this paragraph were used to synthesize (co)polycarbonates and compared with polymers synthesized using diphenyl carbonate. One of the problems when synthesizing polycarbonates in the melt using carbonyl sources such as dimethyl carbonate or diethyl carbonate, is the volatility of these compounds. The DAH bis(ethyl carbonate)s are expected to perform better in this respect.

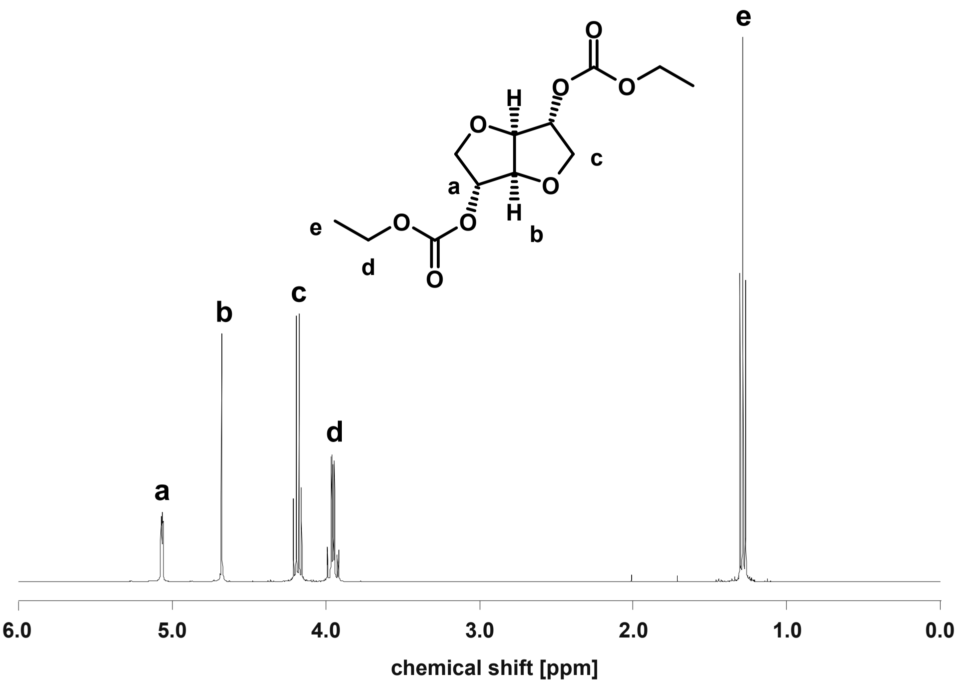


Figure 5-8. ^{1}H NMR spectrum of isoidide bis(ethyl carbonate), recorded in chloroform-*d*.

Transcarbonation of DAH bis(alkyl/aryl carbonate)s with several diols and triols

The previously synthesized DAH bis(alkyl/aryl carbonate)s were reacted with several diols and/or triols to form a range of copolycarbonates. The expected advantage of using these DAH derivatives is that the secondary (and sterically hindered) OH-groups of moderate reactivity have already been converted to carbonate links by the highly reactive chloroformates (Scheme 5-7). During the subsequent transcarbonation polymerizations of these DAH bis(alkyl/aryl carbonate)s with diols/polyols, having primary hydroxyl groups, the control over DAH and comonomer build-in was expected to improve. Furthermore, we anticipated to be able to work at lower temperatures due to the higher reactivity of the primary diols compared to the secondary DAH hydroxyl groups when reacted with bis(phenyl carbonate) compounds. Table 5-5 contains the properties of linear copolycarbonates based on DAH bis(phenyl carbonate)s and DAH bis(ethyl carbonate)s.

The syntheses of the copolycarbonates listed in Table 5-5 resulted in pale yellow transparent polymers. The molecular weights of entries **18-23** are in the desired range, the corresponding T_g values depend on the molecular weights as well as on the compositions of the polycarbonates, as expected. According to the copolymer compositions determined by ^{1}H NMR, the monomers are generally built-in into the polymer chains in the same ratio as the monomer feed. A notable exception is polycarbonate **21**, showing a dramatic loss of ethylene glycol residues during the polycondensation, which was mainly due to the formation of the cyclic monomer ethylene carbonate through an unzipping degradation mechanism. (Scheme 5-8).[42,43]

Table 5-5. Linear copolycarbonates synthesized using several DAH bis(phenyl/ethyl carbonate)s.

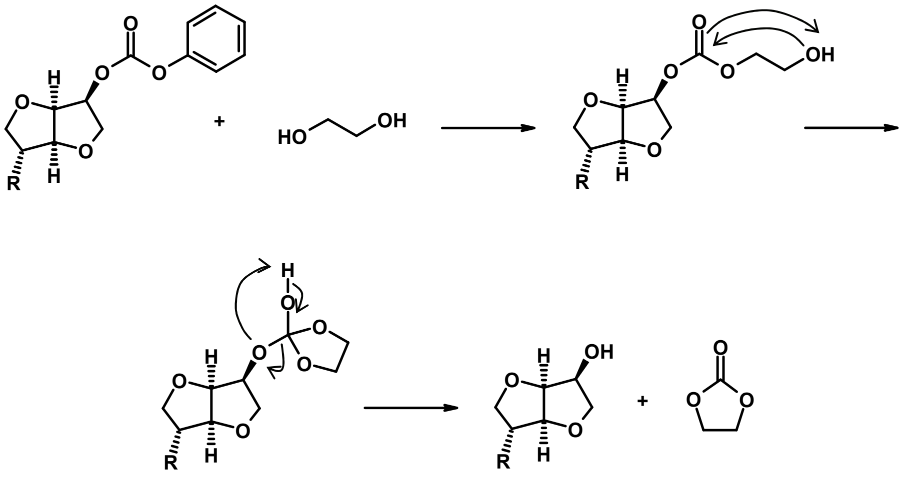
entry [1]	**feed composition** [2]	**composition (NMR)**	T_g **[ºC]**	$\overline{M}_n$ **[g/mol]**	$\overline{M}_w$ **[g/mol]**	***PDI***	***OHV*** **[mg KOH/g]**
		copolycarbonates based on DAH bis(phenyl carbonate)s					
18	ISBPC/IS/1,3-PD [0.42:0.16:0.42]	IS/1,3-PD [0.57:0.43]	89.7	4200	8100	1.9	47.3
19	IIBPC/1,3-PD [0.45:0.55]	II/1,3-PD [0.44:0.56]	35.6	3100	6400	2.1	76.4
20	IMBPC/1,3-PD [0.45:0.55]	IM/1,3-PD [-] [3]	30.9	3700	8000	2.2	n.d. [3]
21	ISBPC/EG [0.48:0.52]	IS/EG [0.92:0.08]	123.8	3600	5500	1.5	28.8
22	ISBPC/1,4-BD [0.45:0.55]	IS:1,4-BD [0.45:0.55]	37.8	5000	9800	2.0	32.1
23	IIBPC/1,4-BD [0.45:0.55]	II:1,4-BD [0.44:0.56]	36.3	6300	14400	2.3	39.0
		copolycarbonates based on DAH bis(ethyl carbonate)s					
24	ISBEC/1,3-PD [0.48:0.52]	IS/1,3-PD [0.55:0.45]	26.9	2000	3600	1.8	n.d. [4]
25	ISBEC/IS/1,3-PD/Ph [0.48:0.05:0.48:0.05]	IS/1,3-PD [0.67:0.33]	64.4	2200	3700	1.7	n.d. [4]
26	IIBEC/II/1,3-PD/Ph [0.48:0.05:0.48:0.05]	II/1,3-PD [0.83:0.17]	67.1	1900	3100	1.6	n.d. [4]

[1] Prepared in the melt, T_{max} = 210 ºC.

[2] ISBPC/IIBPC/IMBPC = isosorbide/isoidide/isomannide bis(phenyl carbonate), 1,3-PD = 1,3-propanediol, EG = ethylene glycol, 1,4-BD = 1,4-butanediol, ISBEC/IIBEC = isosorbide/isoidide bis(ethyl carbonate), Ph = phenol.

[3] Not determined due to insolubility of the resin.

[4] Not determined since there was not enough material available to perform the titrations.



Scheme 5-8. Transcarbonation of a phenyl carbonate end-group with ethylene glycol, followed by so-called unzipping degradation of poly(isosorbide-*co*-ethylene carbonate), yielding ethylene carbonate.[44]

Ethylene carbonate is a stable molecule with a boiling point of 246.7 ºC and it was easily distilled off under vacuum during the second stage of this polymerization at high temperature (approximately 210 ºC). The resulting polymer, containing mainly isosorbide residues, seems to have significant amounts of phenyl carbonate end-groups, as determined by MALDI-ToF-MS. This is obviously due to the fact that, along with ethylene glycol, the initial excess of OH-groups is lost. Similar losses of the flexible diol monomers were not observed in other reactions, indicating that the reaction temperatures were low enough to prevent significant loss of 1,3-propanediol or 1,4-butanediol or the cyclic carbonates derived from these diols.

The copolycarbonates prepared from the DAH bis(phenyl carbonate)s were synthesized at a relatively large scale (10-20 g), so it was possible to perform titrations to determine the number of OH-groups per gram of polymer sample (*OHV*). This is not the case for the materials synthesized starting from the DAH bis(ethyl carbonate)s, since these monomers were only available in small quantities, limiting the scale of the performed reactions. The molecular weights of polymers **24**-**26** are significantly lower than of the polymers synthesized from the DAH bis(phenyl carbonate)s, which is thought to be due to the fact that ethanol is a poorer leaving group than phenol. For this reason, small amounts of phenol were added to reactions **25** and **26**, to promote the transcarbonation reaction. The presence of phenol, however, did not have a noticeable effect on the conversion, judging from the molecular weights of polymers **25** and **26** compared to that of polymer **24**, synthesized without adding phenol. Significant amounts of 1,3-propanediol were lost during these reactions, possibly as a result of a similar degradation reaction as described for ethylene glycol (Scheme 5-8), yielding trimethylene carbonate. Alternatively, the loss of 1,3-propanediol might be due to the prolonged processing under vacuum (see the Experimental section), causing 1,3-propanediol to evaporate from the reactor.

In the MALDI-ToF-MS spectra of copolycarbonates **19**, **22**, **23**, **25** and **26** the main signals can be attributed to linear species having two hydroxyl end-groups. As an example, a section of the MALDI spectrum of poly(isoidide-*co*-butylene carbonate) (entry **23**) is shown in Appendix C, Figure C-4. According to the MALDI spectra of the polycarbonates **18**, **20**, **21** (as already discussed) and **24**, these materials appear to have significant amounts of phenyl carbonate (or ethyl carbonate, in the case of entry **24**) end-groups. By increasing the processing time, especially of the vacuum stage, this problem can probably be overcome. Otherwise, a slightly larger excess of diols may be added to the reaction mixture. No peaks corresponding to ether linkages were detected in the MALDI spectra of entries **21**, **22** and **23**, while the other polymers mentioned in Table 5-5 did show low to moderate levels of signals indicating the presence of ethers.

Branched polycarbonates were also synthesized, based on the three DAH bis(phenyl carbonate)s (Table 5-6). Especially polymers **27** and **28** are promising resins for powder coating applications, since their T_gs are in the proper range, as are their molecular weights and OH-values. Their polydispersities are larger than two, indicating that the introduction of trimethylolpropane (TMP) has indeed led to branching of the polymer chains. Entry **29** has a very high *PDI* which might indicate that, apart from branching due to TMP, also some degradation (possibly: opening of the ether ring) of isomannide has occurred. Glycerol appears to be less effective as a branching agent under these reaction conditions, since the PDI of entry **30** is below 2. Also, the molecular weight of this resin is too low and the *OHV* is too high for practical applications.

Table 5-6. Branched copolycarbonates synthesized using several DAH bis(phenyl carbonate)s.

entry [1]	**feed composition** [2]	**composition (NMR)**	T_g **[ºC]**	$\overline{M}_n$ **[g/mol]**	$\overline{M}_w$ **[g/mol]**	***PDI***	***OHV*** **[mg KOH/g]**
27	ISBPC/IS/1,3-PD/TMP [1:0.42:0.70:0.08]	IS/1,3-PD/TMP [1:0.28:0.06]	78.8	3600	11600	3.2	50.4
28	IIBPC/II/1,3-PD/TMP [1:0.42:0.70:0.08]	II/1,3-PD/TMP [1:0.24:0.05]	83.4	2900	6600	2.3	56.8
29	IMBPC/1,3-PD/TMP [1:1.16:0.04]	IM/1,3-PD/TMP [1:1.09:0.04]	40.7	5300	33300	6.3	39.0
30	IIBPC/1,3-PD/GLY [1:1.1:0.07]	II/1,3-PD/GLY [1:0.89:0.07]	51.8	1600	2800	1.7	139.0

[1] Prepared in the melt, T_{max} = 210 ºC.
[2] TMP = trimethylolpropane, GLY = glycerol

In this paragraph we have shown that linear as well as branched polycarbonates with suitable molecular weights, T_gs and functionalities can be synthesized by transcarbonation of DAH bis(phenyl carbonate)s with primary diols and polyols. The reaction stoichiometry and processing conditions are important parameters. The reaction temperature should be as low as possible, to prevent degradation through unzipping reactions (leading to loss of monomer) or decarboxylation (leading to vulnerable ether linkages in the polymer backbone). From the three synthetic routes discussed in this chapter, the approach described in this paragraph shows the most promise and is, thus, the preferred route.

5.3.4 Thermal stability and viscosity profiles of biobased (co)polycarbonates

The thermal stability of several of the (co)polycarbonates prepared in this study was evaluated using thermogravimetric analysis (TGA) (Figure 5-9).

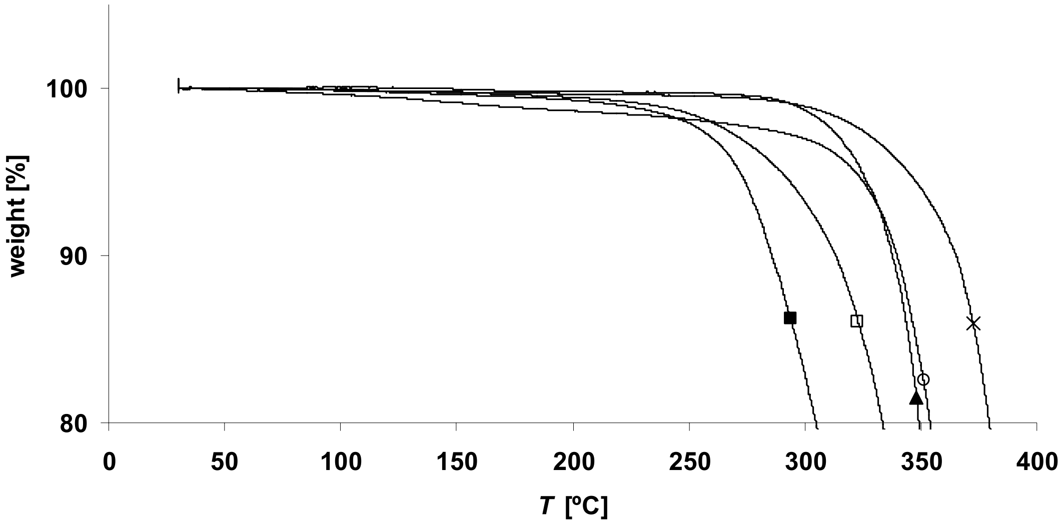


Figure 5-9. Results of thermogravimetric analysis (TGA) of poly(isosorbide carbonate) **14** (○), poly(isoidide carbonate) **15** (▲), poly(isomannide carbonate) **16** (×), poly(isosorbide-*co*-butylene carbonate) **22** (□) and poly(isosorbide-*co*-propylene-*co*-TMP carbonate) **27** (■).

The homopolycarbonates **14**, **15** and **16** based on the 1,4:3,6-dianhydrohexitols are clearly more thermally stable that the copolycarbonates **22** and **27**. It is possible that the copolycarbonates are more prone to degradation by unzipping, since primary hydroxyl end-groups are present in these polymers. For all samples, significant weight loss is not observed below approximately 250 °C, and the homopolycarbonates **15** and **16** are even stable up to 300 °C.

Before evaluating the coating performance of the various polycarbonates described in this chapter, it is interesting to investigate the melt viscosity of these materials. In powder coating systems, film formation occurs through flow and subsequent coalescence of the powder paint. Directly upon flowing and coalescence of the powder particles, the formed film is irregular and the resin needs to flow out over the substrate to obtain a smooth film. If the melt viscosity of the polymeric resin is too high, this process does not occur properly and gelation of the formulation will occur before a smooth film is obtained. The melt viscosity of a polymer depends on the T_g, the molecular weight, the degree of branching and on intermolecular interactions such as hydrogen bonding. Obviously, the addition of additives such as pigments and flow agents will also strongly affect the behavior of the powder paint during film formation.[45] In Figure 5-10, the complex viscosities of several biobased polycarbonates described in this chapter are plotted as a function of temperature. In the same plot, the complex viscosity of a typical commercially available polyester resin, used in powder coatings, is shown.

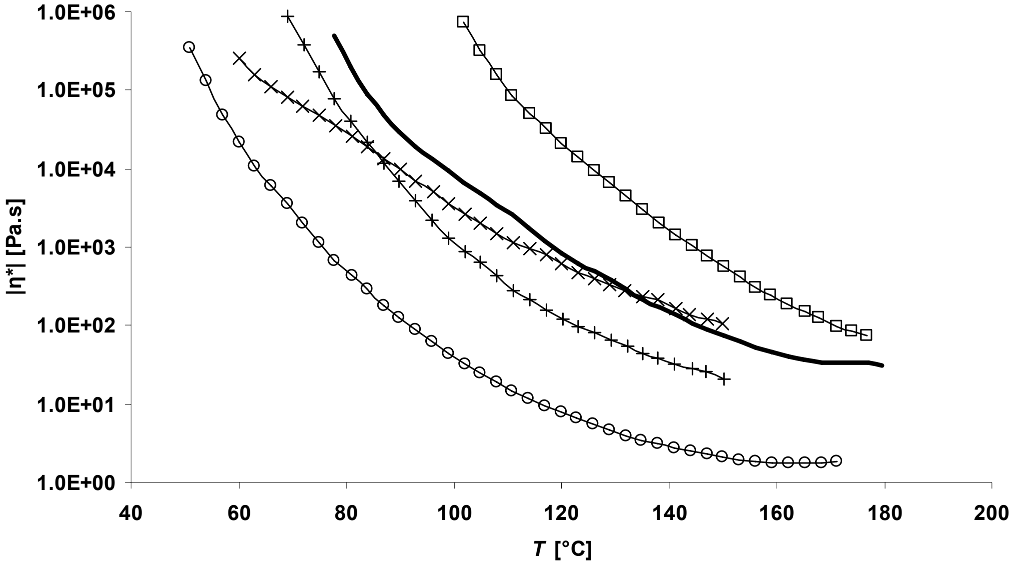


Figure 5-10. Complex viscosity as a function of temperature for polycarbonates **17** (+), **19** (○), **23** (×) and **27** (□) and a typical, commercially available polyester resin (▬), used in powder coatings.

Poly(isosorbide-*co*-propylene carbonate) **17** has a similar viscosity profile as the commercial polyester, showing a rapid drop in viscosity between approximately 70 °C and 170 °C to viscosity values between 10^1 and 10^2 Pa.s. The viscosity of poly(isoidide-*co*-butylene carbonate) **23** starts to decrease at slightly lower temperatures around 60 °C, which is probably due to its relatively low T_g (36.3 °C). On the other hand, its drop in viscosity is less steep than for the other resins, which might be a disadvantage in powder coating applications. After all, the resin should show a rapid and dramatic decrease in viscosity upon heating to facilitate sufficient flow before extensive cross-linking occurs. At higher temperatures, also this polymer has a viscosity of the same order of magnitude as the commercial resin. Polymer **19** has a significantly lower melt viscosity over the whole temperature range, which is thought to be caused by its low T_g (35.6 °C) in combination with its moderate molecular weight as compared to polymer **23** ($\overline{M}_n$ = 3100 g/mol vs. $\overline{M}_n$ = 6300 g/mol, respectively). As expected[46], the branched polycarbonate **27** has the highest melt viscosity and its viscosity only starts to decrease at approximately 100 ºC. This might mean that, when this resin would be used in a powder coating formulation, extrusion (to mix the resin with the curing agent, pigments and other additives) and powder paint application would have to be carried out at slightly higher temperatures than for the other polymers described in Figure 5-10. Polycarbonates **17**, **19** and **27** seem to have suitable viscosity profiles for powder coating applications, when compared with the commercial polyester resin. The temperature at which the rapid drop in viscosity occurs can be set by adapting the T_gs of these polycarbonate resins,

5.3.5 Coating properties of cured biobased (co)polycarbonates

Solvent (NMP) borne coating formulations were prepared based on various (co)polycarbonate resins. Due to limited material availability, not all polycarbonates were tested for their coating properties and powder coating experiments were not carried out for these biobased polycarbonates. Table 5-7 lists the coating formulations and some of their properties. The amount of curing agent (0.05 excess) added to the formulations was calculated based on the OH-values of the different resins, determined by titration.

Table 5-7. Solvent cast coating formulations and the resulting coating properties.

film	polycarbonate	curing agent [1]	T_{cure} [ºC]	t_{cure} [min]	acetone resistance [2]	impact test [100 kg×cm] [2]	av. film thickness [µm]
linear OH-functional polycarbonates							
F1	14	II	180	20	+	-	23
F2	15	II	180	20	+	+	24
F3	17	I	200	30	-	-	30
F4	17	II	180	20	-	-	27
F5	18	II	180	20	+/-	+/-	n.d.
F6	19	I	200	30	+	-	35
F7	19	II	180	20	+	+	40
F8	22	II	180	20	+	+	38
F9	23	II	180	20	+	+	29
branched OH-functional polycarbonates							
F10	27	I	200	30	+	-	40
F11	27	II	180	20	+	+	32

[1] I = ε-caprolactam blocked polyisocyanate based on isophorone diisocyanate, II = polyisocyanate based on hexamethylene diisocyanate, see Scheme 2-4.

[2] + = good, +/- = moderate, - = poor.

The coatings obtained upon curing of the polymer/cross-linker mixture onto aluminum substrates are transparent, glossy, colorless or slightly yellow films. Coating **F1**, containing poly(isosorbide carbonate) with a T_g of 138 ºC as the polymeric binder, shows good solvent resistance but poor resistance to rapid deformation. This was expected, since the T_g of the resin and, hence, of the cured coating, is quite high, contributing to the brittle behavior of the cured system. Surprisingly, **F2** did pass the reverse impact test and also showed good solvent resistance. Even though coating **F2** is rather thin, the fact that this coating passes the reverse impact test still indicates that this cured system is a rather tough material. Coatings **F3** and **F4** containing resin **17**, showed poor chemical and mechanical resistances, which was expected since it was previously determined that at least part of the end-groups of this polycarbonate were phenyl carbonate groups (see §5.3.2). Therefore, curing of this polymer certainly results in incomplete network formation and, thus, in poor coating properties. The moderate performance of **F5** can be explained in a similar way as for **F3** and **F4**. Coatings based on resins **19** and **23** perform well, confirming that they have the proper functionality for curing purposes. Coating **F6** does not pass the impact test, which is probably due to the generally observed brittle behavior of DAH-based polymers cured with this particular curing agent based on isophorone diisocyanate (see §2.3.5). The same can be said for coating **F10**, which also shows poor impact resistance. When the same resin (**27**) is cured with the more flexible curing agent **II** (i.e. a polyisocyanate based on hexamethylene diisocyanate), the rapid deformation during the impact test does not cause any damage to the coating. In general, the coatings based on this branched polycarbonate show excellent chemical and mechanical resistances in combination with a good appearance, as demonstrated in Figure 5-11.

