Performance materials by a modular approach

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Table of Contents

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Chapter 1

General introduction

Abstract

There is a continuous search for polymeric materials with improved properties, preferentially prepared by cheap and simple methods. One possibility to cope with these developments is to couple functional linkable additives onto reactive end groups of polymers, to improve the properties of existing polymers or to prepare new polymeric materials.

In the simplest case linkable additives are solely used to couple polymer chains together. A number of such chain extenders is reviewed, whereas a new chain extender, Carbonyl BisCaprolactam (CBC), is described in detail within this work.

CBC enables, besides its use as chain extender, the preparation of functional blocked isocyanates (BIs), by reacting in a highly selective manner with amines. Similar reactions have been reported with other carbonic acid derivatives, but none of them exhibits a high selectivity.

Non-functional BIs are commonly used as crosslinkers in thermosetting resins, but functional BIs are hardly available. Functional BIs can be used for making functional coatings or complex monomers, such as rotaxanes, to prepare the corresponding polyrotaxanes.

1.1 Introduction

In the 1930es the first thermoplastic materials were discovered as a new class of materials to produce fibres, films and other useful products. The growth of these thermoplastic materials was tremendous, up to more than 50 million tons per year in the seventies, and approaching 175 million tons per year today. As time proceeded, specialty polymers of the thirties and later on of the fifties became commodities in the seventies[1]. Commodity polymers were particularly suited for applications at ambient or modestly enhanced temperatures, but in the mean time there was a growing need for plastic materials that could withstand more elevated temperatures. Many academic as well as industrial laboratories were searching for such high performance polymers, and consequently many interesting polymers were discovered. In the seventies quite a number of new high performance resins were commercially launched, such as LCP's (Liquid Crystalline Polymers), polysulfones, polyimides, polyetherimides and aromatic polyamides. At that time, polymers were roughly classified in three categories: a) commodity plastics, b) engineering plastics and c) high performance or specialty polymers. After an initial flood of new products, hardly any new commodity polymer or engineering plastic was introduced in the nineties (figure 1.1)[2].

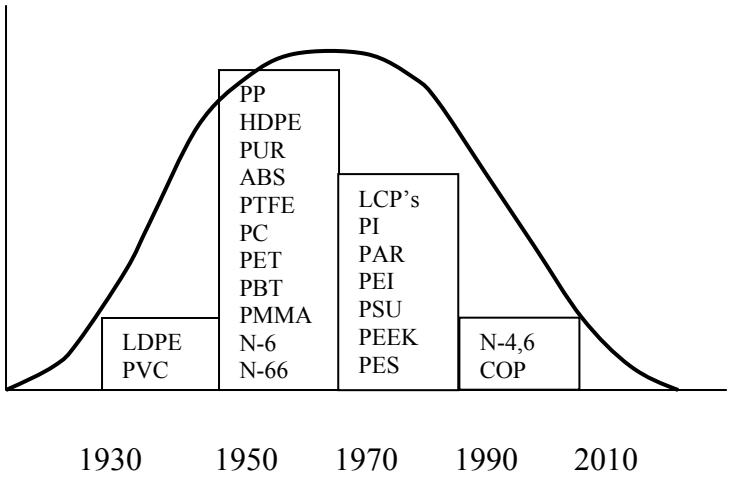


Figure 1.1: Schematic presentation of the introduction of new thermoplastic polymers based on new monomers in time (a non-comprehensive list).

Instead of introducing new polymers, many compounds and blends were developed, mainly based on existing materials[3]. Besides that, there was a growing interest in functional polymers with special optical, electrical, (bio)medical or surface properties. These polymers gained even more attention after the introduction of novel analytical tools, in the eighties, enabling to measure structures with nanometer size dimensions[4]. After that, the development of many

different polymers, with well-defined complex molecular nanostructures, grew steadily. Along with this, there was a growing need for methodologies to synthesise this diversity of new polymers in an economic and convenient way.

In this thesis the preparation of polymeric materials with well-defined molecular structures by using novel well-defined linkable additives was studied, with the objective to improve existing polymers as well as to make new ones.

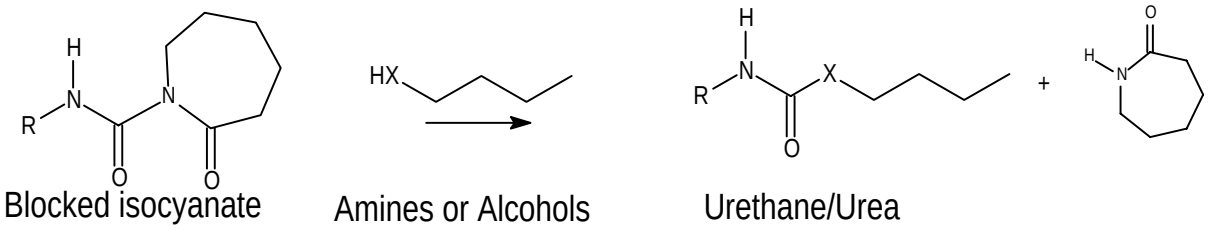
1.2 Linkable additives

1.2.1 Blocked isocyanates

A substantial part of this work is targeted on the development of general routes for making functional reactive additives that are able to link onto the hydroxy or amine end groups of polyesters, polyethers or polyamides.

In the simplest case these linkable additives are only able to couple polymer chains together, giving polymers with a higher molecular weight, and, consequently, with improved mechanical properties. This class of reactive additives (chain extenders) is discussed in paragraph 1.3.1. Amongst these, bislactams of terephthalic or isophthalic acid are the most interesting ones (no branching), and they were the inspiration to study the simplest member of that family, carbonyl biscaprolactam (CBC), in more detail. CBC is one of the many possible derivatives of carbonic acid, but it appears to be a very versatile one.