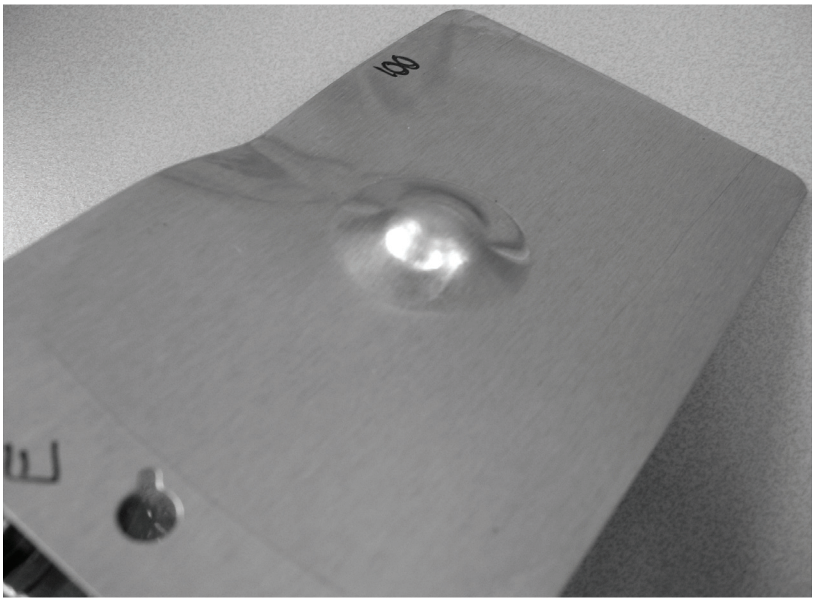


Figure 5-11. Solvent cast coating of the OH-functional, TMP-branched polycarbonate resin **27**, cured with a polyisocyanate based on hexamethylene diisocyanate (**F11**). The dent in the substrate is caused by the reverse impact test. The coating is still completely intact after this rapid deformation.

5.4 Conclusions

Three different synthetic routes were screened towards OH-functional biobased (co)polycarbonates for (powder) coating applications. When using triphosgene (or diphosgene) as a carbonyl source, polymers having suitable molecular weights and T_gs can be prepared by controlling the ratio of 1,4:3,6-dianhydrohexitols and other, more flexible diols that are incorporated into the polymer. However, an important disadvantage of this synthetic method is that it is very difficult to control the type of end-groups obtained, due to the mixture of highly reactive species present during these syntheses. Precipitation of the reaction mixture in a large excess of diols or triols might be a suitable way to enhance the hydroxy-functionality of the obtained polymer. In addition, copolycarbonates made via this route tend to contain significant amounts of cyclic chains, which do not participate in, for example, curing reactions. Interestingly, the reactivity of the *endo*-oriented OH-groups of isomannide and isosorbide appears to be higher than of the *exo*-oriented hydroxyls, which is contrary to the situation in melt polycondensations. This difference is probably caused by the enhanced nucleophilicity of the *endo*-oriented hydroxyl group due to internal hydrogen bonding and the presence of pyridine/pyridine hydrochloride. Homopolycarbonates of isosorbide and isoidide, prepared using the conventional carbonyl source diphenyl carbonate, had mainly hydroxyl end-groups and rather high T_gs. When attempting to synthesize copolycarbonates by adding 1,3-propanediol as a co-monomer, part of this flexible diol was lost from the reactor, mainly due to the required high reaction temperatures. Optimization of the processing conditions might improve the build-in of this monomer via this route. Copolycarbonates were also prepared using prefabricated DAH bis(phenyl carbonate)s. In these melt polymerizations, the reaction temperatures could be chosen significantly lower than when using DPC in combination with the DAHs as such. This synthetic route resulted in several linear and branched copolycarbonates having suitable molecular weights, T_gs and OH-functionalities. Curing of the various biobased linear and branched aliphatic (co)polycarbonates using conventional polyisocyanate cross-linkers yielded colorless to pale yellow, transparent, glossy coatings, having excellent chemical and mechanical resistances. It can be concluded that this last synthetic route is the most promising method to prepare DAH-based polycarbonates, suitable for powder coating applications.

References

(1) Odian, G. *Principles of polymerization* 3 ed: John Wiley & Sons, Inc.: New York, 1991.
(2) Funakoshi, S.; Kawai, K. (Asahi Chemical Ind.). US5703196 1997.
(3) Rokicki, G.; Kowalczyk, T. *Polymer* **2000**, *41,* 9013.
(4) Inoue, S.; Koinuma, H.; Tsuruta, T. *Polym. Lett.* **1969**, *7,* 287.
(5) Kuran, W.; Sobczak, M.; Listos, T.; Debek, C.; Florjanczyk, Z. *Polymer* **2000**, *41,* 8531.
(6) Wang, X. L.; Zhuo, R. X.; Liu, L. J.; He, F.; G., L. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40,* 70.
(7) Dankers, P. Y. W.; Zhang, Z.; Wisse, E.; Grijpma, D. W.; Sijbesma, R. P.; Feijen, J.; Meijer, E. W. *Macromolecules* **2006**, *39,* 8763.
(8) Schutze, E.-C.; Hornung, K.-H.; Nehring, R. (Chemische Werke Huels A.G.). US3547889, 1970.
(9) Bruchmann, B.; Schafer, H. (BASF Aktiengesellschaft). WO2006089940, 2006.
(10) Lowenhielm, P.; Nystrom, D.; Johansson, M.; Hult, A. *Prog. Org. Coat.* **2005**, *54,* 269.
(11) (Courtaulds Limited). NL6405497, 1964.
(12) Chatti, S.; Kricheldorf, H. R.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44,* 3616.
(13) Chatti, S.; Schwarz, G.; Kricheldorf, H. R. *Macromolecules* **2006**, *39,* 9064.
(14) Kricheldorf, H. R.; Sun, S.-J. *Macromol. Chem. Phys.* **1997**, *198,* 2197.
(15) Kricheldorf, H. R.; Sun, S. J.; Chen, C. P.; Chang, T. C. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35,* 1611.
(16) Kricheldorf, H. R.; Sun, S. J.; Gerken, A.; Chang, T. C. *Macromolecules* **1996**, *29,* 8077.
(17) Sun, S. J.; Schwarz, G.; Kricheldorf, H. R.; Chang, T. C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37,* 1125.
(18) Yokoe, M.; Aoi, K.; Okada, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41,* 2312.
(19) Yokoe, M.; Aoi, K.; Okada, M. *J. Appl. Polym. Sci.* **2005**, *98,* 1679.
(20) Ono, A.; Toyohara, K.; Minematsu, H.; Kageyama, Y. (Teijin Limited). EP1640400, 2006.
(21) Kricheldorf, H. R.; Bohme, S.; Schwarz, G. *Macromol. Chem. Phys.* **2005**, *206,* 432.
(22) Kricheldorf, H. R.; Bohme, S.; Schwarz, G. *Macromolecules* **2006**, *39,* 3210.
(23) Kreutzberger, C. B. *Chloroformates and carbonates*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, J. I. Kroschwitz, Editor. 2001, John Wiley & Sons, Inc.
(24) Possidonio, S.; Siviero, F.; El Seoud, O. A. *J. Phys. Org. Chem.* **1999**, *12,* 325.
(25) Foulon, F.; Fixari, B.; Picq, D.; Le Perchec, P. *Tetrahedron Lett.* **1997**, *38,* 3387.
(26) Burgey, C. S.; Vollerthun, R.; Fraser-Reid, B. *Tetrahedron Lett.* **1994**, *35,* 2637.
(27) Sakairi, N.; Wang, L.-X.; Kuzuhara, H. *J. Chem. Soc., Perkin Trans.* **1995**, *4,* 437.
(28) Cowie, J. M. G.; Henshall, S. A. E. *Eur. Polym. J.* **1976**, *12,* 215.
(29) Buck, K. W.; Duxbury, J. M.; Foster, A. B.; Perry, A. R.; Webber, J. M. *Carbohydr. Res.* **1966**, *2,* 122.
(30) Szeja, W. *J. Chem. Soc., Chem. Commun.* **1981**, *5,* 215.
(31) Fleche, G.; Huchette, M. *Starch* **1986**, *38,* 26.
(32) Le Lem, G.; Boullanger, P.; Descotes, G.; Wimmer, E. *Bull. Soc. Chim. Fr.* **1988**, *3,* 567.
(33) Stoss, P.; Hemmer, R. *Adv. Carbohydr. Chem. Biochem.* **1991**, *49,* 93.
(34) Trotzki, R.; Nuchter, M.; Ondruschka, B. *Green Chem.* **2003**, *5,* 285.

(35) Baba, T.; Kobayashi, A.; Kawanami, Y.; Inazu, K.; Ishikawa, A.; Echizenn, T.; Murai, K.; Aso, S.; Inomata, M. *Green Chem.* **2005**, *7,* 159.

(36) Ignatov, V. N.; Tartari, V.; Carraro, C.; Pippa, R.; Nadali, G.; Berti, C.; Fiorini, M. *Macromol. Chem. Phys.* **2001**, *202,* 1941.

(37) Hersh, S. N.; Choi, K. Y. *J. Appl. Polym. Sci.* **1990**, *41,* 1033.

(38) Hsu, J.-P.; Wong, J.-J. *Ind. Eng. Chem. Res.* **2006**, *45,* 2672.

(39) Ardal, D.; Yilgor, E.; Yilgor, I. *Polym. Bull.* **1999**, *43,* 207.

(40) Okada, M.; Yokoe, M.; Aoi, K. *J. Appl. Polym. Sci.* **2002**, *86,* 872.

(41) Montaudo, G.; Puglisi, C.; Rapisardi, R.; Samperi, F. *Polym. Degrad. Stab.* **1991**, *31,* 229.

(42) Liu, B.; Chen, L.; Zhang, M.; Yu, A. *Macromol. Rapid Commun.* **2002**, *23,* 881.

(43) Berti, C.; Bonora, V.; Pilati, F. *Makromol. Chem.* **1992**, *193,* 1679.

(44) Van Meerendonk, W. J., *CO_2 as a monomer for the phosgene-free synthesis of new polycarbonates - catalyst development, mechanistic investigations and monomer screening*, in *Laboratory of Polymer Chemistry*. 2005, Eindhoven University of Technology: Eindhoven.

(45) Misev, T. A. *Powder coatings - chemistry and technology* 1st ed: John Wiley & Sons: New York, 1991.

(46) Marks, M. J.; Munjal, S.; Namhata, S.; Scott, D. C.; Bosscher, F.; De Letter, J. A.; Klumperman, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38,* 560.

6

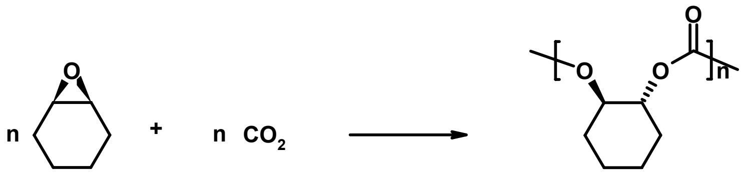
Hydroxy-functional poly(cyclohexene carbonate)s

Abstract

Alcoholysis of high molar mass poly(cyclohexene carbonate) using low molecular weight polyols such as trimethylolpropane or 1,3,5-cyclohexane triol, in the presence of transesterification catalysts, affords functionalized polycarbonates with reduced molecular weights as well as lower glass transition temperatures. MALDI-ToF-MS was used to identify the different polymer species formed during the alcoholysis reactions, showing strongly enhanced hydroxy-functionality compared to the starting high molecular weight PCHC. Formation of cyclic carbonates was also observed, especially in the case of TMP-mediated degradation of PCHC. The properties of cured poly(carbonate urethane)s, based on the alcoholyzed PCHC samples, were moderate with respect to chemical and mechanical stability. The appearance of the coatings, on the other hand, was good. Network formation appeared to be incomplete, which is expected to improve upon optimization of the reaction procedure.

6.1 Introduction

As was already mentioned in Chapter 5, hydroxy-functional aliphatic polycarbonates are very interesting materials for coating applications, thanks to the good transparency, toughness, UV stability and hydrolytic stability of the resulting cured poly(carbonate urethane) networks.[1,2] Apart from polycarbonate synthesis through phosgene or transcarbonation routes, other methods to synthesize polycarbonates have been explored. Aliphatic oxiranes such as propylene oxide, cyclohexene oxide or the biobased limonene oxide[3,4] can be copolymerized with CO_2, a cheap renewable monomer which is non-toxic and non-flammable.[3,5-8] So far, these materials have not been extensively used as engineering plastics, due to their limited toughness and moderate glass transition temperatures. For example, poly(cyclohexene carbonate) (PCHC, Scheme 6-2) has a T_g of approximately 116 ºC, which is low compared to the T_g of poly(bisphenol-A carbonate), being 150 ºC.



Scheme 6-1. Schematic representation of the synthesis of poly(cyclohexene carbonate).

In addition, PCHC displays poor tensile properties, making this aliphatic polycarbonate unfit for many engineering plastics applications.[9,10] On the other hand, PCHC is a highly transparent material with a relatively high chain rigidity, which would make it a suitable candidate for coating applications, provided that the material has sufficient amounts of reactive end-groups for curing purposes. Through the currently used synthetic routes, PCHC is obtained with number average molecular weights between 10,000 and 50,000 g/mol and one hydroxyl end-group per polymer chain. Moreover, when curing PCHC as such, one would not obtain a cross-linked network. At best, the curing agent would act as a chain extender, increasing the polymer molecular weight without significantly improving its mechanical stability or solvent resistance. On the other hand, polymers with $\overline{M}_n$ values in the range of 2000 – 7000 g/mol and having at least two functional groups per chain are suitable for the envisioned application. When curing these polymers with moderate molecular weights, cross-linked networks are obtained, which have sufficient cross-link density to significantly improve impact and solvent resistance. Therefore, a method had to be developed to decrease the molecular weight and the T_g of poly(cyclohexene carbonate), while at the same time functionalizing the material. A method to degrade and functionalize polycarbonates in a controlled way, making use of Bu_2SnO and carboxylic acid chlorides, was described previously.[11] In addition, it is known that carbonate linkages can be hydrolyzed (under basic conditions)[12] and alcoholyzed.[13] Obviously, the synthesis of polycarbonates through transcarbonation of, for example, diphenyl carbonate with diols, is an important example of the alcoholysis of carbonate linkages.

In this chapter, the break-down of poly(cyclohexene oxide) is described, proceeding via alcoholysis (i.e. carbonate interchange) of the carbonate linkages by low molecular weight polyol moieties. The chemistry of these reactions, as well as the characteristics of the obtained polycarbonates is discussed. Furthermore, this study includes an evaluation of the mechanical performance, solvent resistance and appearance of the formed coatings.

6.2 Experimental section

Materials. Trimethylolpropane (TMP), 4-dimethylaminopyridine (DMAP) and acetic anhydride were purchased from Acros Organics. Cyclohexene oxide (98 %) (CHO), D-sorbitol (99+ %), normalized solutions of KOH in methanol and dibutyltin dilaurate (DBTDL) were obtained from Aldrich. 1,3,5-cyclohexanetriol (mixture of *cis* and *trans* isomers, CHT) was bought from TCI Europe. Carbon dioxide (>99.9993 % pure) was purchased from HoekLoos. All solvents were purchased from Biosolve. An isophorone diisocyanate-based, ε-caprolactam blocked polyisocyanate (trade name: Vestagon B1530) was a gift from Degussa GmbH, a hexamethylene diisocyanate-based polyisocyanate (trade name: Desmodur N3600) was a gift from Bayer AG. All chemicals were used as received.

Alcoholysis of poly(cyclohexene carbonate). Poly(cyclohexene carbonate) (PCHC) was synthesized from cyclohexene oxide and CO_2, catalyzed by a β-diketiminato zinc catalyst. The polymerization was performed in an autoclave containing a solution of the catalyst in a mixture of cyclohexene oxide and toluene, which was pressurized with CO_2 (up to 9 bar).[14] PCHC samples were subjected to alcoholysis by several polyols, in the presence of transesterification catalysts such as titanium(IV) n-butoxide or zinc acetate. The followed procedure is described here for the alcoholysis of PCHC by trimethylolpropane: Poly(cyclohexene carbonate) (5.1 g, $\overline{M}_n$ = 14,000 g/mol, 3.6×10^{-4} mol), trimethylolpropane (0.22 g, 1.6×10^{-3} mol) and 0.02 mol% of $Ti(OBu)_4$ (relative to the amount of trimethylolpropane) were mixed and heated up to 200 ºC in a three-neck round bottom flask under an inert atmosphere. Upon formation of a homogeneous, stirrable melt, the reaction temperature was reduced to 180 ºC to limit extensive degradation through decarboxylation and/or unzipping (*vide infra*) of the polymer. The degradation experiment was continued for 10 hours (*note: when using 1,3,5-cyclohexanetriol to alcoholyzed PCHC, the reaction time was longer: approximately 20 hrs*). The development of the molecular weight distribution was monitored by SEC in THF, using PS standards. Yield: 3.3 g (62 %) *N.B. part of the material was lost from the reactor through unzipping degradation, yielding the volatile monomer 1,2-cyclohexanecarbonate.*

Solvent casting and curing of hydroxy-functional polycarbonates. Hydroxy-functional polycarbonates were cured using conventional polyisocyanate curing agents: (1) an ε-caprolactam blocked trimer of isophorone diisocyanate (trade name: Vestagon B1530, NCO equivalent weight = 275 g/mol) and (2) a trimer of hexamethylene diisocyanate (trade name: Desmodur N3600, NCO equivalent weight = 183 g/mol).

Ad 1: A solution of approximately 0.3 g of polycarbonate, 1.05 molar equivalent of the cross-linker (calculated from titration data) and 0.5 wt% (calculated on solid resin) of dibutyltin dilaurate (DBTDL) in 1 mL N-methyl-2-pyrrolidone (NMP) was prepared. Subsequently, a wet film of approximately 250 μm thickness was applied onto an aluminum panel, using a doctor blade. The film was left to dry at room temperature and then cured at 200 ºC for 30 minutes under a nitrogen atmosphere. Ad 2: A solution of approximately 0.3 g of polycarbonate in 0.7 mL of NMP was prepared, as well as a separate solution of Desmodur N3600 (0.05 molar excess, calculated from titration data) in 0.3 mL of NMP. The two solutions were mixed and applied directly to the aluminum substrate as a wet film with a thickness of 250 μm. After drying at room temperature, the film was cured at 180 ºC under N_2 for 20 minutes.

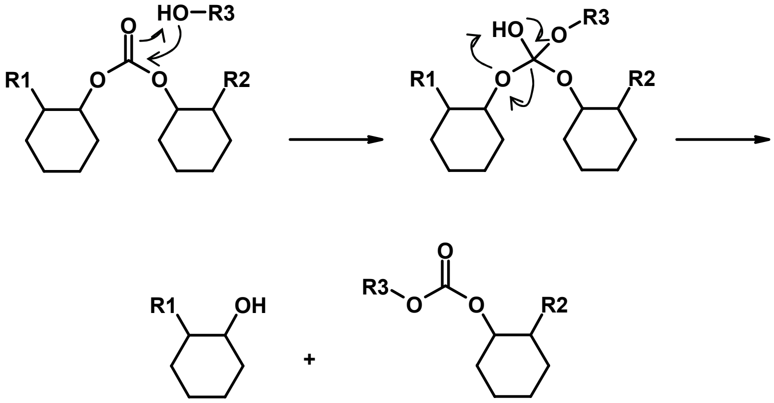
Measurements. SEC analysis was carried out using a Waters GPC apparatus equipped with a Waters 510 pump and a Waters 410 refractive index detector (at 40 °C). Injections were done by a Waters WISP 712 auto injector with an injection volume of 50 μL. Two linear columns, Mixed C, Polymer Laboratories, 30 cm, 40 °C, were used. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min. Calibration curves were obtained using polystyrene standards (Polymer Laboratories, M = 580 g/mol to M = 7.1×10^6 g/mol). Data acquisition and processing were performed using WATERS Millennium32 (v3.2 or 4.0) software. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer, chloroform-*d* was used as a solvent. Glass transition and melting temperatures were determined by DSC measurements, carried out with a DSC Q100 from TA Instruments. MALDI-ToF-MS measurements were performed on a Voyager DE-STR from Applied Biosystems. Calibrations were carried out with poly(ethylene oxide) standards for the lower mass range and polystyrene standards for the higher mass range. The mass accuracy was better than 0.2 Dalton, the mass resolution was approximately m/z 12,000. DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as matrix. Potassium trifluoroacetate (Aldrich, >99 %) was used as cationization agent. Solutions of the matrix (40 mg/mL), potassium trifluoroacetate (5 mg/mL) and the polyester sample (1 mg/mL) in THF were premixed in a ratio of 5:1:5. The mixture was subsequently hand-spotted on the target and left to dry. Spectra were recorded in reflector mode at positive polarity. Potentiometric titrations were carried out using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The carboxylic acid functionality was measured by titration with a normalized 0.1 N methanolic KOH solution. The acid value (*AV*) is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize 1 g of polymer resin. Polyester hydroxyl end-groups were acetylated in solution (NMP) with acetic anhydride at room temperature (4-dimethylaminopyridine was used as catalyst), followed by titration of the resulting acetic acid with a normalized 0.5 N methanolic KOH solution. Blank measurements were necessary to obtain the hydroxyl values. The hydroxyl value (*OHV*) is the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of material. All titrations were carried out in duplo. Cross-linking and coating performance at room temperature were evaluated using the following characterization methods: acetone rub test (Solvent resistance test: the sample is rubbed with a cloth drenched in acetone. If no damage is visible after more than 150 rubs, the coating has good acetone resistance) and rapid deformation test (Reverse impact test, ASTM D 2794).

6.3 Results and discussion

6.3.1 Degradation of poly(cyclohexene carbonate) through alcoholysis

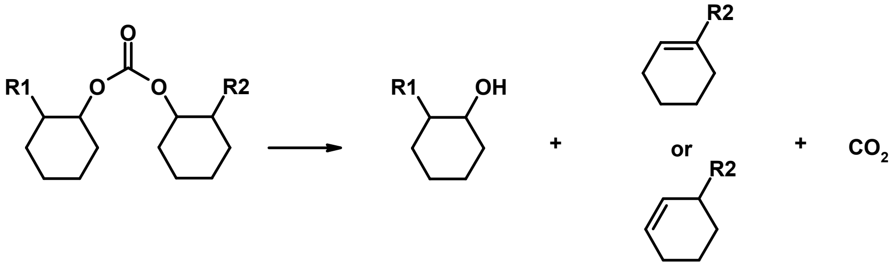
Poly(cyclohexene carbonate) (PCHC) was synthesized via a metal-catalyzed copolymerization of CO_2 and cyclohexene oxide.[14] The resulting polymer is a brittle, colorless material with a glass transition temperature of around 116 ºC (for a sample with $\overline{M}_n$ = 27,000 g/mol). This polymer has an even better transparency than poly(bisphenol-A carbonate), and was also shown to have a lower UV absorption than the commonly used aromatic polymer.[14] For this reason, we expect it to be suitable for coating applications, also with respect to UV stability. PCHC is a linear polymer, implying that it has at most two functional end-groups per polymer chain. However, most PCHC chains are prepared in such a way that generally they only have one hydroxyl end-group capable of participating in curing reactions with, for example, polyisocyanate curing agents. Depending on the type of catalyst used during its synthesis, PCHC can also have a (m)ethyl carbonate or a phenyl ether end-group. In addition, cyclohexyl end-groups may be present.[14] In order to use these polycarbonates in coating applications, their functionalities first have to be enhanced.

Several poly(cyclohexene carbonate)s having different molecular weights, were subjected to transcarbonation with polyols in the melt, in the presence of a catalyst promoting the alcoholysis reaction. Schematically, the reaction proceeds as depicted in Scheme 6-2.



Scheme 6-2. Alcoholysis of a carbonate linkage of PCHC by a hydroxy-functional species. R1 and R2 are polymer chain fragments and R3 is a low molecular weight polyol residue.

Depending on the initial molecular weight of the PCHC sample, several equivalents of triol were added, aiming at a final (theoretical) molecular weight of approximately 3000 g/mol and an average functionality of three. For example, to a PCHC sample with a $\overline{M}_n$ of 37,000 g/mol, 12 molar equivalents of TMP were added assuming that, on average, the average molecular weight value is halved every time a TMP moiety reacts with the PCHC chain. In order to obtain a polymer melt which can be easily stirred, the temperature in the reactor has to be as high as 200 ºC to carry out these transcarbonation experiments. While the reaction proceeds, the melt viscosity decreases due to the breaking up of polymer chains. At these temperatures, the regular degradation mechanisms of PCHC, such as unzipping degradation, chain scission and/or decarboxylation, can also occur. The former degradation pathway has already been described in Chapter 5 (Scheme 5-8) and proceeds through a back-biting reaction involving hydroxyl end-groups, resulting in a cyclic carbonate molecule (1,2-cyclohexane carbonate) and a hydroxy-functional polymer chain. This phenomenon can be accelerated by the presence of residual traces of the polymerization catalyst. A second possible degradation mechanism of polycarbonates is chain scission, which also occurs at elevated temperatures (Scheme 6-3). This degradation pathway leads to release of CO_2 from the degrading polymer chain. Via this route, polymer chains with unsaturated cyclohexyl moieties at the chain end are obtained. In this case, the residual catalyst has little if any influence on the degradation rate.[14,15]

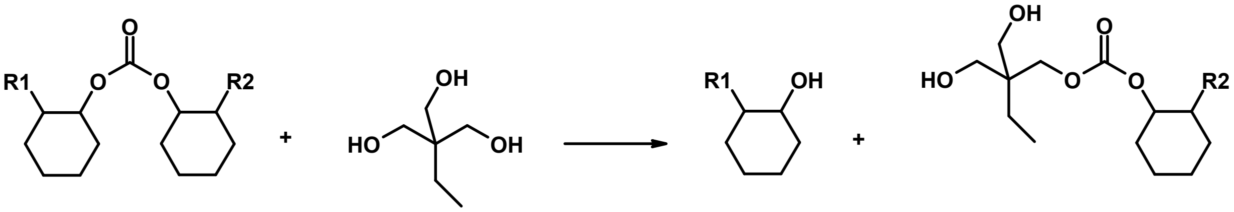


Scheme 6-3. Chain scission of PCHC, resulting in one hydroxy-functional polymer chain and a polymer chain having an unsaturated cyclohexyl end-group. R1 and R2 are polymer chain fragments.[14]

In addition, decarboxylation of the carbonate linkages can occur, leading to ether linkages in the polymer main chain.[16] The three described thermal degradation mechanisms may occur while performing the alcoholysis reactions in the melt, potentially affording a variety of polymer topologies (i.e. linear or branched chains) and end-group structures.

Break-down and in-situ functionalization of PCHC by trimethylolpropane (TMP)

Previously synthesized high molecular weight poly(cyclohexene carbonate) with $\overline{M}_n$ = 14,000 g/mol and *PDI* = 1.11, was broken down through alcoholysis by a trifunctional alcohol, trimethylolpropane (TMP). The primary hydroxyl groups of this monomer are more reactive than the secondary OH-functionalities at the PCHC chain ends. If alcoholysis of the carbonate linkages occurs, a hydroxy-functional linear PCHC chain and a TMP end-functionalized PCHC chain are expected (Scheme 6-4). Obviously, the two remaining hydroxyl groups of the resulting TMP residue, located at the chain end, could react with other carbonate linkages, possibly leading to chain extended, cyclic or branched polymeric structures and a reduced average functionality (i.e. $\overline{F}_n < 3$).



Scheme 6-4. TMP-mediated break-down of PCHC through alcoholysis. R1 and R2 are polymer chain fragments.

The alcoholysis of PCHC was commenced at 200 ºC, until a melt was obtained which could be stirred (see Experimental section) under an inert atmosphere in the presence of TMP. After approximately 2 hours of processing, a clear colorless liquid started to condense and reflux on the reactor wall. Upon cooling, the liquid solidified. By ^{1}H NMR spectroscopy, this side-product was identified as 1,2-cyclohexane carbonate[17,18], the cyclic carbonate monomer resulting from the unzipping reaction. After 210 minutes of processing at 200 ºC, the melt viscosity had decreased significantly and the reaction temperature was lowered to 180 ºC to limit the occurrence of thermal degradation such as decarboxylation. In Figure 6-1, the $\overline{M}_n$ as well as the *PDI* of the PCHC samples are plotted as a function of reaction time. From Figure 6-1 it becomes clear that a strong drop in $\overline{M}_n$ occurs within the first two to three hours of the degradation experiment. Afterwards, the molecular weight decreases at a lower rate. This is thought to be a result of the initial alcoholysis reaction of TMP with the PCHC chains as well as the degradation by chain scission. Both degradation mechanisms imply cutting the polymer chains, leading to a rapid initial reduction in the number average molecular weight. Also, the reaction temperature was at its highest during the first few hours of the reaction, increasing the degradation rate. An increase in the polydispersity index was observed, which is partly caused by the random cutting of polymer chains as well as by branching induced by TMP. The final polymer sample, obtained after 580 minutes of processing, has the following characteristics: $\overline{M}_n$ = 2600 g/mol, *PDI* = 2.34, T_g = 48.7 ºC, *OHV* = 48.4 mg KOH/g.

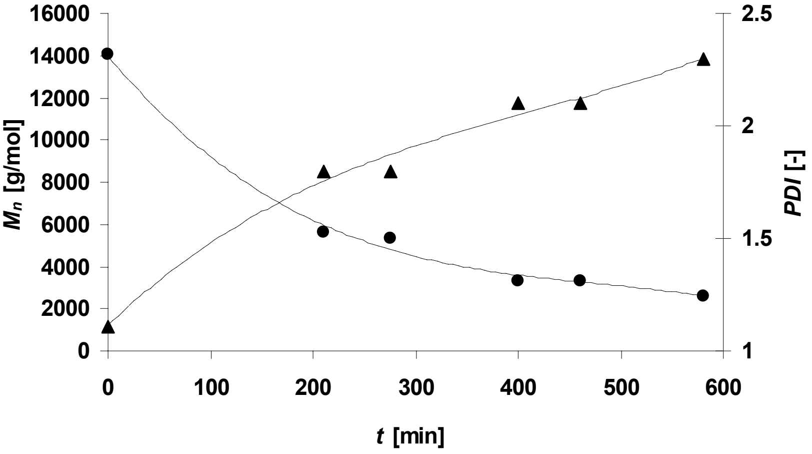


Figure 6-1. TMP-mediated degradation of PCHC. $\overline{M}_n$ (●) and *PDI* (▲) as a function of the reaction time at 180-200 ºC. *N.B. the lines are only meant as guides to the eye.*

The different types of end-groups present in the PCHC starting material, as well as in the material obtained through TMP-mediated degradation, were identified by MALDI-ToF-MS. The spectrum of the starting PCHC showed one main distribution of peaks attributed to linear polycarbonate chains having one hydroxyl and one methyl carbonate end-group, originating from the polymerization initiating catalyst moiety. In the MALDI-ToF-MS spectrum of the TMP-alcoholyzed polycarbonate (Figure 6-2), different distributions of individual molecular peaks are observed between 800 and approximately 5500 g/mol, of which the peaks are separated by the mass of the repeating unit of PCHC (142 Da). Scheme 6-5 depicts the observed types of chain topologies and their end-groups. This spectrum suggests that the main species in the degraded polycarbonate sample are linear chains with two hydroxyl end-groups, but it has been mentioned before in this thesis that MALDI cannot be regarded as a quantitative characterization technique.

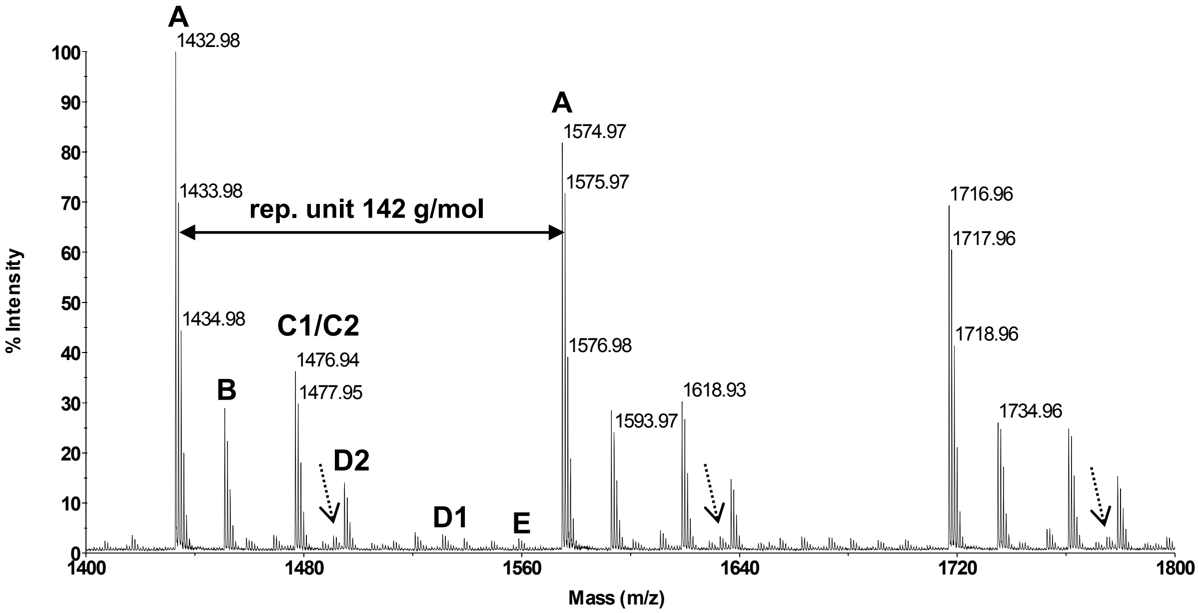
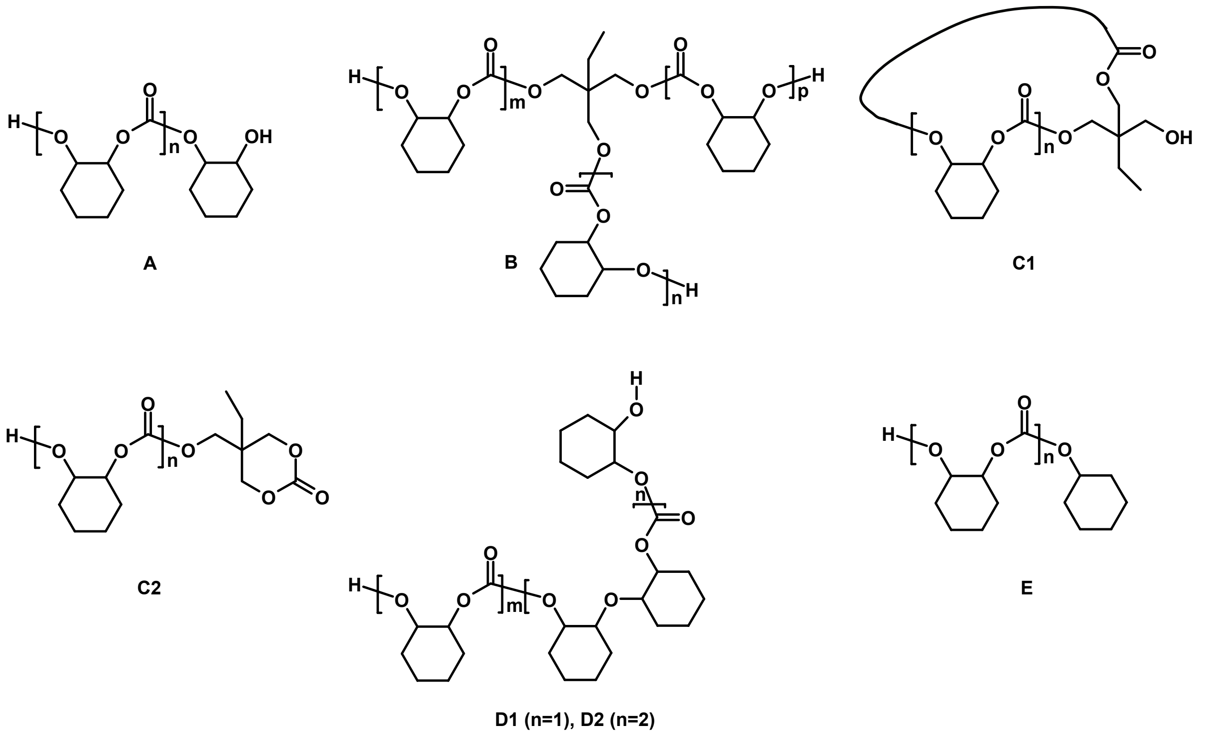


Figure 6-2. Section of the MALDI-ToF-MS spectrum of PCHC after an alcoholysis reaction with TMP. Peak labels refer to the structures depicted in Scheme 6-5. The dotted arrows indicate the masses at which peaks corresponding to residual starting material are visible at low intensity.

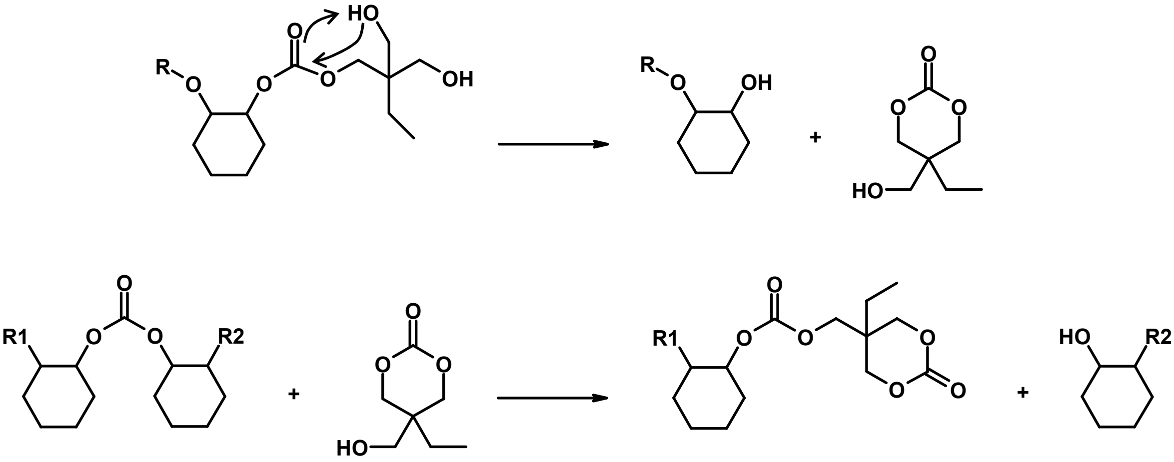
In Figure 6-2, signals of residual starting material, i.e. PCHC chains having one hydroxyl and one methyl carbonate end-group, have almost completely disappeared, as indicated by the arrows in the figure. It is clear that, at least at molecular weights up to 5500 g/mol, the starting PCHC material has been effectively alcoholyzed to form new polymeric species. Since no new species with methyl carbonate end-groups are observed, it is thought that such end-groups have been removed from the reaction mixture through the evaporation of methanol.

Furthermore, it appears that most of the peaks present in the MALDI-ToF-MS spectrum correspond to structures having at least two hydroxyl end-groups. Also, branched polymer chains containing one TMP residue and having three hydroxyl end-groups are observed (signals **B**), at moderate intensity.



Scheme 6-5. Polymeric species observed in the MALDI-ToF-MS spectrum of PCHC after its alcoholysis with TMP: (**A**) linear chains, two hydroxyl end-groups; (**B**) branched chains, three hydroxyl end-groups; (**C1**/**C2**) cyclic chain or linear chain with a cyclic carbonate end-group, one hydroxyl end-group; (**D1**/**D2**) linear chain, one or two ether linkages, two hydroxyl end-groups; (**E**) linear chain with one hydroxyl and one cyclohexyl end-group.

Species **C** corresponds to two different structures (i.e. **C1** and **C2** in Scheme 6-5), since these two types of chains have the same mass. Although it is not impossible that cyclic chains (**C1**) are formed if one TMP moiety attacks the same chain twice at two different locations, structure **C2**, formed through the mechanism shown in Scheme 6-6, is a more likely explanation for signals **C**. Once a TMP molecule has alcoholyzed a PCHC chain, in first instance one of the two remaining primary OH-groups can attack the newly formed PCHC-TMP carbonate linkage, resulting in a hydroxyl end-group at the polymer chain end and a cyclic carbonate monomer, known as 5-ethyl-5-hydroxymethyl-1,3-dioxan-2-one (*mp* = 41 ºC, *bp* = approx. 180 ºC at 1 mbar). This compound is normally synthesized by transesterification (or: transcarbonation) of TMP with dimethyl-, diethyl- or diphenyl carbonate and can be used in lacquers, for example.[19,20] The formation of this cyclic carbonate monomer through the back-biting mechanism proposed in Scheme 6-6 is very similar to the formation of trimethylene carbonate during the thermal degradation of poly(trimethylene carbonate).[21] Once formed, 5-ethyl-5-(hydroxymethyl)-1,3-dioxan-2-one, having one hydroxyl group available for further reactions, can again engage in an interchange reaction with a PCHC carbonate linkage, yielding structure **C2** (Scheme 6-5). Another option would be that the cyclic carbonate monomer is removed from the reactor through evaporation, but considering the reaction temperature and the fact that the reaction is performed under atmospheric conditions (and, thus, not under reduced pressure), this seems unlikely to occur to a large extent.



Scheme 6-6. Formation of a TMP-based cyclic carbonate, 5-ethyl-5-hydroxymethyl-1,3-dioxan-2-one, via a back-biting mechanism and its subsequent carbonate interchange reaction with PCHC, yielding a cyclic carbonate end-group.

From the mechanisms given in Scheme 6-4 and Scheme 6-6, it seems that one molecule of TMP can afford three hydroxy-functionalized chains and one chain with a cyclic carbonate end-group. The latter type of chain terminus is not desired if the subsequent curing reaction involves urethane formation through addition of a polyisocyanate cross-linker. Alternatively, these cyclic carbonate chain ends may be cured with, for example, amines.[22] The signals attributed to species **C1/C2** in the MALDI-ToF-MS spectrum (Figure 6-2) have intermediate intensities, suggesting (but not proving, *vide supra*) that these species are present in significant amounts. We have shown in previous chapters of this thesis that already a small amount of non-functionalized chains or chain ends can seriously affect the final properties of the cured polymeric network, especially if the average functionality of the binder resin is close to two. Apparently, the use of TMP to alcoholyze and functionalize PCHC may lead to deactivated chain ends through the formation of cyclic carbonate moieties. These chain ends do not contribute to the formation of a polymeric network during curing. The same situation was expected for the biobased triol glycerol, which can form a cyclic carbonate species in a similar way as TMP.[23] Therefore, even though the primary hydroxyl groups of TMP seem to be efficient in alcolyzing and functionalizing PCHC, the undesired side-reaction leading to cyclic carbonate structures necessitates the search for an alternative for TMP.

Break-down and in-situ functionalization of PCHC by 1,3,5-cyclohexanetriol (CHT)

To prevent or at least limit the formation of cyclic carbonate end-groups, a more rigid triol was selected to perform the alcoholysis of PCHC: 1,3,5-cyclohexanetriol (referred to as CHT). A potential disadvantage of this molecule is that it has secondary OH-groups, which are thought to be less reactive than the primary hydroxyl groups of, for example, TMP. During the reaction of PCHC with CHT, the decrease of the molecular weight was significantly slower than of the reaction between PCHC and TMP, even though the reaction was performed at the same temperature (Figure 6-3). This is thought to be caused by the limited reactivity of this particular triol. The reaction was stopped after approximately 20 hours (for the reaction of PCHC with TMP, the reaction time was 10 hours) and the $\overline{M}_n$ of the PCHC-sample was still 6500 g/mol, while the T_g had decreased to 77.5 ºC. Also, the *PDI* of the product alcoholyzed by CHT is lower (*PDI* = 1.64) than of the polymer alcoholyzed by TMP (*PDI* = 2.34) (remember that the initial PCHC had a *PDI* of 1.11 and a $\overline{M}_n$ of 14,000 g/mol). These observations indicate that CHT is considerably less efficient during the alcoholysis of PCHC than TMP, as expected.