Besides its applicability as chain extender, CBC offers a new general methodology to make (functional) Blocked Isocyanates (BIs; carbamates). Isocyanates are one of the constituents of polyurethanes, which are well-known for their excellent properties. But isocyanates are difficult to handle due to their too high reactivity and toxicity. In contrast, blocked isocyanates could be an opportunity, because they have a reduced reactivity, but yield finally the same polymers. Blocked isocyanates are widely used in (thermosetting) coating applications[5], but so far hardly utilized in thermoplastic polymers. The blocking groups are only put on to reduce temporarily the reactivity of isocyanates. After the blocking group is removed, by heating, the isocyanate is liberated again and can subsequently react as usual with the hydroxy or amino end groups of polyesters, polyethers or polyamides, forming polyurethanes or polyurea, respectively (scheme 1.1).



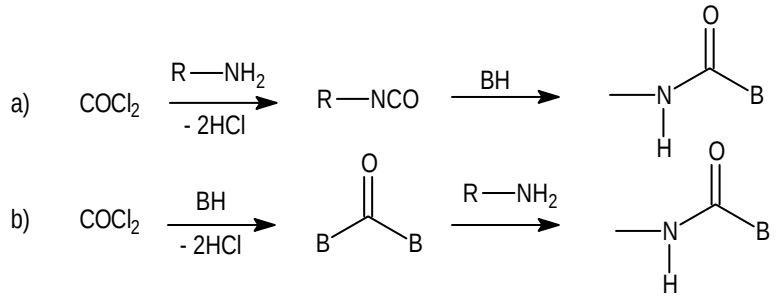
Scheme 1.1: The reaction of ε-caprolactam blocked isocyanates with hydroxy (X = O) or amino (X = NH) polymer end groups.

Blocked isocyanates are usually prepared from isocyanates, and the latter from primary amines and phosgene. This route is not always applicable because it requires special safety conditions, due to the high toxicity of phosgene. In laboratory quantities, isocyanates can be synthesised from triphosgene or tricarbonates[6].

Another method to make functional isocyanates is by reacting compounds, containing hydroxy or amino groups, with an excess of a diisocyanate. One of the isocyanate groups will react with the hydroxy or amino groups, whereas the second isocyanate group remains free. After the excess of the diisocyanate has been removed, this free isocyanate group can be blocked. This procedure is quite laborious, and only applicable for laboratory quantities. Moreover, this method is only feasible if the starting compound does not contain another group that can react with the isocyanate. Thus, BIs can be an opportunity to functionalise polymers, but a convenient method to make them is lacking up to now.

1.2.2 Blocked isocyanates from a retro synthetic point of view

The synthesis of (blocked) isocyanates (carbamates) is approached from a retro synthetic point of view. Conceptually it is conceivable to prepare BIs by making first a blocked isocyanate precursor group, and react this with amines to make in a one step procedure blocked isocyanates. This route circumvents the usual detour via isocyanates. Via this new route every amine-containing compound can be converted in one step into BIs. This procedure requires the availability of a suitable carbonic acid derivative as precursor compound (scheme 1.2). The reaction order as depicted in a) is the common way to make BIs. By changing the order of the consecutive reaction steps (scheme 1.2), the same end products can be made, but in route b) no free isocyanates are involved. In order to get a viable route b) several requirements, concerning reactivity and selectivity of the carbonic acid derivative, have to be fulfilled. The choice of compound BH plays a crucial role in that respect. The substitution of the first B unit must go much faster than that of the second B unit.



Scheme 1.2: a) Conventional route to blocked isocyanates and b) the reversed order option (BH is the blocking agent).

A number of such carbonic acid derivatives have been reported, of which carbonyl diimidazole (CDI) is the most well-known compound. CDI is able to react in good yields along route b), but only with amines with a reduced reactivity[7]. The reactivity of CDI is too high to make blocked isocyanates with ordinary primary amines. In that case the second imidazole ring is substituted as well, yielding ureas. Triphosgene (bis(trichloromethyl) carbonate) yields blocked isocyanates with some amines (with reduced reactivity) by a selective substitution of only one of the trichloromethanol groups[8]. The reactivity of this compound is also too high for primary amines, resulting, consequently, in ureas. Diphenyl carbonate is readily available, but shows only a limited selectivity towards amines[9]. Several other more exotic derivatives of carbonic acid have been mentioned in the literature[10], but only with one of these Katritzky investigated the selectivity with amines. In that case 1,1'-carbonyl bisbenzotriazole was tested, and that compound gave the corresponding blocked isocyanate in rather high yields (70-85 wt%).

Here, in this work, the reactivity and selectivity of carbonyl biscaprolactam (BH in figure 1.2 is ε-caprolactam) with amines is studied, making (caprolactam) blocked isocyanates from amines. It was additionally found that alcohols could give BIs by a ring opening reaction, which had not been reported with the other carbonic acid derivatives. Quite a number of linkable additives have been prepared from CBC, and the applicability of some of them was demonstrated in three different case studies. In a first case CBC itself was tested as chain extender for polyesters and nylons. In a second case blocked isocyanates were prepared and utilised for the manufacturing of specialty coatings. Finally in the last study polyrotaxanes were synthesized, in which CBC played a crucial role in the preparation of rotaxane monomers.