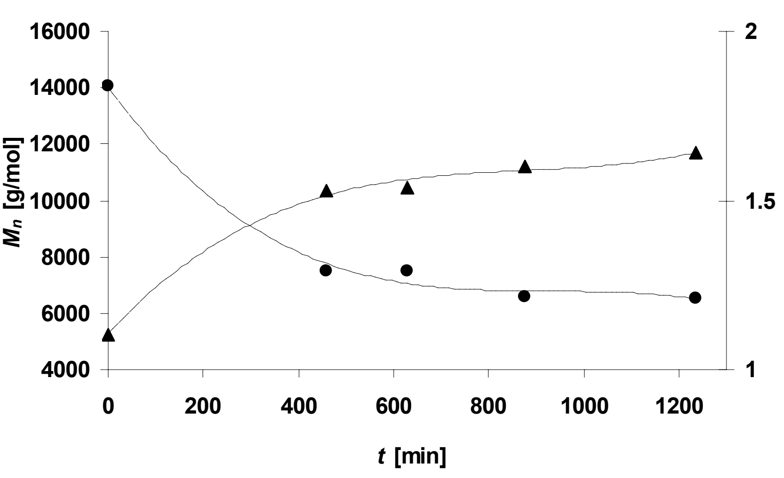


Figure 6-3. CHT-mediated degradation of PCHC. $\overline{M}_n$ (●) and *PDI* (▲) as a function of the reaction time at 180-200 ºC. *N.B. the lines are only meant as guides to the eye.*

The MALDI-ToF-MS spectrum of the product of the alcoholysis of PCHC by CHT (Figure 6-4) shows signals corresponding to similar structures as for alcoholysis by TMP (Scheme 6-5). The main signals correspond to linear, OH-functional chains. The peaks attributed to polymer chains containing one triol residue (i.e. species **B1**, with three hydroxyl end-groups) are slightly more intense than when using TMP. In addition, signals are observed, which correspond to chains containing two triol residues and having four hydroxyl end-groups (**B2**). Cyclic chains or chains having a cyclic carbonate end-group, containing one CHT moiety, are also present (**C**), as well as linear (**D1**/**D2**, having two hydroxyl end-groups) and branched chains (**F1**/**F2**, containing one CHT residue and having three hydroxyl end-groups) having suffered decarboxylation, leading to the formation of ether linkages. The signals corresponding to the cyclic species **C** are only observed at low intensities, suggesting that they are formed less extensively than during TMP-mediated degradation of PCHC. This might be due to the fact that cyclic carbonates are formed less easily from the more rigid CHT than from TMP. The only species having only one hydroxyl end-group is species **E**, having one hydroxyl and one cyclohexyl chain end. All the other observed structures have at least two hydroxyl end-groups. So, in principle, this mixture of polycarbonate species should be suitable for curing reactions with polyisocyanate compounds.

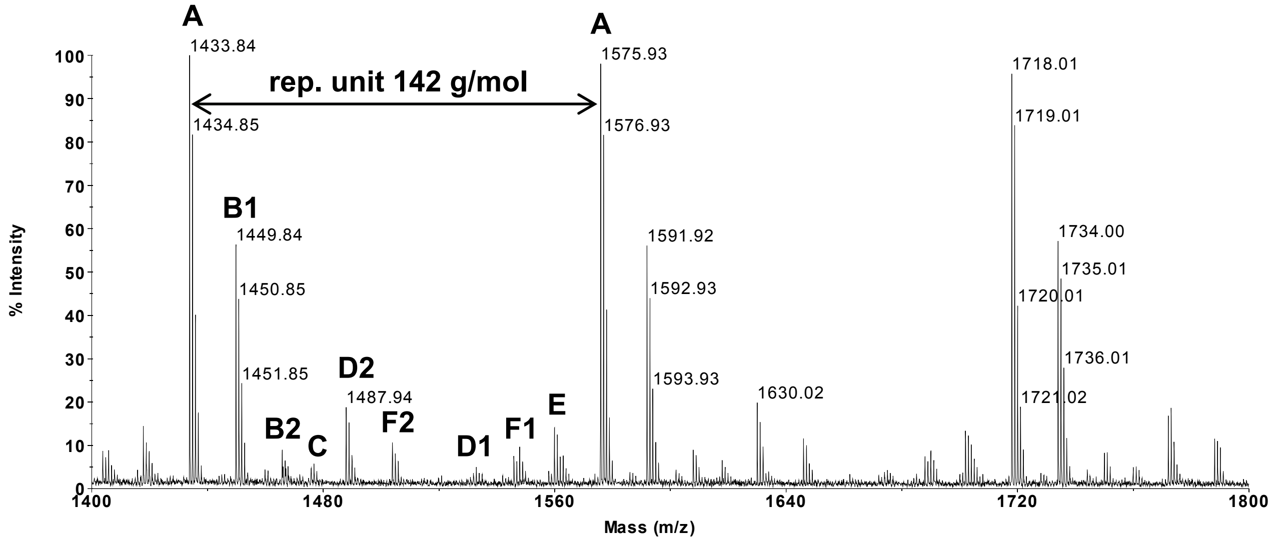


Figure 6-4. Section of the MALDI-ToF-MS spectrum of PCHC after an alcoholysis reaction with CHT. Peak labels refer to structures depicted in Scheme 6-5, with the difference that the TMP-residues are replaced by CHT residues.

6.3.2 Curing of hydroxy-functional poly(cyclohexene carbonate)s and coating properties

The hydroxyl-values (*OHV*) of the different functionalized PCHC samples were determined by titration. Based on these results, the required amount of trifunctional polyisocyanate curing agent was calculated and a 0.05 molar excess was added. The polymers were cured using a trimer of hexamethylene diisocyanate (HMDI) or an ε-caprolactam blocked polyisocyanate based on isophorone diisocyanate (IPDI) (see Chapter 2, Scheme 2-4). The resulting coatings were colorless, transparent and glossy, demonstrating the potential of such materials for coating applications. The films showed intermediate solvent resistance (the coating was visibly damaged after approximately 40 acetone double rubs). Also, the mechanical stability of these PCHC-based coatings is not optimal, since cracking of the coatings was observed after reverse impact testing (100 cm, 1 kg). The moderate results of the solvent test indicate that network formation is not complete. Apparently, not all the polymer chains are hydroxy-functionalized, for which the MALDI-ToF-MS analysis already afforded indications. In the molecular weight range up to approximately 6000 g/mol, the MALDI-ToF-MS spectra do not show considerably large signals for species with a functionality lower than two (see Figure 6-2 and Figure 6-4). Of course, it is possible that the ionization-efficiency of such chains is lower than of the hydroxy-functionalized species, making them less clearly visible in the MALDI spectrum. Another possible explanation for the reduced overall functionality of the PCHC samples might be the presence of inactive chains of higher molecular weight. These chains are not visible in the MALDI-ToF-MS spectra, but might still make up an important fraction (at least in weight) of the total polymer sample. If significant amounts of long chains are present, having only one hydroxyl group per chain, this might have a strong detrimental effect on the solvent resistance of the coating. The moderate impact resistance might also be partly explained by the insufficient levels of cross-linking obtained in these systems. On the other hand, PCHC is known to be a rather brittle material with a low elongation at break even at high molecular weights[10], which could also play an important role in the performance of the poly(carbonate urethane)s based on these functionalized poly(cyclohexene carbonate)s.

In summary, the molecular weights of the alcoholyzed PCHC samples and the coating properties of the resulting poly(carbonate urethane)s are not optimal. Nevertheless, these preliminary results are promising and it is expected that further optimization of reaction conditions to reduce $\overline{M}_n$ and to increase OH-functionality to even higher levels will lead to better network formation and, as a consequence, better chemical and mechanical stability.

6.4 Conclusions

Alcoholysis of high molecular weight poly(cyclohexene carbonate) (PCHC) by trimethylolpropane (TMP) yields OH-functional polycarbonate resins suitable for coating application with respect to polymer T_g and molecular weight distribution. In the resulting alcoholyzed sample, several hydroxy-functional polymer species are present, having at least two reactive end-groups. On the other hand, cyclic carbonate species and cyclohexyl end-groups were also observed, reducing the overall functionality of the sample. When performing similar alcoholysis experiments using 1,3,5-cyclohexanetriol (CHT), it is observed that the decrease in the PCHC molecular weight is slower, due to the lower reactivity of the secondary hydroxyl groups of CHT. The products of such alcoholysis reactions contain mainly OH-functional chains, at least in the molecular weight range up to 6000 g/mol. It appears that cycle formation occurs to a lower extent than when using TMP to alcoholyzed PCHC. Curing experiments resulted in colorless, glossy coatings with intermediate solvent and mechanical resistance. Apparently, the network formation of the PCHC in combination with polyisocyanate curing agents was not yet optimal. This might be due to the presence of relatively large amounts (in weight) of polymer chains having higher molecular weights and limited functionalities. These dangling ends do not contribute to the network formation, resulting in intermediate solvent resistance of the cured films. Furthermore, the limited mechanical performance of the obtained coatings might be due to the inherent brittleness of PCHC. The chemical and mechanical properties of these poly(carbonate urethane)s are expected to be enhanced by improvement of the molecular characteristics of the PCHC resins by optimizing the reaction conditions.

References

(1) Odian, G. *Principles of polymerization* 3rd ed: John Wiley & Sons, Inc.: New York, 1991.

(2) Lowenhielm, P.; Nystrom, D.; Johansson, M.; Hult, A. *Prog. Org. Coat.* **2005**, *54,* 269.

(3) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126,* 11404.

(4) Corma, A.; Iborra, S.; Velty, A. *Chem. Rev.* **2007**, *107,* 2411.

(5) Inoue, S.; Koinuma, H.; Tsuruta, T. *Polym. Lett.* **1969**, *7,* 287.

(6) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28,* 7577.

(7) Van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromol. Rapid Commun.* **2004**, *25,* 382.

(8) Darensbourg, D. J. *Chem. Rev.* **2007**, *107,* 2388.

(9) Duchateau, R.; Van Meerendonk, W. J.; Yajjou, L.; Staal, B. B. P.; Koning, C. E.; Gruter, G.-J. M. *Macromolecules* **2006**, *39,* 7900.

(10) Koning, C. E.; Wildeson, J.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. J. *Polymer* **2001**, *42,* 3995.

(11) Kricheldorf, H. R.; Probst, N.; Langake, D.; Schwarz, G. *Macromol. Rapid Commun.* **2001**, *22,* 750.

(12) Lee, J.-C.; Litt, M. H. *Macromolecules* **2000**, *33,* 1618.

(13) Pinero, R.; Garcia, J.; Cocero, M. J. *Green Chem.* **2005**, *7,* 380.

(14) Van Meerendonk, W. J., *CO_2 as a monomer for the phosgene-free synthesis of new polycarbonates - catalyst development, mechanistic investigations and monomer screening*, in *Laboratory of Polymer Chemistry*. 2005, Eindhoven University of Technology: Eindhoven.

(15) Liu, B.; Chen, L.; Zhang, M.; Yu, A. *Macromol. Rapid Commun.* **2002**, *23,* 881.

(16) Jayakannan, M.; Anilkumar, P. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42,* 3996.

(17) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60,* 725.

(18) Itaya, T.; Iida, T.; Natsutani, I.; Ohba, M. *Chem. Pharm. Bull.* **2002**, *50,* 83.

(19) Buysch, H.-J. *Carbonic esters*, in *Ullmann's Encyclopedia of Industrial Chemistry*. 2005, John Wiley & Sons, Inc.: New York.

(20) Melchiors, M.; Hovestadt, W.; Bruck, J.; Engbert, T.; Buysch, H.-J. (Bayer AG). DE19746379, 1999.

(21) Montaudo, G.; Puglisi, C.; Rapisardi, R.; Samperi, F. *Polym. Degrad. Stab.* **1991**, *31,* 229.

(22) Parzuchowski, P. G.; Kizlinska, M.; Rokicki, G. *Polymer* **2007**, *48,* 1857.

(23) Rokicki, G.; Rakoczy, P.; Parzuchowski, P. G.; Sobiecki, M. *Green Chem.* **2005**, *7,* 529.

7

Fully biobased coating systems using novel curing agents

Abstract

Several biobased bifunctional curing agents were used to prepare polymer networks in combination with previously described renewable polyesters and polycarbonates. Even though the novel curing agents have only two reactive groups per molecule, it was found that poly(ester urethane) and poly(carbonate urethane) networks were formed, provided that the used polymers had average functionalities significantly higher than two. These materials were applied as coatings from solution, affording transparent glossy films with good solvent and mechanical resistance. These results prove that poly(ester urethane)s as well as poly(carbonate urethane)s, completely based on renewable resources, are promising materials for coating applications. Furthermore, isosorbide bis(glycidyl ether) was applied as a curing agent for carboxylic acid-functional polyesters, yielding satisfactory coating properties.

7.1 Introduction

In the previous chapters, the various biobased polyester and polycarbonate resins have been cured using conventional, commercially available curing agents such as hexamethylene diisocyanate- or isophorone diisocyanate-based polyisocyanates. These cross-linkers are well-known in the coating field and often show excellent performance in many commercial systems. The ε-caprolactam blocked polyisocyanates based on isophorone diisocyanate (IPDI) are the main types of polyisocyanates currently being used for curing of hydroxy-functional polymers in powder coating systems. These curing agents are solids at room temperature and are therefore suitable for powder coating applications. In addition to IPDI-based blocked polyisocyanates, blocked cross-linkers prepared from toluene diisocyanate (TDI) can also be used. Due to the high toxicity, poor weatherability and poor yellowing resistance of TDI, however, this material is mainly used in coating systems for indoor applications. Apart from blocked isocyanate compounds releasing caprolactam during curing, internally blocked curing agents are also available, such as uretidiones of IPDI. These materials do not produce volatile side-products during curing.[1]

So far, a limited number of biobased curing agents were described in literature. Linseed oil[2] and castor oil[3] have been epoxidized to prepare cross-linking agents. Although these vegetable oil-based cross-linkers have found commercially use to some extent, an important disadvantage of these materials is that they tend to significantly lower the T_g of the powder coatings systems.

In this study, several novel ε-caprolactam blocked diisocyanates have been prepared, based on renewable resources. In addition, an isosorbide-based bisglycidyl ether was prepared for use as a curing agent for branched, carboxylic acid-functional polymers. By combining these cross-linkers with the biobased polyesters and polycarbonates described in the previous chapters of this thesis, one of the goals of this research project was achieved: to prepare aliphatic network architectures completely derived from renewable resources that are suitable for thermosetting coating applications. This chapter describes the curing characteristics as well as the performance of these bifunctional molecules as curing agents, in fully biobased poly(ester urethane) and poly(carbonate urethane) networks.

7.2 Experimental section

Materials. The following ε-caprolactam blocked diisocyanate curing agents were prepared by the reaction of carbonyl bis(1-caprolactam) (CBC) with the corresponding diamines: (1) 5,5’-

isopropylidenedifurfurylisocyanate (bl-IPDFI, approx. 98 %, mp = 62 ºC), (2) 2,5-isoididediisocyanate (bl-IIDI, 98+ %, mp = 137 ºC) and (3) a diisocyanate derivative of furan-2,5-dicarboxylic acid (bl-FDEDI, approx. 95 %). The main contaminant in these three compounds is CBC. These blocked diisocyanates as well as isosorbide bis(glycidyl ether) (ISBGE, 97+ %) were received as gifts from Agrotechnology and Food Innovations (part of Wageningen University and Research Centre). Dibutyltin dilaurate (DBTDL) and ethyltriphenylphosphonium bromide were purchased from Aldrich. Chloroform-*d* was obtained from Cambridge Isotope Laboratories. The different polyester and polycarbonate resins used for the curing experiments were synthesized as described in previous chapters of this thesis. The used solvents were purchased from Biosolve. All chemicals were used as received.

Solvent casting and curing of hydroxy-functional polyesters and polycarbonates. Hydroxy-functional polyesters and polycarbonates were cured using the following *ε*-caprolactam blocked diisocyanate curing agents (*vide supra*): (1) bl-IPDFI (NCO equivalent weight = 256 g/mol), (2) bl-IIDI (NCO equivalent weight = 211 g/mol) and (3) bl-FDEDI (NCO equivalent weight = 260 g/mol).
A solution of approximately 0.3 g of polymer resin, 1.05 molar equivalent of the curing agent (calculated from titration data) and 0.5 wt% (calculated on solid resin) of dibutyltin dilaurate (DBTDL) in 1 mL N-methyl-2-pyrrolidone (NMP) was prepared. Subsequently, a wet film of approximately 250 μm thickness was applied onto an aluminum panel, using a doctor blade. The film was left to dry at room temperature and then cured at 200 ºC for 30 minutes under a nitrogen atmosphere.

Solvent casting and curing of carboxylic acid-functional polyesters. Carboxylic acid-functional polyesters were cured with isosorbide bis(glycidyl ether). Curing from solution proceeds as described in the following example: a solution of 0.3 – 0.5 g of polyester, 1.05 molar equivalent of the cross-linker (calculated from COOH-value, determined by titration) and 0.5 wt% of ethyltriphenylphosphonium bromide (relative to the amount of solid polyester resin) in 1 mL N-methyl-2-pyrrolidone (NMP) was prepared. Subsequently, a wet film of approximately 250 μm thickness was applied onto the aluminum substrate. The film was left to dry at room temperature, followed by curing at 180 ºC during 20 minutes under nitrogen.

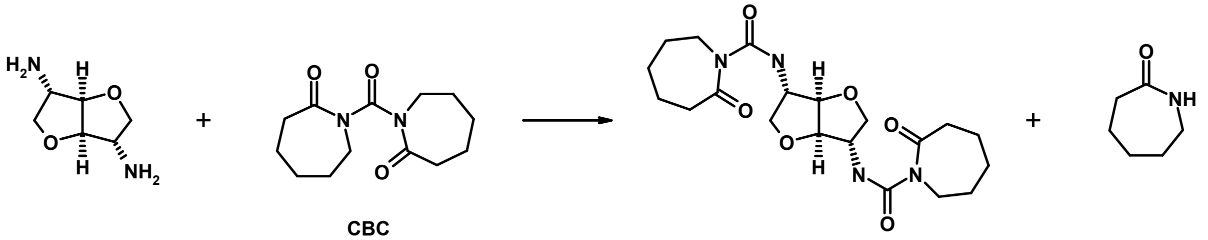
Measurements. SEC analysis in tetrahydrofuran (THF) was carried out using a Waters GPC equipped with a Waters 510 pump and a Waters 410 refractive index detector (at 40 °C). Injections were done by a Waters WISP 712 auto injector, with an injection volume of 50 μL. Two linear columns, Mixed C, Polymer Laboratories, 30 cm, 40 °C, were used. The eluent flow rate was 1.0 mL/min. Calibration curves were obtained using polystyrene standards (Polymer Laboratories, M = 580 g/mol to M = 7.1×106 g/mol). Data acquisition and processing were performed using WATERS Millennium32 (v3.2

or 4.0) software. SEC analysis in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was carried out using a set-up equipped with a Shimadzu LC-10AD pump and a WATERS 2414 differential refractive index detector (at 35 ºC). Injections were done by a MIDAS auto-injector, the injection volume being 50 µL. PSS (2× PFG-lin-XL, 7 µm, 8×300 mm, 40 °C) columns were used. The eluent flow rate was 1.0 mL/min. Calibration curves were obtained using PMMA standards. Data acquisition and processing were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Varian Mercury Vx (400 MHz) spectrometer, where chloroform-*d* was used as a solvent. Glass transition temperatures were determined by DSC measurements, carried out with a DSC Q100 from TA Instruments at a heating/cooling rate of 10 ºC. MALDI-ToF-MS measurements were performed on a Voyager DE-STR from Applied Biosystems. Calibrations were carried out with poly(ethylene oxide) standards for the lower mass range and polystyrene standards for the higher mass range. The mass accuracy was better than 0.2 Dalton, the mass resolution was approximately m/z 12,000. DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) was used as matrix. Potassium trifluoroacetate (Aldrich, >99 %) was used as cationization agent. Solutions of the matrix (40 mg/mL), potassium trifluoroacetate (5 mg/mL) and the polyester sample (1 mg/mL) in THF were premixed in a ratio of 5:1:5. The mixture was subsequently hand-spotted on the target and left to dry. Spectra were recorded in reflector mode at positive polarity. Potentiometric titrations were carried out using a Metrohm Titrino 785 DMP automatic titration device fitted with an Ag titrode. The carboxylic acid functionality was measured by titration with a normalized 0.1 N methanolic KOH solution. The acid value (*AV*) is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize 1 g of polymer resin. Polyester hydroxyl end-groups were acetylated in solution (NMP) with acetic anhydride at room temperature (4-dimethylaminopyridine was used as catalyst), followed by titration of the resulting acetic acid with a normalized 0.5 N methanolic KOH solution. Blank measurements were necessary to obtain the hydroxyl values. The hydroxyl value (*OHV*) is the number of milligrams of potassium hydroxide equivalent to the hydroxyl groups in 1 g of material. All titrations were carried out in duplo. Cross-linking and coating performance at room temperature were evaluated using several characterization methods: acetone rub test (Solvent resistance test: the sample is rubbed with a cloth drenched in acetone. If no damage is visible after more than 150 rubs, the coating has good acetone resistance), rapid deformation test (Reverse impact test, ASTM D 2794) and pendulum damping test (ASTM D 4366, to determine König hardness). The thicknesses of the obtained dry coatings were measured using a magnetic induction coating thickness measuring device (Twin-Check by List-Magnetik GmbH).

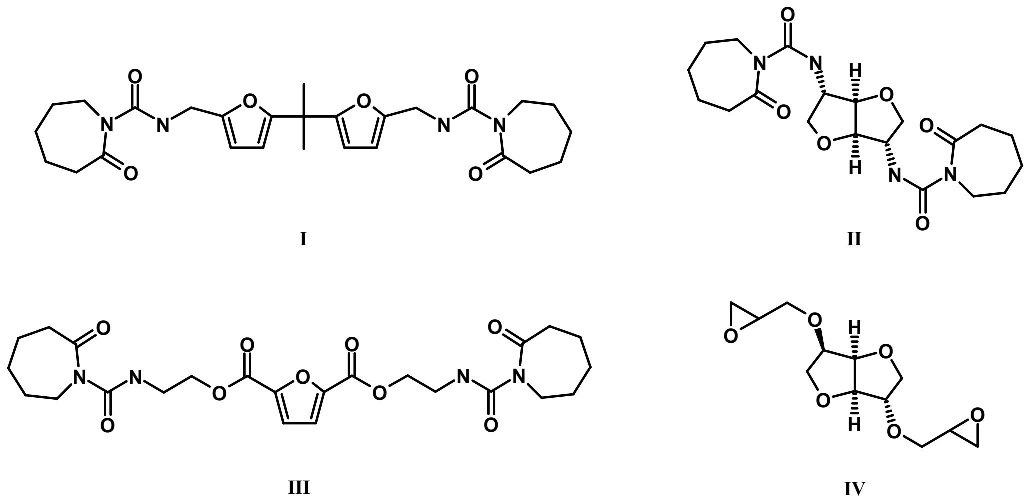
7.3 Results and discussion

7.3.1 Novel biobased curing agents

The compounds described here were developed and prepared at Agrotechnology and Food Innovations (A&F) (Wageningen, the Netherlands) and used as received. First of all, three different *ε*-caprolactam blocked diisocyanates were synthesized by the reaction of biobased diamines with carbonyl bis(1-caprolactam) (CBC)[4] as schematically depicted for the *ε*-caprolactam blocked 2,5-isoididediisocyanate in Scheme 7-1. The following materials were prepared by A&F according to the CBC-route: *ε*-caprolactam blocked 5,5'-isopropylidenedifurfurylisocyanate (bl-IPDFI, curing agent **I**), *ε*-caprolactam blocked 2,5-isoididediisocyanate (bl-IIDI, curing agent **II**) and an *ε*-caprolactam blocked diisocyanate derivative based on a diester of furan-2,5-dicarboxylic acid (bl-FDEDI, curing agent **III**). In addition, isosorbide bis(glycidyl ether)[5] (ISBGE, curing agent **IV**) was prepared (Scheme 7-2).