1.3 Chain extension

High molecular weight polycondensates are currently prepared by a solid-state post-condensation process (SSP). Reactive extrusion could be a more convenient alternative way to make these polymers. Reactive processing is in particular well developed for polyolefins, but not for polycondensates. The chemistry that is used to modify polyolefins results in ill-defined mixtures of polymers[11]. The polyolefins are modified in a random way because of the lack of groups with a discernible reactivity. Polycondensates however, such as polyethers, polyesters and polyamides, do have well-defined reactive end groups (OH, NH_2, COOH), which make it possible to change their properties in a more controlled way.

Chain extension is common practice in polyurethanes, but hardly used in polyesters or polyamides, probably because of the higher processing temperatures. At these temperatures there is a considerable risk for side reactions (branching), because of the necessarily high reactivity of chain extenders.

Quite a number of chain extenders for polyesters and nylons have been reported. Diphenyl carbonate[12] reacts fast with hydroxy and amino end groups and increases the viscosity within a short time, without branching. Nevertheless this compound is not acceptable for industrial applications, because of the emission of phenol (toxicity and stench). Bisoxazolines[13] look very attractive, since they do not produce volatiles, while reacting with carboxylic acids. But, their reactivity is too low to be useful in reactive extrusion (1 – 3 min). 2,2'-Bisoxazoline is an exception within this family, but is not commercially used, probably due to its moisture sensitivity[14]. Bisepoxides[15] are commercially readily available products and they do not produce volatiles in their reaction with carboxylic groups, but they give only minor increases in viscosity during the processing step. Diisocyanates[16] are cheap, and give a very fast increase of the molecular weight during reactive processing. Unfortunately, isocyanates are toxic and can give many side reactions. Tris-caprolactam[17] and tri-esters[18] of phosphorous acid are described as chain extenders. Unlike other chain extenders, they promote the ester or amide formation by consuming the condensation water, forming phosphorous acid as a side product. Free phosphorous acid is a disadvantage, because it is a catalyst for the hydrolytic degradation. Bisketene imines[19] are described as suitable chain extenders, but their toxicity and colour make them hardly useful. Dianhydrides[20], like pyromellitic dianhydride (PMDA), give a fast increase in molecular weight with polyesters. In the first reaction step an ester-acid is formed and the acid groups will continue to react, giving branched polymers. PMDA is in fact a four functional acid. Fardet et al.[21] described the coupling of polymer chains with bis-oxazolinones. These chemicals are only suitable if the processing temperature is not too high

(200 ^{o}C), because of their limited thermal stability. They obtained good results with nylon-11 or -12, because of the low processing (melting) temperatures of these polymers. Dicyanates[22] react too slowly, particularly with polyesters, to be useful under practical conditions. Finally, among all the chain extenders that have been described in literature, aromatic bislactams[23] were perhaps the best (no branching), and they were therefore the inspiration for this work.

1.4 Functional coatings

Coatings formed the second class of materials for which the applicability of linkable additives was studied. Coatings are already blends of reactive oligomers and low molecular weight reactive additives (crosslinkers), and thus the addition of other linkable additives can easily be done in practice. The most important reasons for using coatings is to protect substrates against environmental influences and to make a product, from an aesthetic point of view, more appealing[24]. But, there is a growing interest in functional coatings, whereby additional properties are incorporated. The surface of products determines to a large extent the performance of the whole product.

In this work functional additives are prepared, and used for making self-crosslinkable coatings and coatings with a low surface energy. Self-crosslinkable coatings are one-component systems that are stable at room temperature, but will give a fast crosslinking reaction on heating, without adding a crosslinking agent. The addition of crosslinkers to coating resins requires an additional processing step, and can give compatibility problems. Furthermore, built-in crosslinkers are also preferred from an environmental point of view because they are not able to evaporate or to leach out (toxicity). Poly(meth)acrylates, with BIs as crosslinkers, are widely used in coating resins for two component systems. One component self-crosslinkable poly(meth)acrylate coating resins containing hydroxy functional (meth)acrylates and blocked isocyanate functional (meth)acrylates, have been reported[25]. These polymers are prepared by ordinary radical polymerisation procedures at about 100 ^{o}C. At that temperature blocked isocyanates do not react with hydroxy groups. On heating the coating above 140 ^{o}C, the deblocking of the blocked isocyanate starts and, consequently, crosslinking takes place. Isocyanate functional (meth)acrylates are commercially available, but very expensive, due to a cumbersome synthesis[26]. The possibility to make blocked isocyanates via the reversed order route (1.2.2.) may provide a more convenient method to make these interesting monomers in a cheap way.

Coatings with low surface energies are known to have a low dirt take-up (anti-fouling). Fluorine containing polymers, such as Teflon, possess low surface energies, and exhibit,

consequently, anti-fouling properties. Since the surface energy is only dependent on the composition of the top layer, there is no need to have the expensive fluorine present in the bulk. One possibility to create a high concentration of low surface energy compounds at the surface of coatings is by self-stratification. Self-stratification is a process in which a gradient arises due to a partial de-mixing process of a blend. De-mixing is driven by the differences in surface tension of the compounds in the mixture. The kinetics of this process depend, amongst other parameters, on the molecular weight of the compounds. Lower molecular weight products diffuse faster than high molecular weight compounds.

A number of authors have reported the preparation of coatings with a low surface energy by mixing resins with and without fluorine, and showed that coatings with low surface energy were obtained[27]. Here in this work, coatings containing low molecular weight, fluorine containing, blocked isocyanates were prepared and tested.