Scheme 7-1. Synthesis of the *ε*-caprolactam blocked 2,5-isoididediisocyanate (i.e. the carbonyl bis(1-caprolactam) (CBC) adduct of 2,5-isoididediamine), with caprolactam as a side product.[4]



I

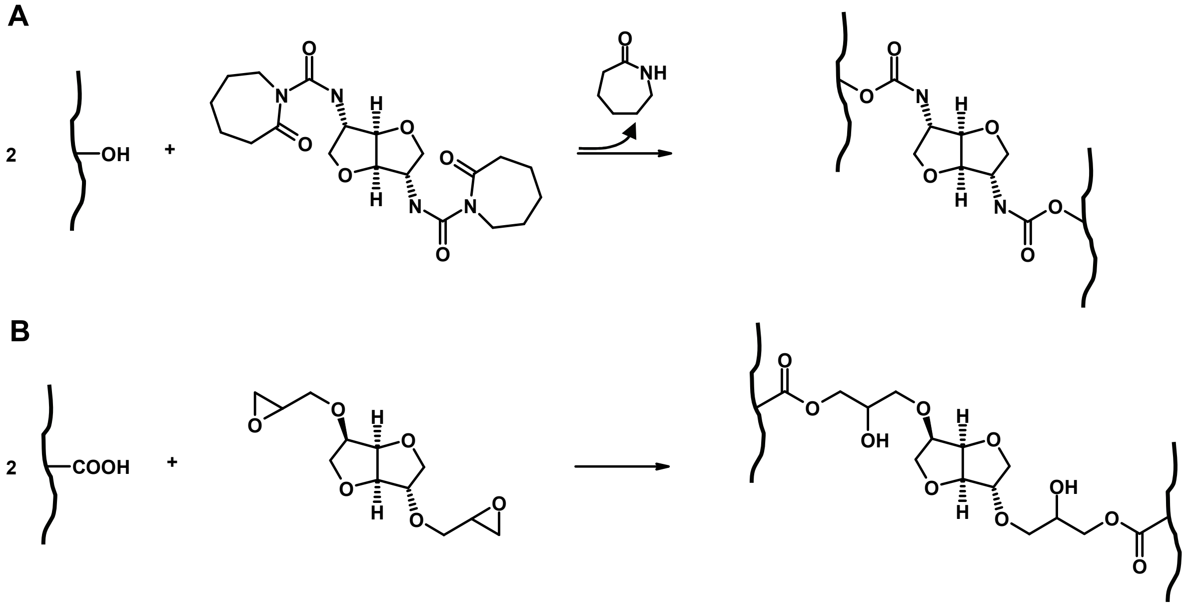
II

III

IV

Scheme 7-2. Bifunctional curing agents based on renewable resources: (**I**) bl-IPDFI, (**II**) bl-IIDI, (**III**) bl-FDEDI and (**IV**) ISBGE.

Curing agents **I-III**, which are all solids at room temperature, can be used to cure hydroxy-functional polymers, while structure **IV** can cross-link carboxylic acid or anhydride functional materials, as described in Chapter 2 and Chapter 4, respectively. Isosorbide bis(glycidyl ether) is a liquid at room temperature. Similar to conventional ε-caprolactam blocked polyisocyanates, curing agents **I-III** become deblocked at temperatures above 160 – 180 ºC.[6] Their reactions with OH-functional polymers can be catalyzed by adding, for example, dibutyltin dilaurate (DBTDL). Reactions between curing agent **IV** and carboxylic acid/anhydride terminal polymers can be catalyzed by adding quaternary ammonium or phosphonium salts, such as ethyltriphenylphosphonium bromide or hexadecyltrimethylammonium bromide. Schematic representations of the formation of poly(ester urethane) or poly(carbonate urethane) and polyester networks using these curing agents are shown in Scheme 7-3.



Scheme 7-3. Schematic representation of the formation of poly(ester urethane), poly(carbonate urethane) and polyester networks through the curing of (**A**) a hydroxy-functional polymer with ε-caprolactam blocked 2,5-isoididediisocyanate and (**B**) a carboxylic acid-functional polyester with isosorbide bis(glycidyl ether).

Since it is important to determine if these curing agents, having a maximum functionality of two, indeed bring about gelation (i.e. network formation) of polymer resins with functionalities $\overline{F}_n > 2$, gelation experiments were performed. The functionality of a polymer resin can be estimated from its composition (determined by ^{1}H NMR) combined with its $\overline{M}_n$. For example, polymer **2** in Table 7-1 (*vide infra*) contains one trimethylolpropane (TMP) moiety for every 10 succinic acid (SA) residues and 11 isosorbide (IS) residues. Such a polymer chain would have a molecular weight of approximately 2600 g/mol. The $\overline{M}_n$ of polymer **2** is 2100 g/mol, implying that, on average, each chain contains 0.8 TMP units. If a polymer chain contains one TMP moiety, the functionality of this chain is $\overline{F}_n$ = 3, provided that the three end-groups are all the same. An average content of 0.8 TMP moieties per chain implies an average functionality of approximately 2.8. The curing reaction between this polymer and a bifunctional curing agent has to proceed to 75 % conversion to reach the gel-point of the formulation (see Appendix B for exemplary calculations).[7]

Initially, polymer **2** was cured with curing agent **I** at a relatively low temperature (160 ºC) in order to follow the development of the molecular weight distribution (Figure 7-1) and T_g (Figure 7-2). At this temperature, deblocking of the curing agent already occurred. Relative to the amount of hydroxyl end-groups of the polymer (determined by titration), 1.05 equivalent of curing agent was added (i.e. for every OH-group, there are 1.05 blocked isocyanate groups).

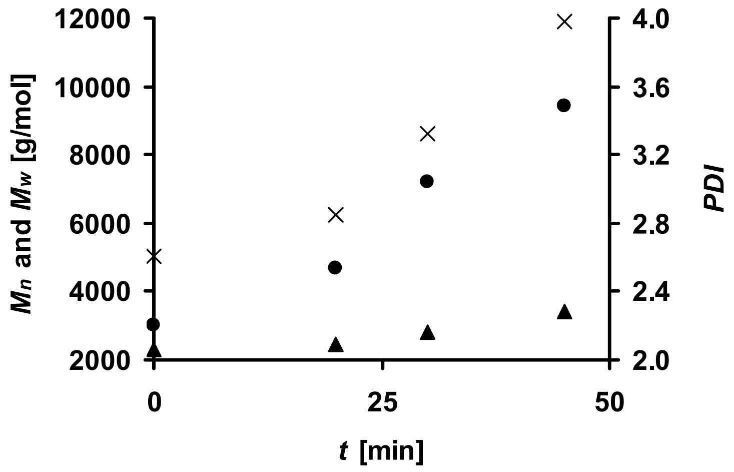


Figure 7-1. $\overline{M}_n$ (▲), $\overline{M}_w$ (×) and PDI (●) as functions of reaction time for the curing reaction between polymer **2** (Table 7-1) and curing agent **I** (Scheme 7-2) at 160 ºC.

The increase of the $\overline{M}_n$ and the $\overline{M}_w$ during this curing reaction proceeds rather slowly at 160 ºC, as expected. It is clear, however, that the reaction between the polyester hydroxyl end-groups and the diisocyanate cross-linker occurs. Samples taken after reaction times longer than 45 minutes are not soluble, indicating that the formation of a poly(ester urethane) network has taken place. The same curing reaction was also followed using ^{1}H NMR spectroscopy (as long as the samples were soluble). At $t = 0$, the ratio polyester:curing agent was 2.2:1 (wt/wt), a ratio which was based on the titration data as mentioned previously. For this particular polymer, having a relatively low molecular weight, this means that there is one molecule of curing agent **I** for every 5.6 succinic acid/isosorbide repeating units. After 45 minutes of curing, new resonances had appeared in the ^{1}H NMR spectrum, attributed to ε-caprolactam, as expected. From the NMR data, it was calculated that 11 % of the initial amount of ε-caprolactam moieties were still connected to the curing agent, blocking the isocyanate group. In addition, 42 % of the starting amount of ε-caprolactam units were present in the reaction mixture as free molecules. The rest, i.e. 47 %, had been removed from the reaction mixture through evaporation. It is known that a significant fraction of the ε-caprolactam, released during the curing reaction, does not leave the coating through evaporation but remains present in the cured film.[8] The conversion (at $t = 45$ min.) of the hydroxyl end-groups of the polyester, resulting in urethane linkages, was approximately 56-60 %, as approximated from the ^{1}H NMR data.

During the first stages of the curing reaction, the T_g of the resin/curing agent mixture is low, probably due to the plasticizing effect of the curing agent and the released ε-caprolactam. After 45 minutes of reaction, a T_g of 14.4 °C is observed, followed by an increase of the T_g to a final value of 57.8 °C, which is 14.3 °C higher than the T_g of the initial polyester resin **2** (Figure 7-2).

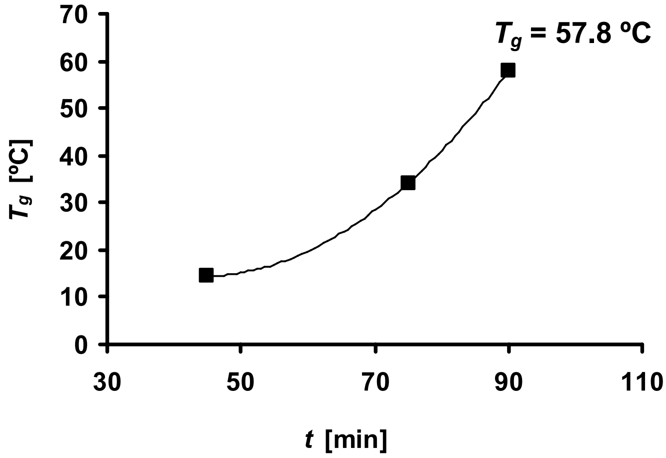


Figure 7-2. T_g as a function of reaction time for the curing reaction between polymer **2** (Table 7-1) and curing agent **I** (Scheme 7-2) at 160 °C.

In this paragraph, we have shown that bifunctional curing agents can be used to prepare poly(ester urethane) networks with increased T_gs. Furthermore, it appears that deblocking and subsequent urethane formation already occurs at 160 ºC, albeit at a relatively low rate. The next step is to evaluate these different curing agents in coating formulations.

7.3.2 Coating properties of biobased poly(ester urethane), polyester and poly(carbonate urethane) networks

Poly(ester urethane) and polyester coatings

The described bifunctional curing agents were used to cure 1,4:3,6-dianhydrohexitol-based polyesters and polycarbonates as well as commercially available aromatic polyester resins. A 0.05 molar excess of curing agent (calculated based on the hydroxyl / carboxylic acid values determined by titration) was added to the polymer resins, calculated from the titration data. All the coatings were applied from NMP solution onto standard aluminum substrates and tested for hardness, reverse impact resistance and solvent resistance. Several branched polyesters were selected from the various polymers presented in Chapters 2, 3 and 4 and their most relevant properties are summarized in Table 7-1. The exact compositions of commercially available resins **3**, **4** and **6** are not available, but the most important difference regarding their compositions is the fact that polyesters **3** and **6** are based on terephthalic acid (TPA), while **4** is based on isophthalic acid (IPA). Furthermore, the OH-functional resins **3** and **4** are more extensively branched than the COOH-functional polymer **6**.

Table 7-1. Branched polyester resins selected for coating application using biobased curing agents.

resin	composition (NMR) [1]	T_g [ºC]	$\overline{M}_n$ [g/mol]	*PDI*	*AV* [mg KOH/g]	*OHV* [mg KOH/g]
		hydroxy-functional polyesters				
1	SA/II/GLY [1:0.98:0.06]	42.4	2200 [2]	2.2	7.8	97.2
2	SA/IS/TMP [1:1.1:0.1]	43.5	2100	2.3	1.3	91.7
3	TPA/NPG-based	43.8	5400	4.3	4.6	51.0
4	IPA/NPG-based	49.9	4100	6.7	5.1	85.3
		carboxylic acid-functional polyesters				
5	SA/IS/CA [1:1.09:0.2]	59.0	2200 [2]	2.7	101.8	65.2
6	TPA/NPG-based	38.4	5000	2.3	35.7	5.4

[1] SA = succinic acid, II = isoidide, IS = isosorbide, GLY = glycerol, TMP = trimethylolpropane, TPA = terephthalic acid, IPA = isophthalic acid, NPG = neopentyl glycol, CA = citric acid.

[2] Determined by SEC in HFIP, using PMMA standards.

Gelation experiments revealed that a formulation based on resin **1** cured with curing agent **I** (Scheme 7-2) formed a gel within 20 minutes at 200 ºC, while curing the same polyester with curing agent **II** (Scheme 7-2) already led to gelation within 10 minutes. The T_g values of the poly(ester urethane)s resulting from these gel tests also show a considerable difference: T_g = 48.7 ºC for resin **1** cured with **I** versus T_g = 70.3 ºC for resin **1** cured with **II**. This is mainly a result of the more flexible nature of curing agent **II** compared to compound **I**. Table 7-2 lists the results for several biobased poly(ester urethane) coatings prepared by curing the selected polymers with the different curing agents. The reactions between the ε-caprolactam blocked curing agents were catalyzed by addition of 0.5 wt% dibutyltin dilaurate (calculated relative to the amount of polyester resin) to the formulation. Curing reactions involving isosorbide bis(glycidyl ether) (ISBGE) were catalyzed by 0.5 wt% ethyltriphenylphosphonium bromide (calculated relative to the amount of polyester resin). Further details concerning the coating application procedure are given in the Experimental section.

Table 7-2. Poly(ester urethane) and polyester coating formulations and their properties.

film	resin	curing agent [1]	T_{cure} [ºC]	t_{cure} [min]	acetone resistance [2]	impact test [1 kg, 100 cm] [2]	av. film thickness [µm]
				poly(ester urethane) networks			
F1	1	I	200	30	-	-	56
F2	1	II	200	30	+	+	28
F3	1	III	200	30	-	-	39
F4	2	I	200	30	+	+/-	52
F5	2	II	200	30	+	+	36
F6	2	III	200	30	+/-	-	47
F7	3	I	200	30	+/-	+	55
F8	3	II	200	30	+	+/-	50
F9	3	III	200	30	+/-	+/-	52
F10	4	I	200	30	+	-	42
F11	4	II	200	30	+	-	45
F12	4	III	200	30	+	-	49
				polyester networks			
F13	5	IV	180	20	+/-	-	35
F14	5	IV/TGIC	180	20	+	+/-	34
F15	6	IV	180	20	+/-	+	36

[1] See Scheme 7-2. TGIC = triglycidyl isocyanurate.
[2] + = good, +/- = moderate, - = poor.

As expected, curing of linear polyesters with these bifunctional curing agents led to poor coating properties, since only chain extension can occur and no networks are formed. These results are not shown in Table 7-2. In general, coatings cured with curing agent **II** perform considerably better than those cross-linked using blocked diisocyanates **I** or **III**, with respect to appearance as well as mechanical and chemical stability. All the coatings are glossy, transparent films. The coatings cured with **I** and **III** show strong discoloration, which may be partly due to impurities present in these curing agents as well as to degradation involving the activated methylene groups present in these molecules. Coatings cured with curing agent **II** are pale yellow. The good performance of coatings **F2**, **F5**, **F7** and **F8** is striking and it shows that these new blocked diisocyanates are promising compounds when used in combination with branched polymers. The TPA-based coatings **F7**-**F9** have better mechanical properties than the IPA-based coatings **F10**-**F12**, which is mainly due to the inherently superior mechanical stability of coating systems prepared from TPA-based polyesters compared to comparable IPA-based systems.[9] The polyester network based on the biobased carboxylic acid-functional polyester **5**, cured with ISBGE (Scheme 7-2, structure **IV**) shows moderate chemical and mechanical stability. Curing the same resin with a 60/40 (mol/mol) mixture of ISBGE/triglycidyl isocyanurate (TGIC) significantly enhances the coating properties, as expected.

Poly(carbonate urethane) coatings

In addition to the polyester and poly(ester urethane) systems, three different biobased, OH-functional polycarbonates (Table 7-3) were selected for application as poly(carbonate urethane) coatings, cured by the novel blocked diisocyanates. Linear polycarbonates were also included in this study, to demonstrate the differences between chain extension and cross-linking. In this case, no commercial polycarbonate resins, used for coating purposes, were available for comparison purposes.

Table 7-3. Linear and branched polycarbonate resins selected for coating applications using biobased curing agents.

resin	composition (NMR) [1]	T_g [ºC]	$\overline{M}_n$ [2] [g/mol]	*PDI*	*OHV* [mg KOH/g]
7	II/1,3-PD [0.44:0.56]	35.6	3100	2.1	76.4
8	IS/1,4-BD [0.45:0.55]	37.8	5000	2.0	32.1
9	IS/1,3-PD/TMP [1:0.28:0.06]	78.8	3600	3.2	50.4

[1] II = isoidide, IS = isosorbide, 1,3-PD = 1,3-propanediol, 1,4-BD = 1,4-butanediol, TMP = trimethylolpropane.
[2] Determined by SEC in HFIP, using PMMA standards (see Experimental section).

The obtained poly(carbonate urethane) coatings are glossy and transparent. As was already observed for the poly(ester urethane)s, curing agents **I** and **III** result in stronger discoloration during curing than compound **II**. Other properties are listed in Table 7-4 below.

Table 7-4. Poly(carbonate urethane) coating formulations and their properties.

film	resin	curing agent [1]	T_{cure} [ºC]	t_{cure} [min]	acetone resistance [2]	impact test [1 kg, 100 cm] [2]	av. film thickness [µm]
F16	7	I	200	30	-	+/-	29
F17	7	II	200	30	+/-	+/-	31
F18	7	III	200	30	-	-	36
F19	8	I	200	30	-	+	39
F20	8	II	200	30	-	+	36
F21	9	I	200	30	+	-	43
F22	9	II	200	30	+	+/-	29
F23	9	III	200	30	+	+/-	30

[1] See Scheme 7-2.
[2] + = good, +/- = moderate, - = poor.

The fact that formulations **F16**, **F19** and **F20** are resistant to rapid deformation is probably mainly due to the low T_gs of polycarbonates **7** and **8**, affording flexibility of the coatings at room temperature. Obviously, no network structures can be formed when curing a linear polymer with a bifunctional curing agent, which explains the poor solvent resistance of **F16-F20**. The enhanced performance of the coatings prepared from the branched polycarbonate **9** was expected. Coatings based on the branched polymer **9** do show good solvent resistance, indicating efficient network formation in these systems. In addition, the coatings perform fairly well with respect to impact resistance, confirming the fact that these novel bifunctional curing agents are promising molecules for application in coating systems. Novel curing agents based on renewable resources, having functionalities larger than two, are currently being developed. It is expected that the performance of fully biobased polymer networks cured with these compounds will be even better.

7.4 Conclusions

Novel, biobased *ε*-caprolactam blocked diisocyanate curing agents were evaluated for their curing characteristics and performance in solvent cast coating systems. When reacting such compounds with hydroxy-functional branched polyesters at 160 ºC in the melt, there is a clear increase in the molecular weight and polydispersity index, eventually leading to insoluble polymer networks. At 200 ºC, gel tests show that network formation occurs within 10 – 20 minutes if resins with sufficiently high functionalities are selected. Solvent cast poly(ester urethane) and poly(carbonate urethane) coatings are transparent and glossy and are resistant to solvent and rapid deformation. Especially coatings containing 2,5-isoidideddiisocyanate residues perform well. Biobased and commercially available carboxylic acid-functional polyesters, cross-linked using isosorbide bis(glycidyl ether), also have suitable properties for coating applications. Most of the polymeric networks described in this chapter are fully biobased, demonstrating the potential of renewable monomers and the resulting polymeric structures.

References

(1) Misev, T. A. *Powder coatings - chemistry and technology* 1st ed: John Wiley & Sons: New York, 1991.
(2) Overeem, A.; Buisman, G. J. H.; Derksen, J. T. P.; Cuperus, F. P.; Molhoek, L.; Grisnich, W.; Goemans, C. *Ind. Crop. Prod.* **1999**, *10,* 157.
(3) Park, S.-J.; Jin, F.-L.; Lee, J.-R. *Macromol. Chem. Phys.* **2004**, *205,* 2048.
(4) Maier, S.; Loontjens, T.; Scholtens, B.; Mulhaupt, R. *Macromolecules* **2003**, *36,* 4727.
(5) Zech, J. D.; Le Maistre, J. W. (Atlas Chemical Industries). US3272845, 1966.
(6) Maier, S.; Loontjens, T.; Scholtens, B.; Mulhaupt, R. *Angew. Chem. Int. Ed.* **2003**, *42,* 5094.
(7) Tiemersma-Thoone, G. P. J. M.; Scholtens, B. J. R.; Dusek, K.; Gordon, M. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29,* 463.
(8) Richart, D. S. *Coating processes, powder technology*, in *Kirk-Othmer Encyclopedia of Chemical Technology*. 2001, John Wiley & Sons, Inc.: New York.
(9) Van der Linde, R.; Belder, E. G.; Perera, D. Y. *Prog. Org. Coat.* **2000**, *40,* 215.

8

Epilogue

8.1 Highlights

This study concerning biobased polyesters, polycarbonates and the cured networks based on these step-growth polymers, has afforded interesting insights into the chemistry, functionality and applicability of materials from renewable resources. Polycondensates prepared from the 1,4:3,6-dianhydrohexitols (DAHs), combined with several comonomers such as succinic acid, 1,3-propanediol and glycerol, have fascinating properties with respect to reactivity, thermal transitions and rheological behavior. One of the main challenges was to develop synthetic procedures towards mechanically and chemically stable polymeric architectures, making use of sugar derivatives that often have limited reactivity and, in some cases, limited thermal stability. We have shown that linear as well as branched polyesters and polycarbonates with sufficiently high molecular weights, tunable T_gs and functionalities for (thermosetting) coating applications can be prepared from the mentioned monomers. In addition, the influence of the orientation (i.e. *endo* or *exo*) of the hydroxyl groups of the different DAH isomers was investigated and appears to be highly dependent on the reaction conditions. In melt polycondensations, the *exo*-oriented hydroxyl groups are more reactive in esterification and transcarbonation reactions, while during the pyridine-promoted solution polymerizations the *endo*-oriented hydroxyl groups react more readily. Citric acid was found to be a very useful molecule to prepare carboxylic acid-functional polymers, while simultaneously enhancing the functionalities of said polymers. Poly(cyclohexene carbonate)s that were given suitable molecular weights, T_gs as well as functionalities by alcoholysis using polyols, proved to be promising resins for coating applications. Furthermore, cured polyester, poly(ester urethane) and poly(carbonate urethane) networks, applied by solution casting or as powder paints, have good or even excellent appearances and are resistant towards solvents and rapid mechanical deformation. Apart from conventional curing agents, novel biobased cross-linkers were efficient with respect to network formation in solution cast films and resulted in chemically and mechanically stable coatings, fully based on renewable resources.

8.2 Technology assessment

It is clear that part of this research has direct links to industrial application of polymers as coating materials. In industry, there is a strong development towards implementation of new products and processes, based on renewable feedstock. Several of the materials investigated during this study may correspond well to the industrial ambitions with respect to biobased polymer production. Most of the described polymers have been prepared in the melt via classical polycondensation procedures. Provided that effective precautions are taken to limit degradation and discoloration of these sugar-derived polymers by running the production processes at moderate reaction temperatures, under an inert reaction atmosphere and using the proper stabilization methods (e.g. anti-oxidants), these polymers can be produced in the same reaction vessels as the conventional polyester resins. Furthermore, the subsequent processing of these resins to produce the final powder paints can be carried out using the same equipment as is currently used. A patent application describing such biobased polyesters was filed, based on the results obtained during this project. Instead of manufacturing fully biobased polyesters, it is of course possible to replace part of the conventionally applied diols or carboxylic di- or polyacids with alternative starting compounds such as isosorbide, succinic acid or citric acid. For example, reducing the aromatic content of a terephthalic acid/neopentyl glycol-based polyester by incorporating considerable amounts of succinic or adipic acid and DAHs may lead to enhanced UV stability of the final coatings, while at the same time achieving potential environmental benefits by using less petrochemicals. Another interesting opportunity of the presented biobased polycondensates is the possible application of fully aliphatic polycarbonates as coating resins. This is an exciting new development, potentially affording UV-stable, tough poly(carbonate urethane) coating systems with enhanced hydrolytic and solvent stability. The importance of these findings was recognized by industrial partners involved in this project and a patent application concerning these systems has been filed.

So far, the polymers containing 1,4:3,6-dianhydrohexitols have been presented as potential constituents of powder coating systems. Alternatively, these materials can also be regarded as promising polyols for use in, for example, waterborne dispersions and as useful construction resins. Preliminary experiments, performed at one of the industrial partners involved in this project, have shown the potential applicability of the DAH-based polyesters as toner resins.

Their tunable thermal characteristics and favorable melt viscosities match the requirements for their potential use in solid printing formulations. Another observation that was made in this respect, is that the aliphatic biobased polyesters may enhance the stability of certain fluorescent dyes used in toner formulations. These results were not discussed in this thesis due to their preliminary character but these issues certainly merit further investigation.

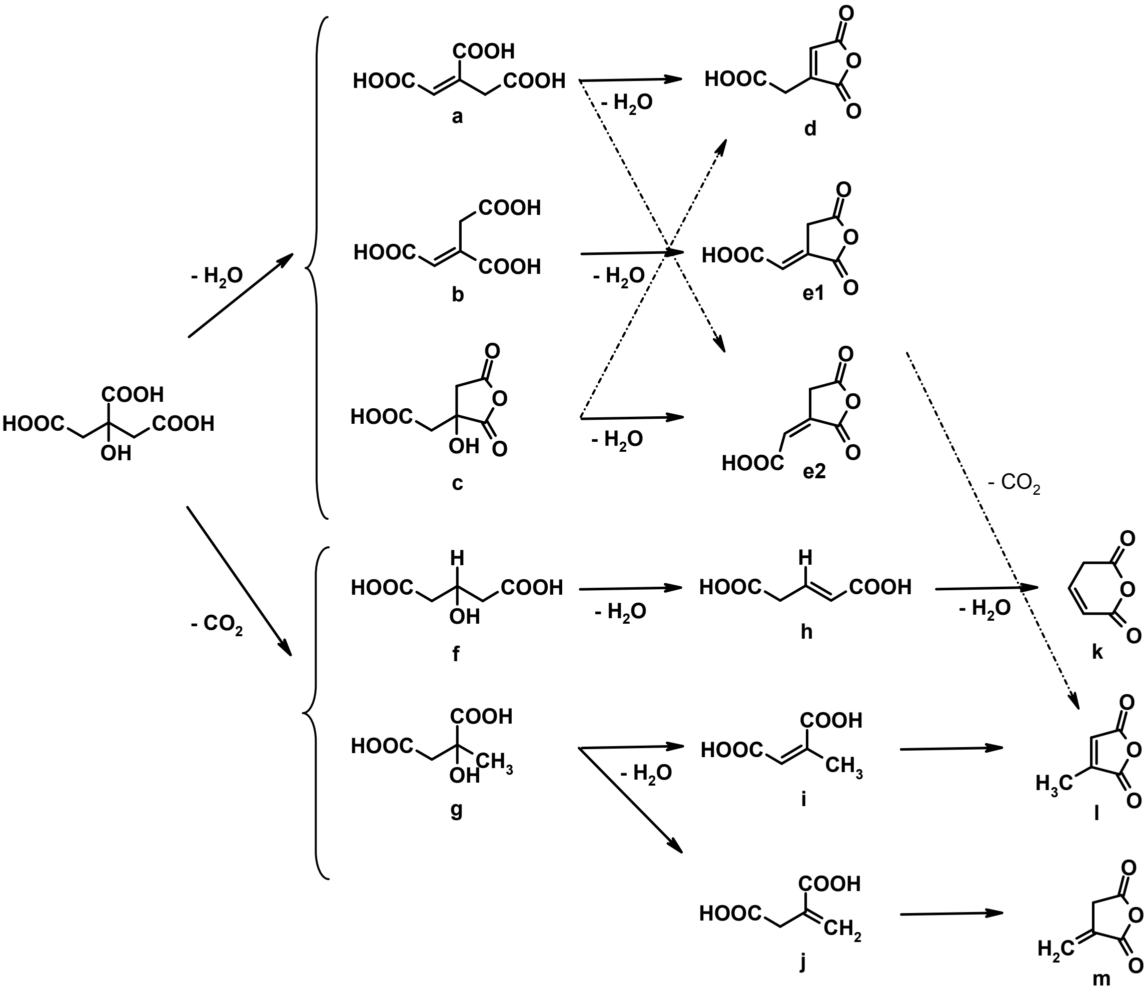
At this point, the main drawbacks of using the 1,4:3,6-dianhydrohexitols on a industrial scale are their availability and price. Isosorbide is currently the only isomer that is produced with sufficiently high purity on a multi-ton scale, but its price is still rather high compared to, for example, neopentyl glycol and terephthalic acid. Of course, prices may decrease upon further upscaling and maturation of the production processes. Isoidide is not yet commercially available on any appreciable scale, due to its more complex and, thus, more costly preparation. On the other hand, monomers such as citric acid and glycerol are available on large scales at low prices. In the case of glycerol, the low pricing is mainly due to the large amount of glycerol produced as a side-product of biodiesel.

8.3 Outlook

The 1,4:3,6-dianhydrohexitols have been the subjects of several studies in the polymer field, focusing on biodegradable polymers, optically active materials and performance polymers. In addition, fundamental studies into the formation of cyclic versus linear polymers have been carried out. This thesis adds to the numerous publications concerning DAH-based polymers, in the area of performance materials. Even though many different aspects of these materials have been discussed in open and patent literature, further research into this field is necessary to reveal, for example, the possibilities of using DAH-based polyols in aqueous dispersions as part of polyurethane resins. As was already mentioned, additional research is needed to investigate biobased polymers as constituents in toner particles, with respect to thermal and rheological properties as well as with respect to interactions with the other components present in the toner, such as pigments, magnetic particles and such. In addition, the development of new polyfunctional curing agents based on renewable resources is expected to lead to fully biobased coating formulations with even better properties than those described in this study. Functionalized aliphatic polycarbonates have already shown to be promising materials for coating applications. A more efficient and well-controlled route towards functional polycarbonates from, e.g., biobased oxiranes and CO_2, is another very interesting topic for future research.

Appendix A

- supporting information with Chapter 4 of this thesis -



Scheme A-1. Degradation pathways of citric acid by dehydration and/or decarboxylation. Compounds formed: (**a**) *cis*-aconitic acid, (**b**) *trans*-aconitic acid, (**c**) citric acid anhydride, (**d**) *cis*-aconitic anhydride, (**e1/e2**) *trans*-aconitic anhydrides, (**f**) 3-hydroxyglutaric acid, (**g**) 2-hydroxy-2-methyl succinic acid, (**h**) glutaconic acid, (**i**) citraconic acid, (**j**) itaconic acid, (**k**) glutaconic anhydride, (**l**) citraconic anhydride and (**m**) itaconic anhydride (structures **d** and **e** can isomerize spontaneously). Further degradation can occur at more extreme conditions, but this is outside the scope of Chapter 4.[1,2]

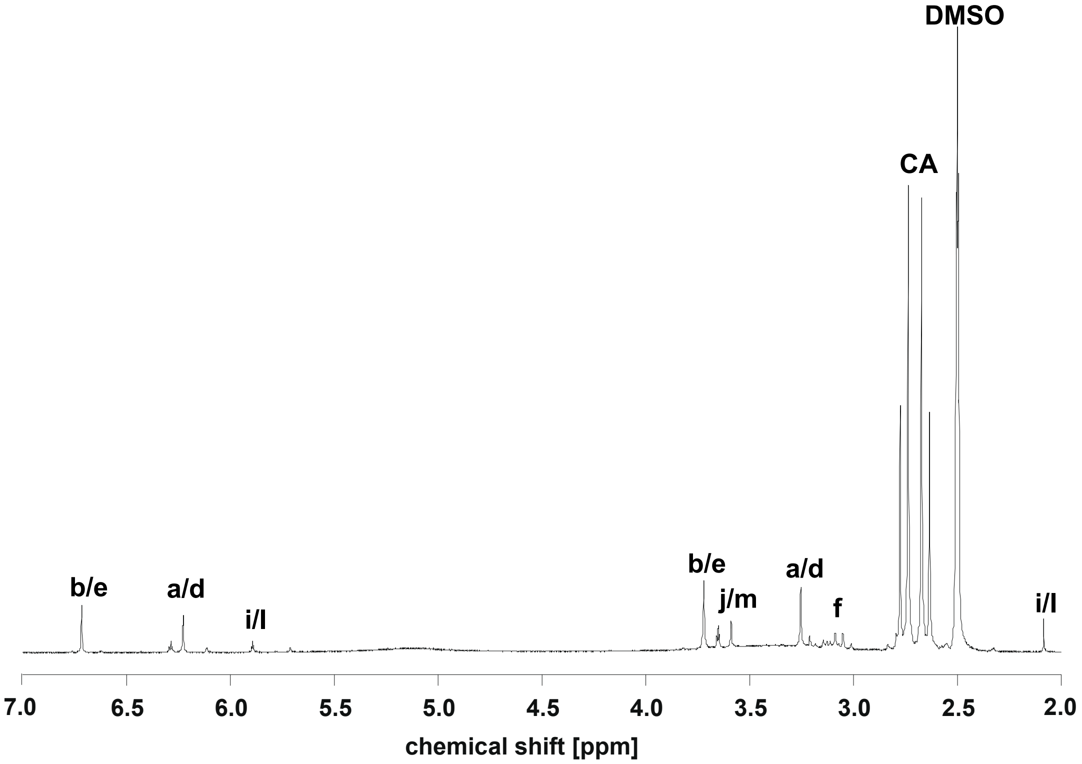


Figure A-1. ^{1}H NMR spectrum of citric acid (CA) after a heat treatment at 180 ºC during 2 hours, including peak attributions (letters correspond to structures drawn in Scheme A-1).

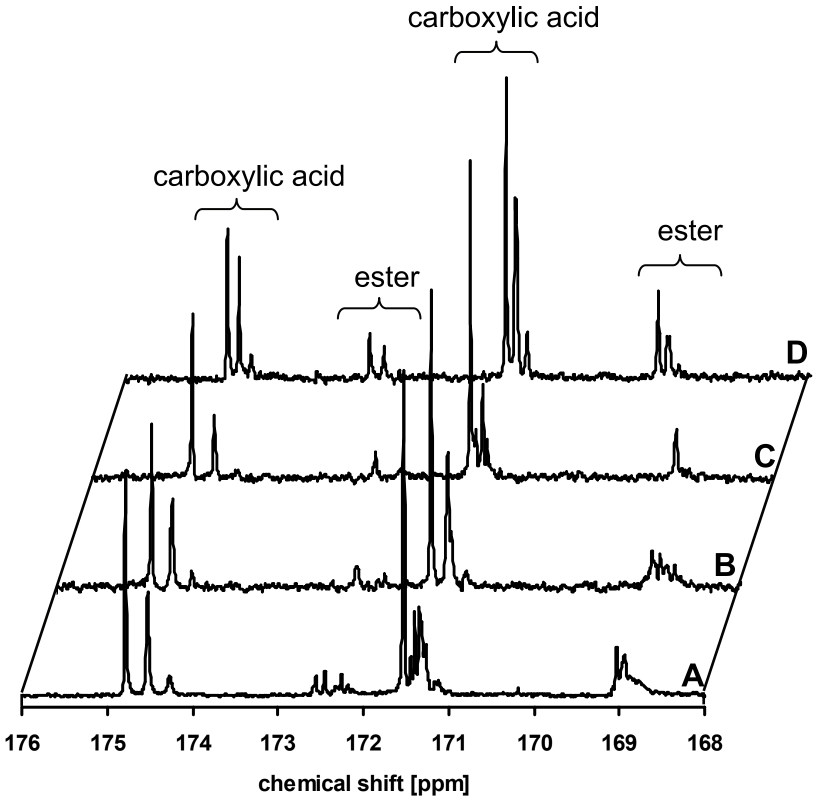


Figure A-2. Carbonyl regions of the ^{13}C NMR spectra of the model reactions of citric acid with (**A**) isosorbide, (**B**) isoidide, (**C**) isomannide and (**D**) 1,4-butanediol at 160 ºC after 170 minutes.

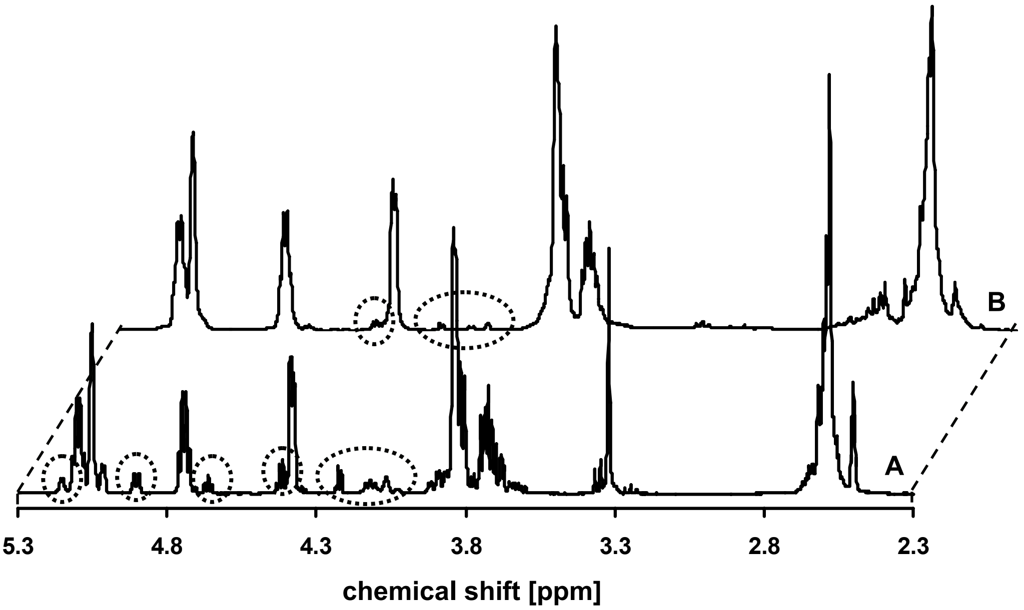


Figure A-3. ^{1}H NMR spectra of (**A**) OH-functional SA/IS copolyester **1** (Table 4-2) and (**B**) its CA-modified product **2** (Table 4-2). The signals indicated by circles originate from IS end-groups. The signals at 4.9 ppm and 5.15 ppm in spectrum **A** are attributed to the *endo*- and the *exo*-oriented hydroxyl groups, respectively. The signals caused by IS end-groups decrease significantly upon CA-modification.

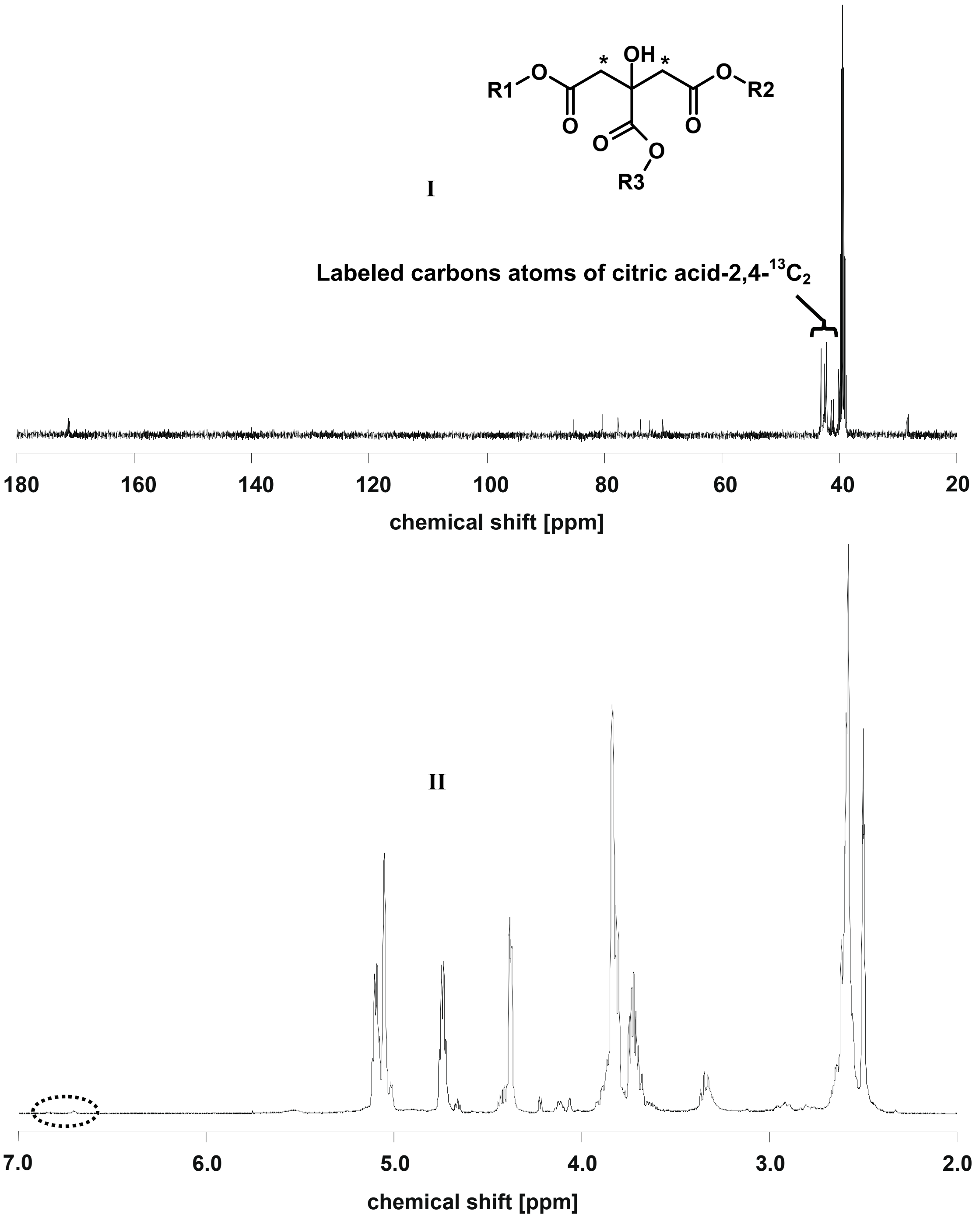


Figure A-4. ^{13}C NMR (**I**) and ^{1}H NMR (**II**) spectra of an OH-functional resin reacted with citric acid-2,4-$^{13}C_2$ after heating at 155 ºC during 4 hours. The ^{13}C spectrum shows no significant signals between 125 and 145 ppm caused by unsaturated structures. The ^{1}H NMR spectrum shows only very faint traces of species such as the aconitic anhydrides around 6.8 ppm (indicated by the ellipse).

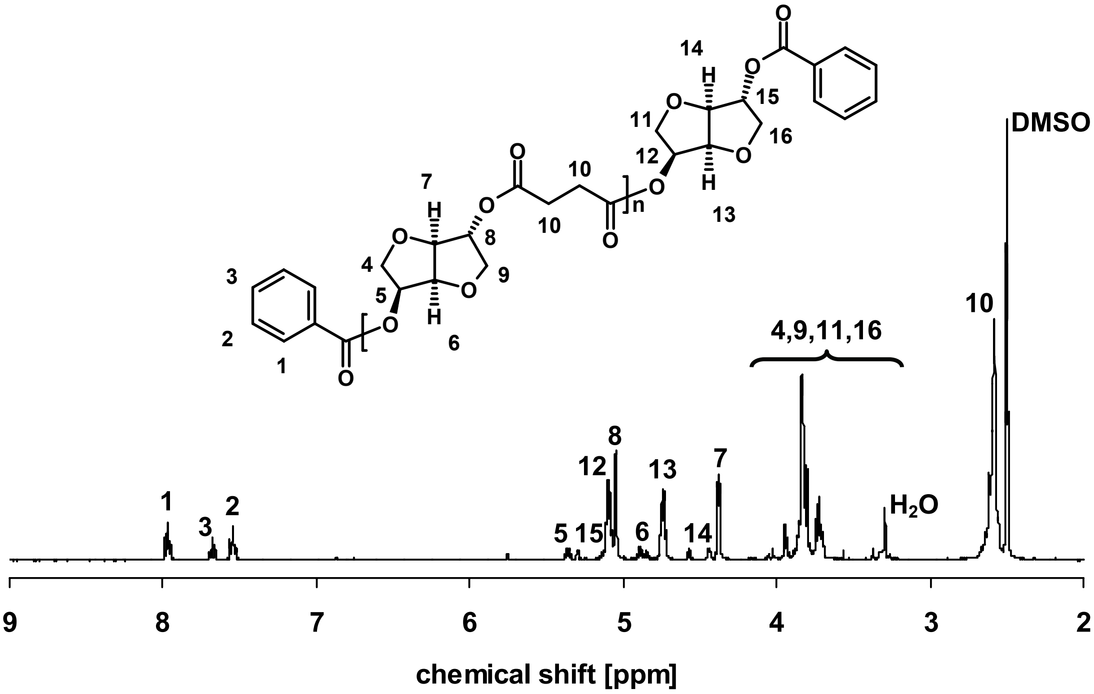


Figure A-5. ^{1}H NMR spectrum of the product of the reaction between an OH-functional poly(isosorbide succinate) and benzoyl chloride (recorded in DMSO-d_6).