1.5 Polyrotaxanes

Complex polymers, such as polyrotaxanes, were selected to investigate the scope and limitations of the new methodology to make linkable additives. The target was to prepare rotaxane monomers, containing blocked isocyanates as reactive bulky stopper groups, and to use these monomers to make polyrotaxanes. Rotaxanes are compounds in which a macrocyclic component circumscribes a linear thread molecule to which the macrocycle is not covalently attached and is therefore free to spin or to shuttle up and down along the thread. Bulky stopper groups at either end of the thread provide steric hindrance to prevent the macrocycle from falling off. If the polymer chain does not contain blocking groups, to prevent the macrocycle falling off, these materials are pseudo-polyrotaxanes. So far polyrotaxanes have been prepared by threading polymers with macrocyclic compounds in solution, or by making the polymer threads in the presence of macrocycles[28]. In these cases polyrotaxanes are prepared in a statistical way, with no control on the number and location of the macrocycles along the thread. To get a better control on the structure of polyrotaxanes, complementary complexing units have been built-in in the polymer and in the macrocycle. For that purpose hydrophobic-hydrophilic interactions, hydrogen bonds, π-π stacking and metal templates are used. Although this has improved the extent of control, this approach still gives a statistical distribution of the macrocycles along the polymer thread.

There was still a lack of methods to make well-defined rotaxane monomers with blocking groups that prevents dethreading, and to convert them into corresponding polyrotaxanes.

1.6 The aim of this thesis: The synthesis of performance materials by a modular approach

The prime objective of this work was to develop an enabling technology to synthesise a whole family of linkable additives, containing moieties with special properties. These additives are designed to react in a fast and controlled way with hydroxy or amino end groups of polyesters, polyethers or polyamides. These linkable additives are used to add new properties to existing polymers or coatings, and to make novel polymeric materials. This modular approach concept is schematically depicted in figure 1.2.

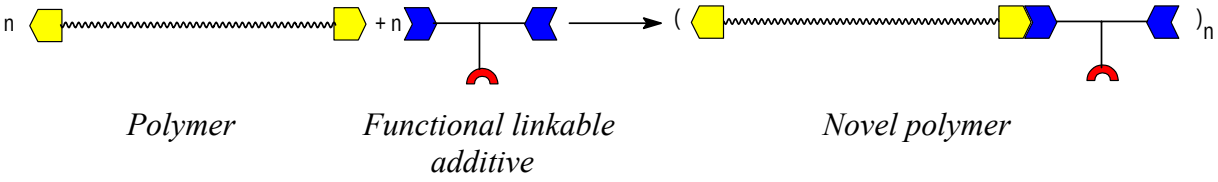


Figure 1.2: Schematic representation of the modular approach for making performance materials with special properties.

1.7 Outline of this thesis

A large part of this work is based on the unique properties of 1-[(2-oxo-1-azepanyl)carbonyl]-2-azepanone (Carbonyl BisCaprolactam, CBC, ALLINCO®; figure 1.3). It will be shown that this simple molecule, consisting of two caprolactam rings bridged by a carbonyl moiety, is very versatile, and offers many possibilities to make a whole range of linkable additives.

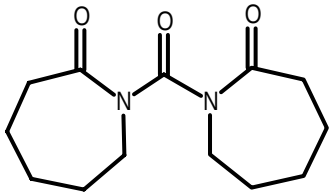


Figure 1.3:1-[(2-oxo-1-azepanyl)carbonyl]-2-azepanone or Carbonyl BisCaprolactam (CBC)

To obtain more information on the chemistry of hydroxy functional compounds with CBC, model reactions were carried out with low molecular weight alcohols. Along with this, the influence was studied of a large number of catalysts on the reaction rate as well as on the reaction pathway (*chapter 2).*

In *chapter 3* the applicability of CBC as chain extender for polyesters and polyamides is described. Chain extension is an alternative method for the laborious and expensive Solid-State Post-condensation process (SSP). The objective is to make polymers with the same

range of viscosities and the same performance as can be obtained via the SSP process, by adding small amounts of CBC during the final processing step.

Chain extension is a two-step process, in which the reactive intermediates of the first step react for a second time, giving coupled products. In *chapter 4* it is described how these reactive intermediates of this first step are isolated. This offers an enabling technology to make blocked isocyanates (caprolactam carbamates) in one step from amines. It will be shown that a ring opening reaction of the first caprolactam ring of CBC by alcohols yields also blocked isocyanates.

Chapter 5 describes the double selectivity of the reaction of CBC with amino alcohols or with compounds comprising primary and secondary amino groups. As a result, this method offers the possibility to prepare BIs, still having a free hydroxy or amino group, which can be used to make functional BIs.

Chapter 6 describes the preparation of coatings with special properties by using blocked isocyanates with special moieties. In one example the preparation of coatings with a low surface tension is studied. In another example the use of functional BIs is demonstrated by preparing self-crosslinkable poly(meth)acrylate coatings.

Finally in *chapter 7* the strength and versatility of this methodology, to make functional BIs, is further explored, by making sophisticated polymers like polyrotaxanes. This route resulted in a novel methodology to synthesize polyrotaxanes.

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Model reactions of alcohols and acids with CBC, in the presence of catalysts

Abstract

Carbonyl biscaprolactam (CBC) is a new chemical that is used for increasing the molecular weight of polycondensates during reactive extrusion (chapter3). Model reactions were carried out to get more detailed information on the chemistry of these reactions and on the possibility to catalyse them. The screening of a large number of catalysts is more convenient with model compounds than with polymers. Ethylene glycol monobenzoate was selected as one of the model compounds to mimic poly(ethylene terephthalate).

More than sixty catalysts were tested at 175, 200 and 275 ^{o}C and quite a number are able to enhance the reaction rate considerably. The best results are obtained with $MgBr_2$, $Ti(OR)_4$, $Zr(OR)_4$ and $Zr(acac)_4$, which are subsequently tested in poly(ethylene glycol terephthalate) (chapter 3).

The analysis, of the linking units in the reaction products of the model alcohols with CBC, reveals that the urethane bond is the main linkage (one ring opens, one is substituted).