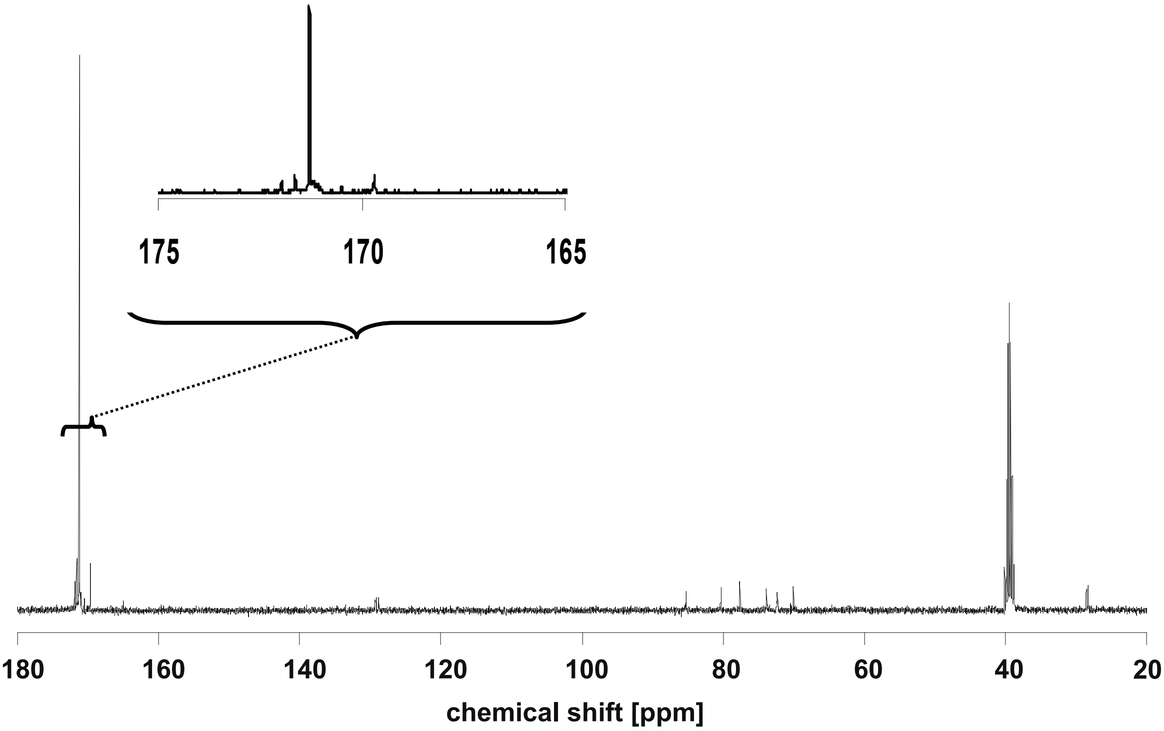
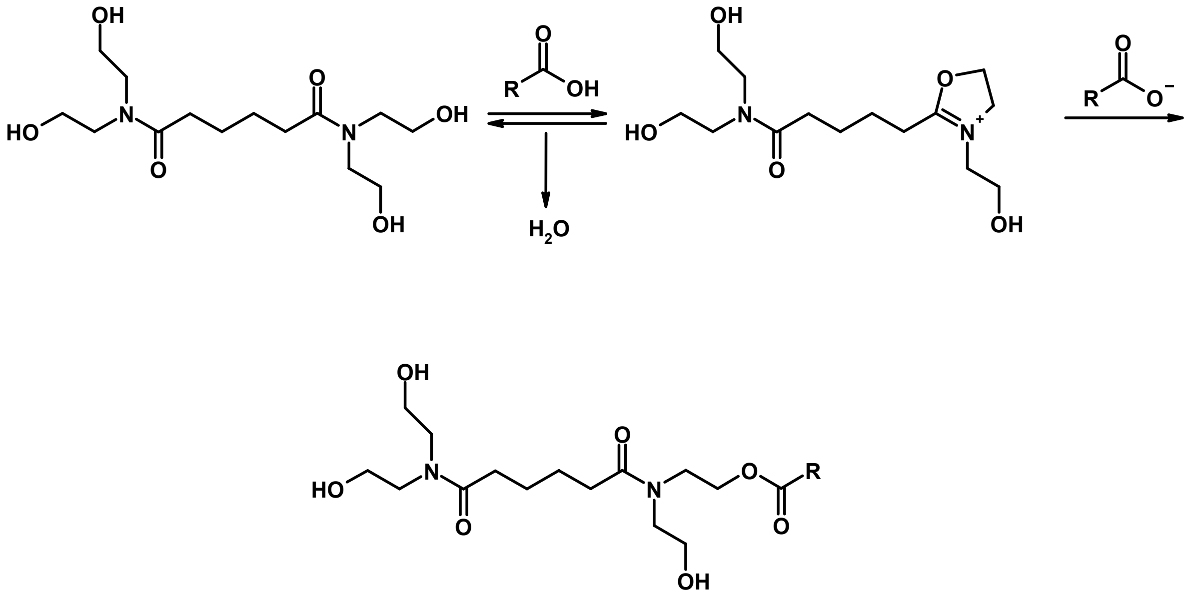


Figure A-6. ^{13}C NMR spectrum of the product of the reaction between CA-1,5-$^{13}C_2$ and a polyester end-capped with a benzoyl chloride residue.



Scheme A-2. Curing mechanism of N,N,N',N'-tetrakis(2-hydroxyethyl)adipamide (trade name: Primid XL-552, EMS Chemie) with a carboxylic acid-functional polymer, proceeding through an oxazolinium cation.[3]

References

(1) Fischer, J. W.; Merwin, L. H.; Nissan, R. A. *Appl. Spectrosc.* **1995**, *49,* 120.
(2) Koning, C. E.; Van Duin, M.; Pagnoulle, C.; Jerome, R. *Prog. Pol. Sci.* **1998**, *23,* 707.
(3) Stanssens, D.; Hermanns, R.; Wories, H. *Prog. Org. Coat.* **1993**, *22,* 379.

Appendix B

- calculation of conversion at the gel-point for A_x / B_y systems[1,2] *-*

The level of conversion p_c at which gelation occurs (or: critical conversion point) in a thermoset coating formulation can be calculated using the following equation:

$$p_c = \frac{1}{[r(f-1)(g-1)]^{0.5}}$$

With $r = \frac{\#A}{\#B}$ (i.e. the ratio of the two different types of functional groups present in the reaction mixture); N.B.: $r \leq 1$

And f and g are the functionalities of the resin and the curing agent:

$$f = \frac{\Sigma \nu_i f_i^2}{\Sigma \nu_i f_i}$$ (analogous for g)

<u>Examples:</u>

1) Linear OH-functional chains (A_2) cured with a trifunctional polyisocyanate (B_3): $1A_2 + 0.66B_3$

$$r = \frac{1 \times 2}{0.66 \times 3} = 1$$ (i.e. stoichiometric conditions)

$f = 2$, $g = 3$

Resulting in: $p_c = \frac{1}{[1(2-1)(3-1)]^{0.5}} = 0.71$ → gelation occurs at <u>71 %</u> conversion.

2) COOH-functional chains (A_3), cured with triglycidyl isocyanurate (B_3): $1A_3 + 1B_3$

$r = \frac{1\times 3}{1\times 3} = 1$ (i.e. stoichiometric conditions)

$f = g = 3$

Resulting in: $p_c = \frac{1}{[1(3-1)(3-1)]^{0.5}} = 0.50$ → gelation occurs at 50 % conversion.

3) COOH-functional chains (A_3), cured with a β-hydroxyalkylamide (B_4): $1A_3 + 0.75B_4$

$r = \frac{1\times 3}{0.75\times 4} = 1$ (i.e. stoichiometric conditions)

$f = 3, g = 4$

Resulting in: $p_c = \frac{1}{[1(3-1)(4-1)]^{0.5}} = 0.41$ → gelation occurs at 41 % conversion.

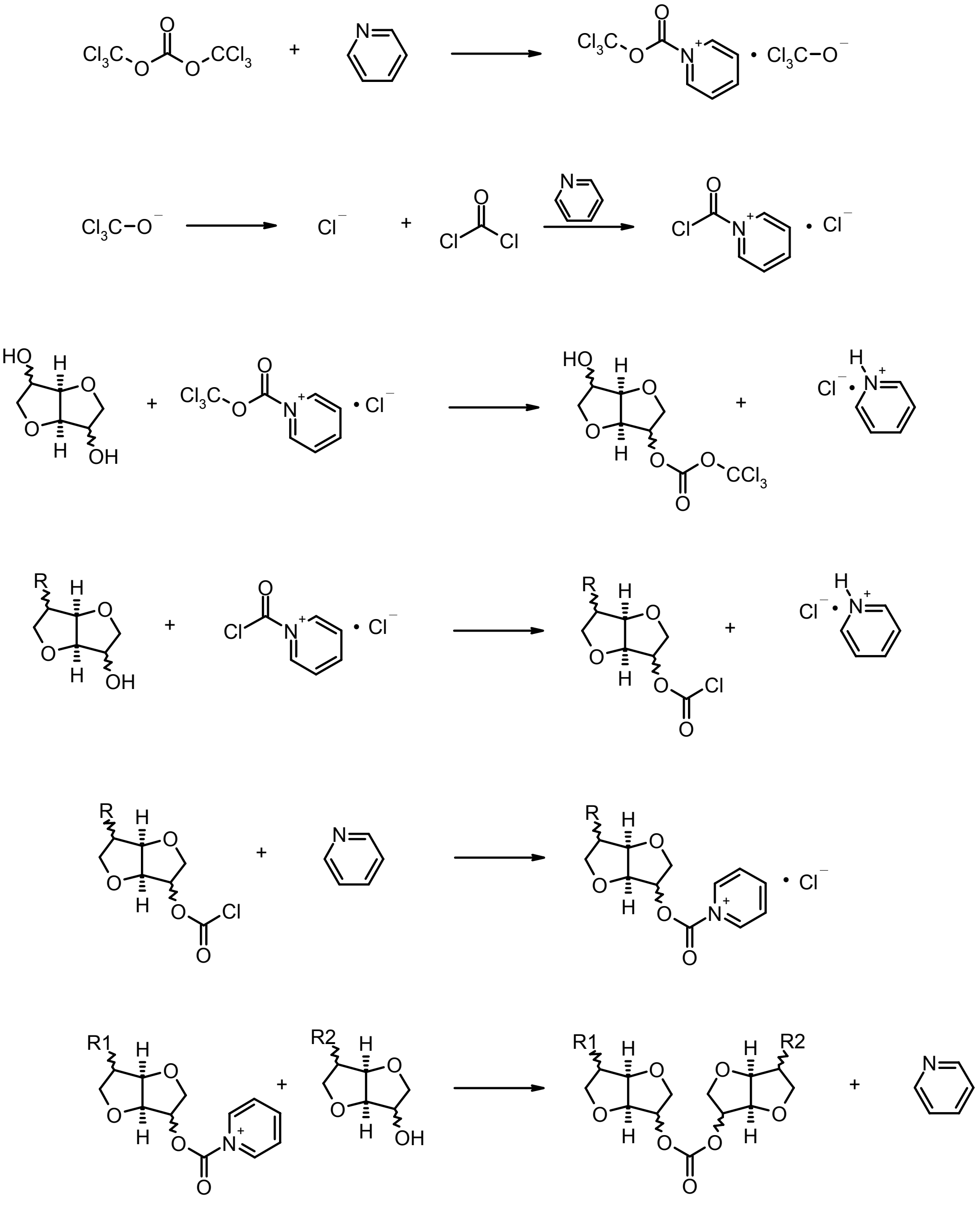
References

(1) Tiemersma-Thoone, G. P. J. M.; Scholtens, B. J. R.; Dusek, K.; Gordon, M. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29,* 463.

(2) Van Benthem, R. A. T. M., *Branched polymer architectures of coating resins (course material)*. 2004.

Appendix C

- supporting information with Chapter 5 of this thesis -



Scheme C-1. Reaction mechanism of the polycondensation of 1,4:3,6-dianhydrohexitols with triphosgene (TPh).[1-4]

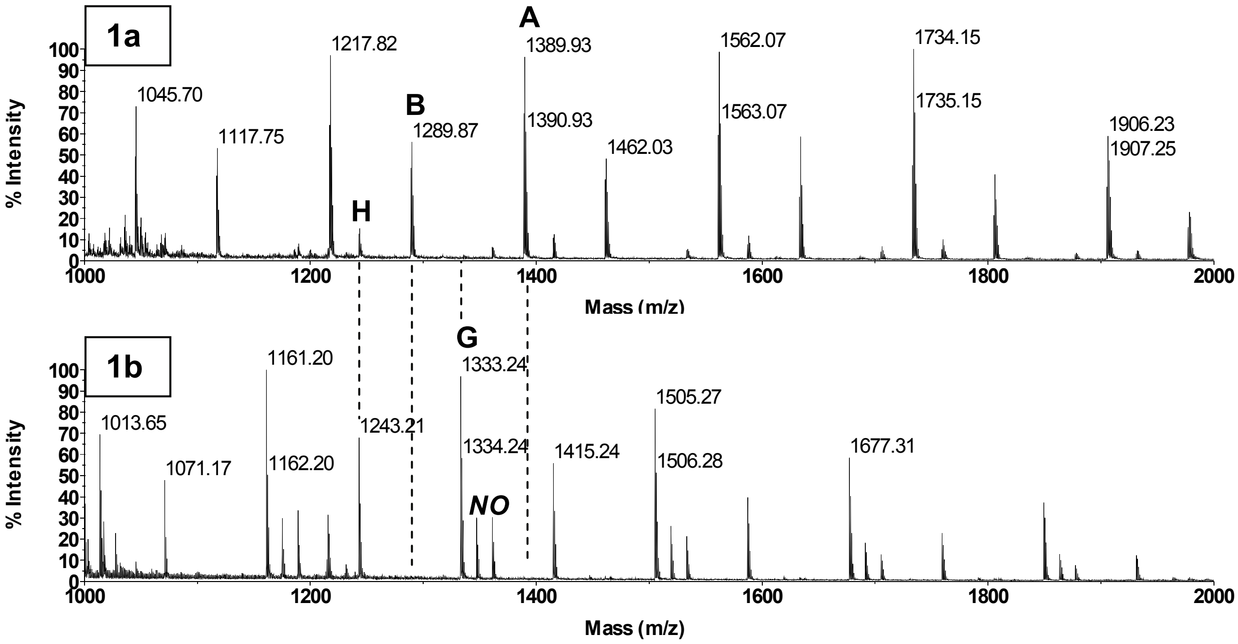


Figure C-1. Sections of the MALDI-ToF-MS spectra of polycarbonates **1a** and **1b** (Table 5-1). Species: (**A**) linear chains, two hydroxyl end-groups; (**B**) cyclic chains; (**G**) linear chains, two methyl carbonate end-groups; (**H**) linear chains, one methyl carbonate and one methyl ether end-group; (**N**/**O**) linear chains, one or two ethyl carbonate end-groups instead of methyl carbonate end-groups, as a result of using dichloromethane stabilized with ethanol. Peak labels **A**, **B**, **G** and **H** refer to structures depicted in Scheme 5-3.

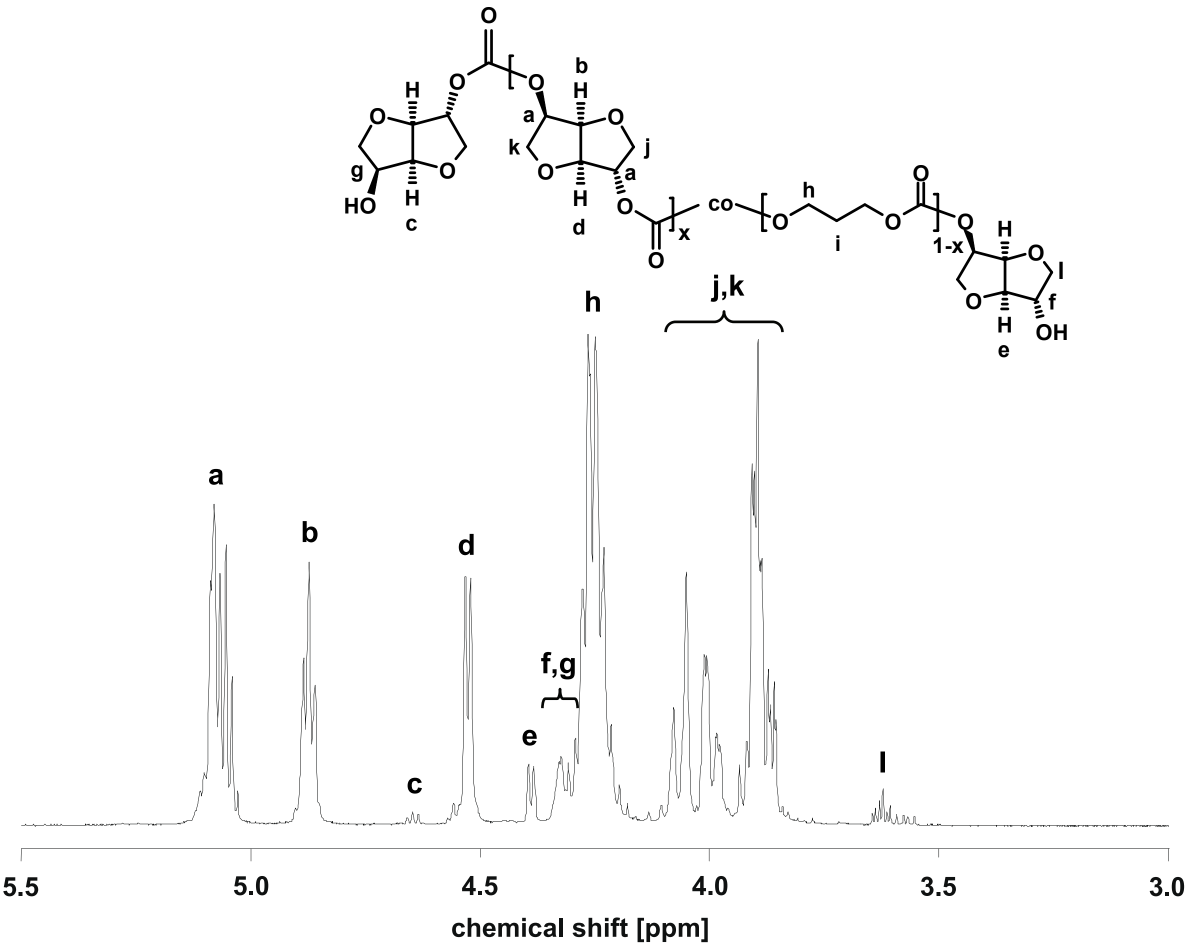


Figure C-2. Section of the ^{1}H NMR spectrum of poly(isosorbide-*co*-propylene carbonate), entry **4** in Table 5-2. This spectrum shows that the conversion of the *endo*-oriented OH-group (96 %) of isosorbide is significantly higher than of the *exo*-oriented OH-group (83 %). *N.B. The resonance for the protons in position **i** is present at 2.05 ppm of this spectrum (not shown here).*

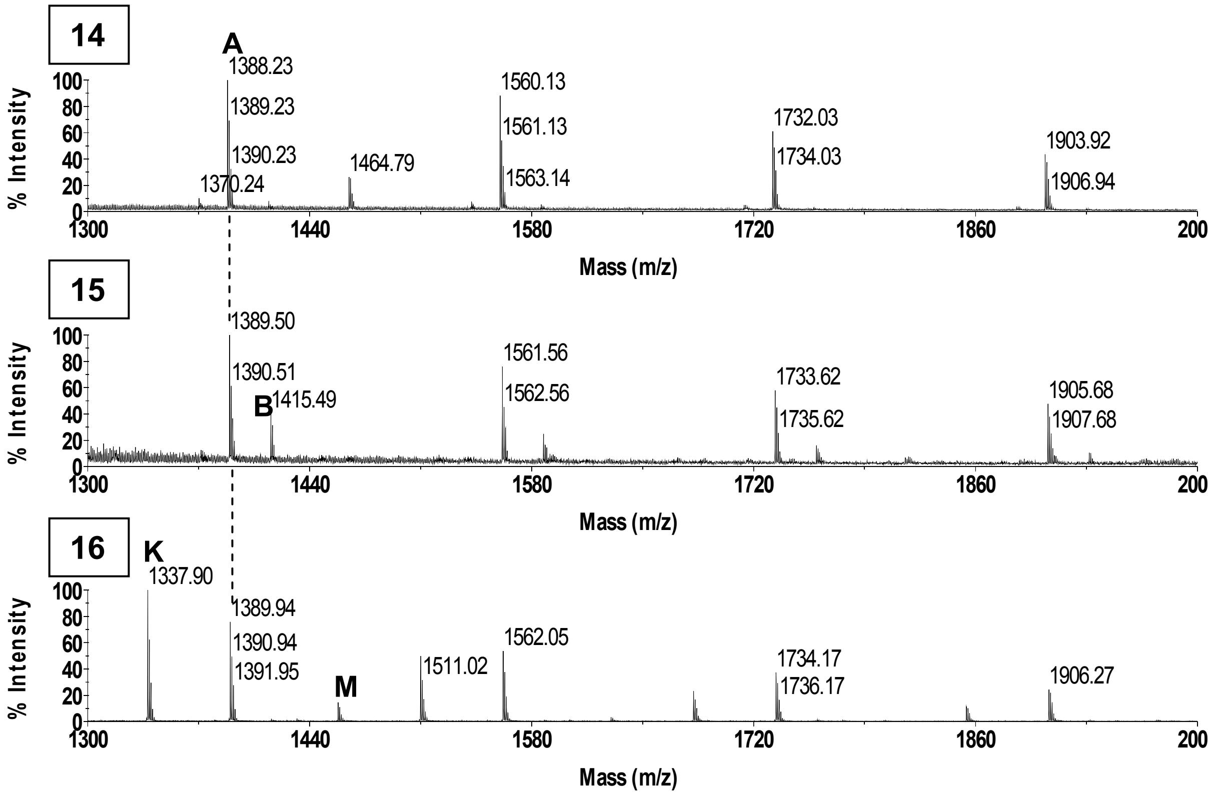


Figure C-3. Sections of the MALDI-ToF-MS spectra of polycarbonates **14**, **15** and **16** (Table 5-4). Species: (**A**) linear chains, two hydroxyl end-groups; (**B**) cyclic chains; (**K**) linear chains, one hydroxyl and one phenyl carbonate end-group; (**M**) linear chains, two phenyl carbonate end-groups.