2.1 Introduction

2.1.1 Mimicking chain extension processes of polyesters by model reactions of alcohols with carbonyl biscaprolactam (CBC)

Chain extension is an emerging technology to prepare high molecular weight polycondensates by a chemical coupling reaction, during a reactive extrusion step. Chain extension comprises a physical (mixing) and a chemical process, and both require a certain residence time. The total residence time in extruders is about ten minutes in some commercial processes (spinning lines), which is more than enough to finish the coupling reactions. In other processes such as extrusion or injection moulding, however, residence times are often about one minute, or sometimes even less.

CBC is a new chain extender that reacts fast with the amino end groups of nylons, so that the coupling reaction is finished within one minute. But the reaction of CBC with hydroxy end groups of polyesters takes about three minutes (*chapter 3*). In order to realize an economically feasible process, it was necessary to carry out a study on the influence of catalysts on the reaction rate of hydroxy functional compounds and CBC. Since no information was available on that reaction, it was not predictable whether this reaction could be catalysed at all.

Model reactions seemed the best way to screen within a short time a large number of catalysts. However, these results have to be handled with care, since model experiments will give only a definite answer on the chemistry of the reactions, and not on the chain extension process in an extruder, because then physical parameter will play a very important role as well. The results have to be reproduced and verified under extruder conditions *(chapter 3)*.

An additional advantage of model reaction is that the products can be characterized in a reliable way. The amount of chain extender applied in polymers will always be less than 1 wt%. This makes it extremely difficult to obtain reliable information on the chemistry, since the concentration of the newly formed chemical bonds is too low to be analysed properly. Thus, the reactions with low molecular weight alcohols and CBC will also provide information on the nature of the chemical linkage.

2.1.2 Literature on CBC

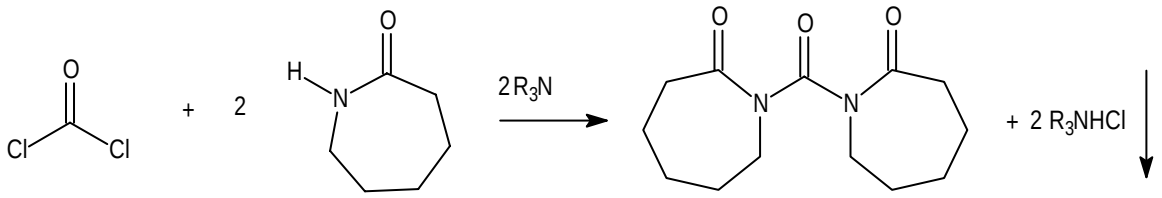
The number of publications and patents on CBC was rather limited, and consequently little or no information on the chemistry of CBC with polyesters or nylons was available. Meyer[1], who was the first to mention CBC in the literature (in 1956), described its preparation from caprolactam and phosgene (scheme 2.1). If no catalyst was used hardly any CBC was formed. By replacing caprolactam by the sodium salt of caprolactam, the yield of CBC improved

considerably (from 0.6 to 40 %). This paper also describes the preparation of polymers by reacting CBC with diamines. However, unfortunately, little information is given on the chemistry, on the nature of the polymeric products and on their characterisation. Okada[2] et al. filed a patent on the preparation of CBC (in 1965), in which they described an improved preparation procedure. The yield of CBC was increased if the reaction of caprolactam with phosgene was done in the presence of a tertiary amine. In this patent, again, no information is given on the chemistry of CBC. Nagai et al.[3] filed a patent on the applicability of compounds such as CBC, as accelerator for the anionic polymerisation of caprolactam. Monsanto filed some patents[4] on a similar topic in which they claim the use of a whole list of N-acyl lactams, amongst which CBC, as an accelerator for the anionic polymerisation of lactams and copolymers of lactams and lactones. It was Mateva[5] et al. who actually showed that CBC could successfully be used as accelerator in the anionic polymerisation of caprolactam. A few methods were reported to improve the preparation of CBC from phosgene and caprolactam, mainly by replacing triethyl amine by more appropriate tertiary amines as acid scavengers[6,7]. Some patents were filed in which the use of a large number of N-acyl lactams was claimed, amongst which CBC, as accelerator for bleaching agents in detergents[8]. From 1999 until 2003, S. Maier performed his PhD study on the applications of CBC[9]. Our investigations on CBC started in 1998 and have been documented extensively[10].

Only the earlier mentioned publication of Meyer[1] gave some information on the chemistry of CBC with amines, but no information was available on the reaction of CBC with alcohols, nor on the influence of catalysts.

2.1.3 Synthesis of carbonyl biscaprolactam

The publication of Meyer contained hardly any information on the synthesis of carbonyl biscaprolactam (CBC)[1], but Okuda et al. gave a more detailed description in their patent[2] (scheme 2.1).



Scheme 2.1: Preparation of carbonyl biscaprolactam from phosgene and caprolactam.

Their procedure to make CBC starts by dosing a solution of phosgene in benzene into a solution of caprolactam in the presence of triethyl amine (as acid scavenger) in benzene. After the triethyl amine-HCl precipitate had been filtered off, the solution was washed several times with water to remove the excess of phosgene, HCl, caprolactam and triethyl amine, and finally the solvent was evaporated to collect CBC.

CBC was, at the start of this study, not commercially available, and therefore the preparation was studied on small as well as on large scale[10]. On a small scale CBC has successfully been made from caprolactam and triphosgene. Nevertheless, all the work throughout this thesis was carried out with the commercial CBC from DSM (purity > 99%), which became in the mean time available, and was used without further purification.