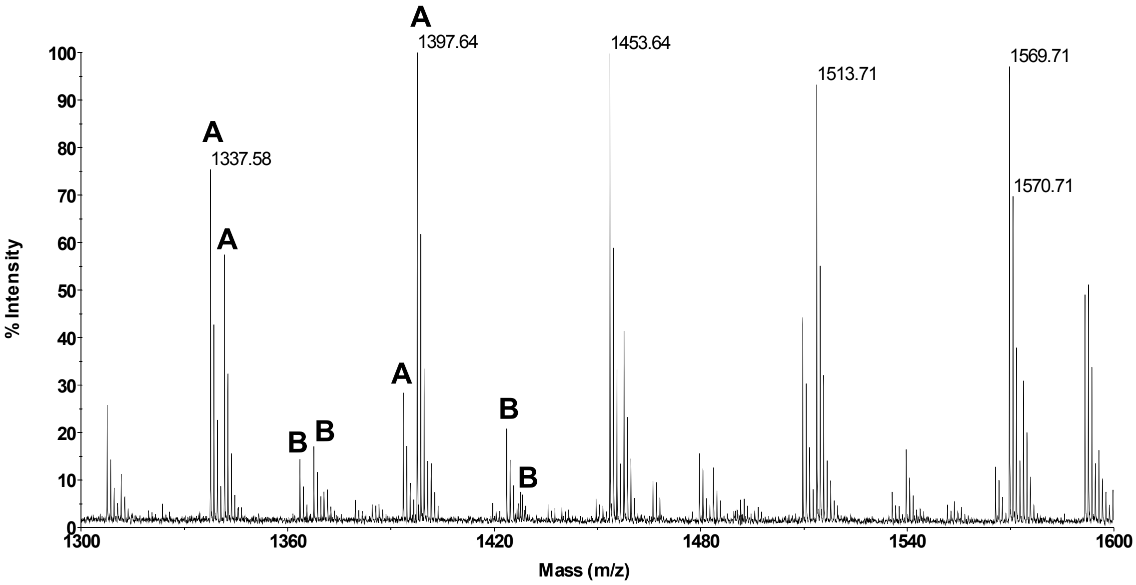


Figure C-4. Section of the MALDI-ToF-MS spectrum of polycarbonate **23** (Table 5-5). Species: (**A**) linear chains, two hydroxyl end-groups; (**B**) cyclic chains.

References

(1) Kricheldorf, H. R.; Bohme, S.; Schwarz, G.; Schultz, C.-L. *Macromolecules* **2004**, *37,* 1742.
(2) Chatti, S.; Schwarz, G.; Kricheldorf, H. R. *Macromolecules* **2006**, *39,* 9064.
(3) Chatti, S.; Kricheldorf, H. R.; Schwarz, G. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44,* 3616.
(4) Kricheldorf, H. R.; Bohme, S.; Schwarz, G. *Macromol. Chem. Phys.* **2005**, *206,* 432.

Glossary

Abbreviations and symbols

1,3-PD	1,3-propanediol
1,4-BD	1,4-butanediol
^{13}C NMR	carbon-13 Nuclear Magnetic Resonance spectroscopy
^{1}H NMR	hydrogen-1 Nuclear Magnetic Resonance spectroscopy
2,3-BD	2,3-butanediol
AA	adipic acid
ATR-FTIR	Attenuated Total Reflection Fourier-Transform InfraRed spectroscopy
AV	acid value, determined by titration [mg KOH/g]
bl-FDEDI	diisocyanate derivative of furan dicarboxylic acid
bl-IIDI	diisocyanate derivative of isoidide
bl-IPDFI	diisocyanate derivative of 5,5'-isopropylidenedifurfurylamine
BPA	bisphenol-A
CA	citric acid
CA-1,5-$^{13}C_2$	citric acid labeled with ^{13}C-atoms in the 1 and the 5 position
CA-2,4-$^{13}C_2$	citric acid labeled with ^{13}C-atoms in the 2 and the 4 position
CBC	carbonyl bis(caprolactam)
$CDCl_3$	deuterated chloroform
$CHCl_3$	chloroform
CHO	cyclohexene oxide
CHT	1,3,5-cyclohexanetriol
DAH	1,4:3,6-dianhydrohexitol
DBTDL	dibutyltin dilaurate
DCM	dichloromethane
DGT	diglycidyl terephthalate
DMA	Dynamic Mechanical Analysis
DMAP	4-dimethylaminopyridine
DMSO-d_6	deuterated dimethyl sulfoxide
DPC	diphenyl carbonate
DPh	diphosgene
EG	ethylene glycol
EtOAc	ethyl acetate
EtOH	ethanol
η^*	complex viscosity [Pa s]
$\overline{F}_n$	average functionality
G'	shear modulus (or: storage modulus) [Pa]
G''	loss modulus [Pa]
GLY	glycerol
GPC	Gel Permeation Chromatography
HCl	hydrochloric acid
HFIP	1,1,1,3,3,3-hexafluoro-2-propanol
HMDI	hexamethylene diisocyanate
II	1,4:3,6-dianhydro-L-iditol (or: isoidide)
IIBEC/ISBEC	isoidide/isosorbide bis(ethyl carbonate)
IIBPC/ISBPC/IMBPC	isoidide/isosorbide/isomannide bis(phenyl carbonate)
IM	1,4:3,6-dianhydro-D-mannitol (or: isomannide)

IPA	isophthalic acid
IPDI	isophorone diisocyanate
IS	1,4:3,6-dianhydro-D-glucitol (or: isosorbide)
ISBGE	isosorbide bis(glycidyl ether)
K	contant from the Fox-Flory equation, related to the thermal expansion coefficients above and below T_g
KOH	potassium hydroxide
MALDI-ToF-MS	Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry
MeOH	methanol
mp	melting point [ºC]
$\overline{M}_n$	number average molecular weight [g/mol]
$\overline{M}_w$	weight average molecular weight [g/mol]
n	number of repeating units in a polymer chain
NCO	isocyanate group
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear Magnetic Resonance spectroscopy
NPG	neopentyl glycol
v_e	concentration of elastically effective network chains [mol/m^3]
OHV	hydroxyl value, determined by titration [mg KOH/g]
PCHC	poly(cyclohexene carbonate)
PDI	polydispersity index
PMMA	poly(methyl methacrylate)
PS	polystyrene
R	gas constant [$m^3\ Pa\ K^{-1}\ mol^{-1}$]
SA	succinic acid
t	time [s]
t_{cure}	curing time
T	temperature [ºC]
T_{cure}	curing temperature
T_{flow}	flow temperature
T_g	glass transition temperature
T_g^{∞}	glass transition temperature at infinite molecular weight
T_m	melting temperature
TBGE	*tert*-butyl glycidyl ether
TDI	toluene diisocyanate
TGA	ThermoGravimetric Analysis
TGIC	triglycidyl isocyanurate
TGT	triglycidyl trimellitate
THF	tetrahydrofuran
TMA	trimellitic anhydride
TMP	trimethylolpropane
TPA	terephthalic acid
TPh	triphosgene
UV	ultraviolet

Samenvatting

Geïnspireerd door de mogelijkheid om materialen te verkrijgen met interessante nieuwe eigenschappen en verder gestimuleerd door de toenemende olieprijs en de groeiende ongerustheid met betrekking tot het milieu, heeft zich de laatste jaren een hernieuwde interesse voor biogebaseerde polymeren ontwikkeld. Er worden uitgebreide inspanningen gedaan om bruikbare uitgangsstoffen te winnen uit hernieuwbare grondstoffen en om uit deze moleculen vervolgens nieuwe polymeren te synthetiseren. Het doel van dit onderzoek was om het potentieel te bestuderen van verscheidene biogebaseerde monomeren als uitgangsstoffen voor de synthese van polycondensaten die geschikt zijn voor coating- of tonertoepassingen. Een diepgaande studie van de chemie, functionaliteit en de structuur-eigenschap relaties van dergelijke polymeren is uitgevoerd.

Stapgroei polymeren met specifieke eigenschappen wat betreft molecuulgewicht en molecuulgewichtsdistributie, eindgroepstructuur en thermische eigenschappen werden nagestreefd. Dit deel van het project omvatte een gedetailleerde bestudering van de geschikte reactieomstandigheden om de biogebaseerde grondstoffen, die vaak gekenmerkt worden door beperkte reactiviteit en thermische stabiliteit, te polymeriseren. Polyesters werden bereid door de 1,4:3,6-dianhydrohexitolen (DAHs, te weten: isosorbide, isoidide en isomannide) te laten reageren met dicarbonzuren zoals barnsteenzuur. De bicyclische structuren van de DAHs zorgen voor voldoende ketenstijfheid en dus ook voor voldoende hoge glasovergangstemperaturen (T_g), zelfs voor de relatief lage molmassa's die voor coating harsen gebruikelijk zijn. Series lineaire en vertakte terpolyesters zijn gesynthetiseerd, waarvan het gemiddelde aantal reactieve eindgroepen kon worden ingesteld door de hoeveelheid polyolen aanwezig in het reactiemengsel te variëren. Het is gebleken dat de *exo*-georiënteerde hydroxy-groepen aanwezig in isoidide en isosorbide reactiever zijn in smeltpolycondensatie reacties, gebruikmakend van niet-geactiveerde dicarbonzuren, dan de *endo*-georiënteerde hydroxy-groepen die voorkomen in isomannide en isosorbide. Bovendien hebben we gevonden dat de anhydro ether ringen van isomannide onderhevig zijn aan ring-opening bij verhoogde temperatuur, in tegenstelling tot de ether ringen van isosorbide en isoidide, welke stabiel lijken te zijn onder deze omstandigheden. Wanneer isoidide of isomannide worden gebruikt om co- en terpolyesters te synthetiseren, resulteert dit in semikristallijne polymeren, terwijl polymerisatie van isosorbide met dicarbonzuren tot amorfe materialen leidt.

Om carbonzuur-functionele materialen te verkrijgen, werden reacties tussen eerder bereide hydroxy-functionele polyesters en citroenzuur uitgevoerd in de smelt. Modelreacties dienden om de chemie van deze modificatiereactie en de verkregen eindgroepstructuur te bestuderen. Interessant genoeg wordt uit citroenzuur een reactief anhydride gevormd rond het smeltpunt van citroenzuur van 153 ºC. Daardoor kan de modificatie van hydroxy-functionele polymeren met het thermisch instabiele citroenzuur bij relatief lage temperaturen worden uitgevoerd. Tevens kunnen de gemodificeerde producten bij gematigde temperaturen worden vernet met conventionele cross-linkers (*vide infra*), waarschijnlijk ten dele als gevolg van anhydridevorming aan de polyester keteneindes, wat de vernettingsreactie versnelt.

Alifatische, biogebaseerde polycarbonaten werden bereid door de polymerisatie van de DAHs in combinatie met anders diolen en/of triolen, gebruik makend van verschillende carbonylbronnen zoals trifosgeen, difenyl carbonaat en bis(ethyl/fenyl carbonaat) monomeren afgeleid van de DAHs. Het bleek moeilijk om de eindgroepstructuren van de polycarbonaten te controleren wanneer gebruik werd gemaakt van zeer reactieve fosgeenderivaten, terwijl de uitwisselingsreacties van de biogebaseerde diolen met difenyl carbonaat hoge reactietemperaturen noodzakelijk maakten om tot voldoende conversie te komen. Thermische degradatie vond plaats via zgn. unzipping en decarboxylatie mechanismen. Om deze nadelige nevenreacties te voorkomen werden de hydroxy-groepen van de DAHs eerst omgezet in carbonaat bindingen met chloroformaten, gevolgd door uitwisselingsreacties van de verkregen moleculen met primaire diolen en/of polyolen in de smelt. De vereiste reactietemperaturen voor deze polymerisaties zijn niet te hoog, wat degradatie beperkt en resulteert in de gewenste hydroxy-functionele copolycarbonaten met bevredigende T_gs en molecuulgewichten. Tevens is een andere route om tot gefunctionaliseerde, alifatische polycarbonaten te komen onderzocht. Deze methode is gebaseerd op de alcoholyse van hoogmoleculair poly(cyclohexeen carbonaat) door polyolen zoals trimethylolpropaan en 1,3,5-cyclohexaantriol. De zo verkregen polycarbonaten hebben significant verbeterde functionaliteiten, evenals geschikte molecuulgewichten en T_gs voor coating toepassingen.

De verschillende hydroxy-functionele polyesters en polycarbonaten werden gemengd met vrije of met ε-caprolactam afgeblokte polyisocyanaten en aangebracht als coatings uit oplosmiddel of als poederverf. Polymeren met carbonzuur eindgroepen werden vernet met epoxy-verbindingen of β-hydroxyalkylamiden. De resulterende polyester, poly(ester urethaan) en poly(carbonaat urethaan) coatings zijn getest op chemische, mechanische en UV stabiliteit. Tevens werden de rheologische eigenschappen van de harsen en de netwerken bepaald. De netwerken verkregen door vernetting van vertakte polymeren presteren beter dan die bereid uit lineaire polymeren, wat vooral het gevolg is van de hogere cross-linkdichtheid van de eerstgenoemde systemen. Maar toch bleek het mogelijk om coatings, bestand tegen oplosmiddelen en snelle vervorming, te maken uit zowel lineaire als vertakte, biogebaseerde, alifatische polycondensaten. Naast de commercieel beschikbare vernettingsreagentia zijn ook verschillende nieuwe, biogebaseerde, met ε-caprolactam afgeblokte diisocyanaten in staat gebleken om vertakte polyesters en polycarbonaten op een efficiënte manier te vernetten. Dit heeft geleid tot chemisch en mechanisch stabiele coatings met veelbelovende eigenschappen, volledig gebaseerd op hernieuwbare grondstoffen.

Summary

Inspired by the opportunity to obtain materials with interesting new properties and further stimulated by the increasing oil prices and the augmenting environmental concerns, renewed interest in biobased polymers has recently arisen. Extensive efforts are being invested in extracting useful starting materials from renewable resources and to use these molecules to synthesize novel polymers. The aim of this study was to investigate the potential of several biobased monomers as starting compounds to synthesize polycondensate resins suitable for coating or toner applications. An in-depth study of the chemistry, functionality and the structure-property relations of such polymers was performed.

Step-growth polymers with specific characteristics with respect to molecular weight (distribution), end-group structure and thermal properties were targeted. This part of the project included a detailed study of the suitable reaction conditions to polymerize the biobased starting materials, which often have limited reactivity and thermal stability. Polyesters were prepared by reacting the 1,4:3,6-dianhydrohexitols (DAHs, i.e. isosorbide, isoidide and isomannide) with dicarboxylic acids such as succinic acid. The bicyclic structures of the DAHs introduce sufficient chain rigidity and, thus, already for the relatively low molar masses required for coating resins sufficiently high glass transition temperatures (T_g) were obtained. Series of linear and branched terpolyesters were synthesized, of which the average number of reactive end-groups per polymer chain could be adjusted by varying the amount of polyols present in the reaction mixture. It was shown that the *exo*-oriented hydroxy-groups present in isoidide and isosorbide are more reactive in melt polycondensation reactions, using non-activated dicarboxylic acids, than their *endo*-oriented counterparts present in both isomannide and isosorbide. In addition, we found that the anhydro ether rings of isomannide are susceptible to ring-opening at elevated temperatures, in contrast to the ether rings of isosorbide and isoidide, which appear to be stable under these conditions. When using isoidide or isomannide to synthesize polyesters, semi-crystalline polymers are obtained, while polymerization of isosorbide with dicarboxylic acids yields amorphous materials.

To obtain carboxylic acid-functional polyesters, linear hydroxy-functional polyesters were reacted with citric acid in the melt. Model reactions were carried out to investigate the chemistry of this modification reaction and the resulting end-group structures. Interestingly, citric acid is transformed into a more reactive anhydride species close to its melting

temperature of 153 ºC. Therefore, the modification of hydroxy-functional polymers with the thermally labile citric acid can be performed at relatively low temperatures. In addition, the modified products can be cured with conventional cross-linkers (*vide infra*) at moderate temperatures, which is probably partly due to anhydride formation at the polyester chains ends, accelerating the curing reaction.

Aliphatic, biobased polycarbonates were prepared by polymerization of the DAHs, in combination with other diols and/or polyols, using several types of carbonyl sources such as triphosgene, diphenyl carbonate and bis(ethyl/phenyl carbonate) species derived from the DAHs. It proved to be difficult to control the end-group structures of the polycarbonates when using the highly reactive phosgene derivatives, whereas the interchange reactions of the biobased diols with diphenyl carbonate required high reaction temperatures to achieve sufficient conversion. Thermal degradation occurred through an unzipping mechanism and decarboxylation. To prevent these detrimental side reactions, the hydroxy-groups of the DAHs were first converted to carbonate linkages using chloroformates, followed by melt interchange reactions of the resulting molecules with primary diols and/or polyols. These polymerizations do not require too high reaction temperatures, thereby limiting degradation and resulting in the desired hydroxy-functional copolycarbonates with satisfactory T_gs and molecular weights. Another route to functionalized, aliphatic polycarbonates was investigated, involving alcoholysis of high molecular weight poly(cyclohexene carbonate) by polyol species such as trimethylolpropane and 1,3,5-cyclohexanetriol. The obtained polycarbonates have significantly enhanced functionalities as well as reduced molecular weights and T_gs, all suitable for coating applications.

The various hydroxy-functional polymers were mixed with free or ε-caprolactam-blocked polyisocyanate curing agents and applied as coatings by either solution casting or powder coating. Polymers with carboxylic acid end-groups were cured using epoxy-compounds or β-hydroxyalkylamides. The resulting polyester and poly(ester/carbonate urethane) coatings were tested for chemical, mechanical and UV stability. In addition, the rheological properties of these materials were investigated. Networks obtained by curing branched polymers perform better than those prepared from linear polymers, which is mainly due to the enhanced cross-link density of the former systems. Solvent and impact resistant coatings were prepared from linear and branched, biobased polycondensates. In addition to the conventional curing agents used in this study, several novel, biobased, ε-caprolactam-blocked diisocyanates proved efficient in cross-linking branched polyesters and polycarbonates, leading to fully biobased, chemically and mechanically stable, glossy coatings with very promising properties.

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Ruim vier jaar geleden verhuisde ik van Enschede naar Eindhoven en in december 2003 begon ik met mijn promotieonderzoek aan de TU/e in het Brabantse land. Het is een leerzame en vooral ook erg leuke tijd geweest en ik wil dan ook graag een aantal mensen bedanken, zonder wie deze afgelopen jaren in Eindhoven lang niet zo aangenaam zouden zijn geweest.

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Het project, waarvan de resultaten in dit proefschrift zijn beschreven, was een samenwerking tussen de TU/e en Agrotechnology & Food Innovations (onderdeel van het Wageningen University and Research Centre). Hierbij wil ik Jacco van Haveren, Daan van Es, Roelof Koelewijn en Guus Frissen hartelijk bedanken voor hun input en de prettige samenwerking gedurende dit project.

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Curriculum Vitae

Bart Noordover werd op 7 juni 1979 geboren te Heemskerk. In Castricum volgde hij het voortgezet onderwijs aan het Bonhoeffer College. Na het behalen van zijn gymnasiumdiploma begon hij in 1997 aan de studie Chemische Technologie aan de Universiteit Twente te Enschede. In juli 2003 studeerde hij af in de groep 'Synthese en Technologie van Engineering Plastics' van dr. Reinoud Gaymans, op het onderzoek getiteld: 'Structuur-eigenschap relaties van gesegmenteerde polyurethanen met uniforme harde segmenten'. Van september tot en met november 2003 was hij werkzaam als onderzoeker binnen de capaciteitsgroep Polymeerchemie aan de Technische Universiteit Eindhoven, op het gebied van geleidende koolstof nanobuisjes/polyethyleen nanocomposieten. Aansluitend begon hij aan zijn promotieonderzoek binnen diezelfde groep, begeleid door prof.dr. Cor E. Koning en dr. Rob Duchateau. Het onderzoek werd uitgevoerd in samenwerking met de groep Coatingstechnologie, onderdeel van de capaciteitsgroep Materiaal- en Grensvlakchemie. Binnen deze groep waren prof.dr. Rolf A. T. M. van Benthem en dr. Weihua Ming zijn begeleiders. De belangrijkste resultaten van het onderzoek zijn in dit proefschrift beschreven. Per 1 februari 2008 is hij werkzaam bij Dow Europe GmbH in Zwitserland.

Bart Noordover was born on the 7th of June 1979 in Heemskerk. He received his secondary education in Castricum at the Bonhoeffer College. After obtaining his gymnasium diploma in 1997, he started his Master studies at the faculty of Chemical Engineering of the University of Twente in Enschede. In July 2003, he graduated within the group 'Synthesis and Technology of Engineering Plastics' of dr. Reinoud Gaymans, on the research entitled: 'Structure-property relations of segmented polyurethanes having uniform hard segments'. From September until November 2003, he worked as a researcher in the Laboratory of Polymer Chemistry at the Eindhoven University of Technology, in the field of conductive carbon nanotube/polyethylene nanocomposites. Subsequently, he started his PhD research within the same group, supervised by prof.dr. Cor E. Koning and dr. Rob Duchateau. The research was carried out in collaboration with the Coatings Technology group, which is part of the Laboratory of Materials and Interface Chemistry. Within this group, prof.dr. Rolf A. T. M. van Benthem and dr. Weihua Ming were his coaches. The most important results of this study are described in this thesis. From the 1st of February 2008, he is employed by Dow Europe GmbH in Switzerland.

List of publications

Noordover, B. A. J.; Duchateau, R.; Koning, C. E.; Van Benthem, R. A. T. M.; Ming, W. 'Enhancing the functionality of biobased polyester coating resins through modification with citric acid' *Biomacromolecules* **2007**, *in press*.

Noordover, B. A. J.; Duchateau, R.; Koning, C. E.; Van Benthem, R. A. T. M.; Haveman, D. *patent application: Polycarbonate and process for producing the same*, EP07116306 to the Dutch Polymer Institute (filed in September **2007**).

Van Haveren, J.; Oostveen, E. A.; Miccichè, F.; Noordover, B. A. J.; Koning, C. E.; Van Benthem, R. A. T. M.; Frissen, A. E.; Weijnen, J. G. J. 'Resins and additives for powder coatings and alkyd paints, based on renewable resources' *J. Coat. Technol. Res.* **2007**, 4 (2), 177.

Noordover, B. A. J.; Van Staalduinen, V.G.; Duchateau, R.; Koning, C. E.; Van Benthem, R. A. T. M.; Mak, M.; Heise, A.; Frissen, A. E.; Van Haveren, J. 'Co- and terpolyesters based on isosorbide and succinic acid for coating applications: Synthesis and characterization' *Biomacromolecules* **2006**, 7 (12), 3406.

Noordover, B. A. J.; Sablong, R. J.; Duchateau, R.; Van Benthem, R. A. T. M.; Ming, W.; Koning, C. E.; Van Haveren, J. *patent application: Process for the production of a dianhydrohexitol based polyester*, EP07007979 to the Dutch Polymer Institute (filed in September **2006**).

Van der Schuur, J. M.; Noordover, B. A. J.; Gaymans, R. J. 'Polyurethane elastomers with amide chain extenders of uniform length' *Polymer* **2006**, 47 (4), 1091.*

Gaymans, R. J.; Van der Schuur, J. M.; Noordover, B. A. J. *Polyurethanes, polyurethaneureas and polyureas and use thereof,* WO2005068528 to the Dutch Polymer Institute (**2005**).*

The results concerning (powder) coating application of biobased polyesters (described in Chapters 2, 3 and 4) as well as the results related to biobased polycarbonates will be published as separate papers.

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* These publications did not result from the research described in this thesis.