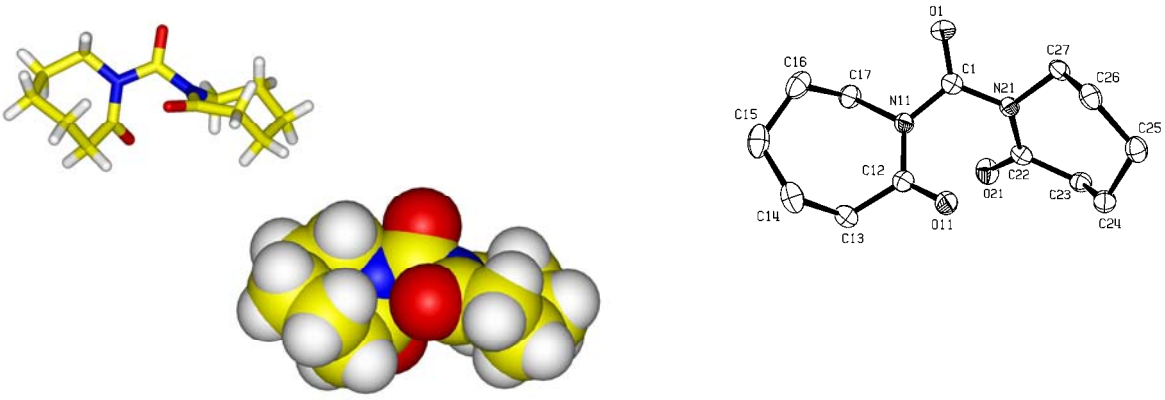


Figure 2.1: Molecular model (left and middle) and the crystal structure (right) of carbonyl biscaprolactam.

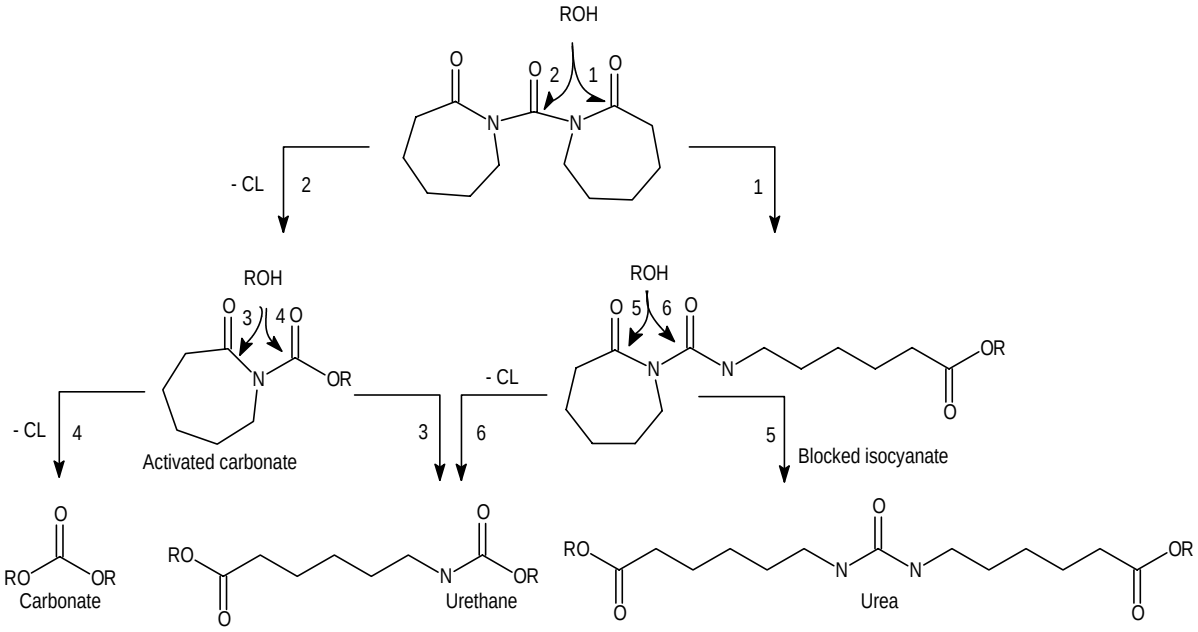
CBC is a white, freely flowing powder with a melting point of 115 ^{o}C. The crystal structure of this compound (figure 2.1) reveals that the three carbonyl groups are organized in a helical way, in which all three carbonyl groups are accessible for a nucleophilic attack. This is important, as will be shown later on, since under certain conditions the central carbonyl group is attacked, while under other conditions the carbonyl groups of the caprolactam rings are targeted.

2.2 Chemistry of carbonyl biscaprolactam with alcohols

2.2.1 Possible reaction pathway

In *chapter 3* it will be shown that CBC is suitable as a chain extender for polycondensates. Chain extension reactions imply the occurrence of two consecutive steps. First one polymer chain has to react with CBC, giving a reactive intermediate, which then subsequently reacts

with another polymer chain end. In scheme 2.2 a possible reaction scheme for the chemistry of alcohols with CBC is depicted.



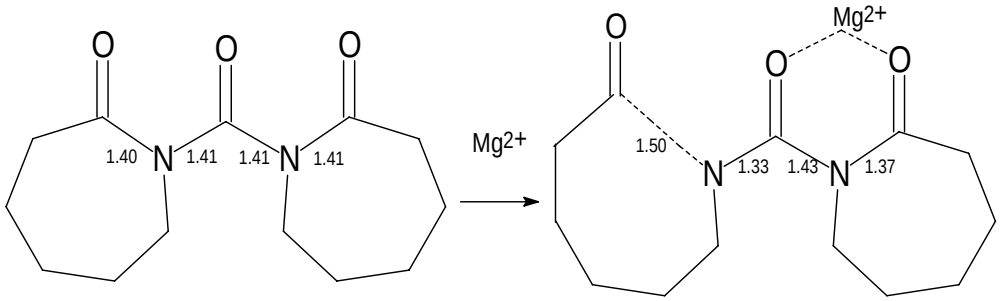
Scheme 2.2: Theoretically possible reactions of alcohols with CBC (CL = ε-caprolactam)

The nucleophilic attack of an alcohol group can take place either on the central carbonyl group or on one of the carbonyl groups of (one of) the caprolactam rings. The carbonyl groups of both caprolactam rings are of course identical (figure 2.1). The reactive intermediates are formed either by substitution or by opening of one of the caprolactam rings. More detailed information on these intermediates is given in *chapter 4*. These reactive intermediates (carbamates (= blocked isocyanates) and/or activated carbonates) will react under the polymer processing conditions -above 150 ^{o}C- in a consecutive step forming carbonates, and/or urethanes and/or ureas. By analysis of the reaction products in model systems more information will be obtained on the reaction path during the chain extension reaction of polyesters.

2.2.2 Molecular modelling

To obtain a better understanding of the possible influence of catalysts on the alcohol-CBC reaction, some molecular modelling calculations were carried out. These calculations[11] revealed (scheme 2.3) that the coordination of two carbonyl groups of CBC with metal ions (in the given example Mg^{2+}) is energetically favourable. The central carbonyl group and one of the ring carbonyl groups operate as a bi-dental ligand and form a complex with the metal ion. According to the calculations the carbon-nitrogen bond length in the second, non-

complexed caprolactam ring is enlarged from 1.41Å to 1.50 Å, suggesting that this bond is weakened.



Scheme 2.3: The calculated atom-atom distances (in Å*) in the complex of CBC with Mg^{2+} ions.*

Due to this weakening it is reasonable to expect that this caprolactam ring is more reactive, meaning that ring opening will be promoted. Thus these results indicate that the catalyst may have an influence on reaction rate as well as on the reaction pathway between CBC and alcohols, leading consequently to other reaction products.

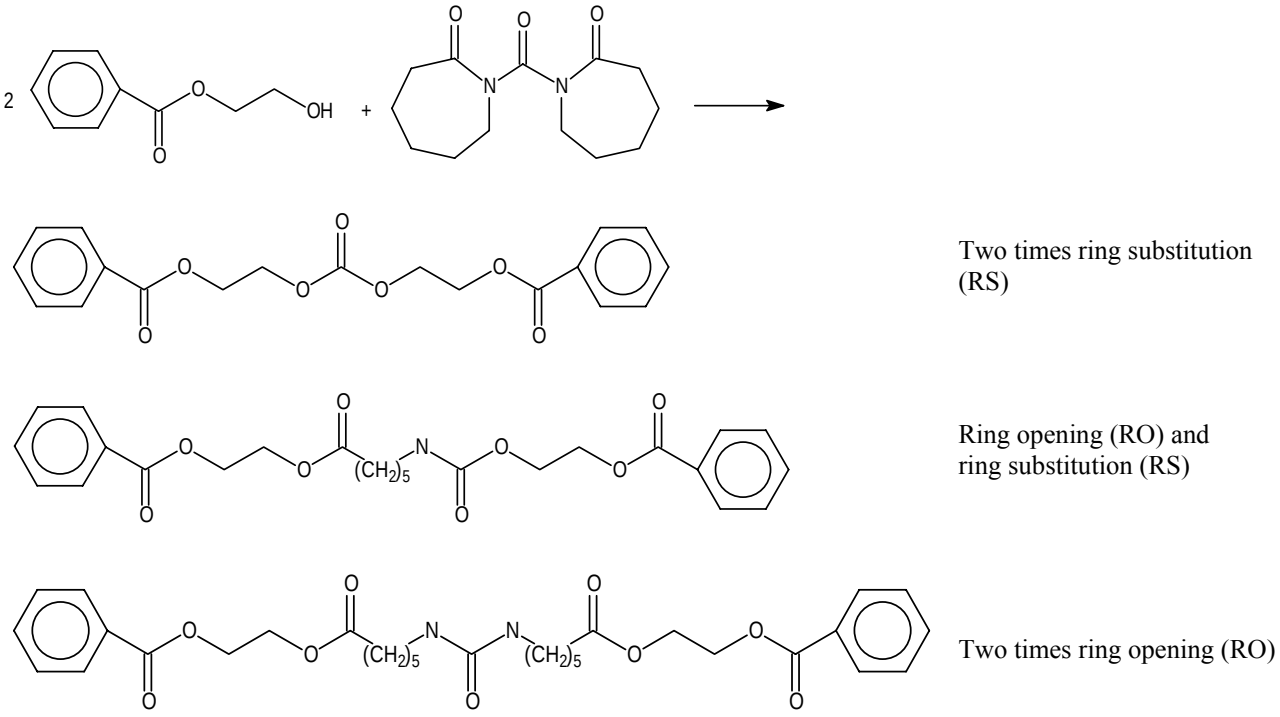
2.3 Model reaction of Ethylene Glycol Mono Benzoate (EGMB) with CBC at 175 ^{o}C

In the first series of experiments EGMB was chosen as a (high boiling) model compound to mimic the end groups of hydroxy functional aromatic polyesters, particularly of PET. The reactions with CBC were carried out in propylene carbonate as a polar non-reactive diluent to mimic a polyester environment.

This first series only aimed at a rough screening of a large number of catalysts to see if they had any effect at all and, if so, to rank them in order of efficiency with respect to the conversion rate of the reactants. Each experiment (see appendix 2.1) was carried out only once, and, consequently, the results are only indicative.

In a typical experiment 2 equivalents of EGMB and 1 equivalent of CBC, in the presence of 1 wt% of a catalyst (with respect to CBC) were heated at 175 ^{o}C in propylene carbonate for 10 minutes. The reaction temperature was lower than during PET processing in an extruder, but it enabled us to work in open vessels under atmospheric pressure. The concentration of the hydroxy groups was 500 mmol/l, which is about 10 times higher than in the corresponding polymer system. This high concentration is necessary to be able to perform reliable analysis of the reaction mixtures. After the heating, the reaction mixture was quickly cooled down and the concentrations of CBC, EGMB and caprolactam (formed during the reaction) in the

mixture were measured with HPLC. The possible reaction products are depicted in scheme 2.4, supposing that the reaction between EGMB and CBC goes to completion.
More than fifty-five catalysts were tested and the results are compiled in the table in appendix 2.1 (at the end of this chapter). Basically, most catalysts were selected from the group of metal salts (transition and non-transition metals), since the calculations predicted an influence of metal ions. A few strong acids and bases were tested as well for comparison. It was found that many of the catalysts that were tested have a considerable activating effect on this model reaction.



Scheme 2.4: Possible products of the reaction of 2 moles of ethylene glycol monobenzoate with 1 mole of CBC, if the reaction goes to completion (caprolactam is not depicted).

In appendix 2.1 all the results are given, ordered with increasing conversion of EGMB. To make the results more surveyable a smaller table (table 2.1) is extracted from appendix 2.1, in which only the experiments are given with EGMB conversions higher than 50 %. In columns 3, 4 and 5 (table 2.1) the analytical data of the concentrations of EGMB, CBC and caprolactam, respectively, are given. In column 6 the calculated value of caprolactam is given supposing that all consumed EGMB reacts only by substituting caprolactam and that no ring opening (RO) takes place (which is actually not the case). In all cases less caprolactam is formed than calculated, suggesting that the rest of the caprolactam rings is opened. In column 7 the percentage ring opening is calculated from the amount of caprolactam that was actually

formed and the amount of caprolactam that could be formed, if only substitution had taken place.

The conversion of CBC is always higher (except with DBU (= 1,8-diazabicyclo-[5.4.0]undec-7-ene)) than that of EGMB, as expected, since two moles of EGMB per mole CBC were used, whereas only one mole of EGMB can already consume all CBC. The conversion of CBC is complete when the best catalysts are used, whereas only 21 to 24 % is converted without using catalysts, which demonstrates the large effect of catalysts. The fact that with DBU as catalyst the EGMB conversion is higher than that of CBC indicated that in this experiment also other reactions take place (see below) than those given in scheme 2.4.

Table 2.1: HPLC results of the reaction mixture of EGMB with CBC after 10 minutes at 175 ^{o}C, with conversions of EGMB higher than 50 %.

Sample	Catalyst [1]	Conversion EGMB [2] (%)	Conversion CBC [2] (%)	Caprolactam Measured (wt%)	Caprolactam Calculated [3] (wt%)	RO (Ring opening) [4] (%)
1a	Non	9.5	21	0.45	0.61	26
1b	Non	9.0	24	0.45	0.58	22
2	$MgCl_2$	58	94	2.1	3.8	45
3	Li(t-OBu)	66	100	2.8	5.4	48
4	$Ti(OiPO)_4$	75	100	3.3	4.8	31
5	DABCO	75	78	2.1	4.8	56
6	DBU	75	60	0.7	4.7	85
7	$TiCl_3$	77	99	2.5	4.9	49
8	$Ti(OBu)_4$	84	100	4.1	5.4	24
9	LiCl	85	93	2.3	4.2	45
10	LiOEt	91	100	3.3	5.9	44
11	NaOEt	95	95	3.4	6.1	44

[1] 1 wt % of catalyst with respect to CBC; DABCO = 1,4-diazabicyclo[2,2,2] octane, DBU = 1,8-diazabicyclo[5,4,0] undec-7-ene.
[2] Percentage with respect to the starting amount of material.
[3] The calculated wt% of caprolactam in the mixture is based on the conversion of EGMB, supposing that only ring substitution takes place.
[4] The percentage of RO (ring opening) is calculated according to the formula: $[(\text{Caprolactam}_{\text{calculated}} - \text{caprolactam}_{\text{measured}})/\text{caprolactam}_{\text{calculated}}]*100\%$.

The results given in table 2.1 have to be handled with care, since some of the assumptions are not fully correct. For instance, if some caprolactam is converted into nylon-6 oligomers then it is wrongly interpreted as having been incorporated into the end product and addressed as a ring opening reaction. Another point of concern is that EGMB can react with itself and form ethylene glycol dibenzoate and ethylene glycol. If that takes place the assumed conversion of

EGMB is overestimated. This latter reaction could for instance explain why the conversion of EGMB is higher than that of CBC in the presence of DBU.

Nevertheless, the results are useful and some important preliminary conclusions can be drawn. The most important one is that catalysts have a profound influence on the conversion of EGMB and CBC. It can be seen that the reaction rate is much higher in the presence of catalysts, yielding a complete conversion of CBC in 10 minutes, whereas without catalysts this is only about 23 %. This is extremely important since the aim was to find catalysts that reduce substantially the residence time in extruders. It has, of course, still to be verified whether similar results can be obtained with polymers in extruders, but the effect on the chemistry (at 175 ^{o}C) has been demonstrated. Catalysts seem to promote the ring opening reaction, since without them (sample 1a and b) the extent of the ring opening is significantly lower. This is very important as well, since this implies that, in the presence of catalyst, less caprolactam is formed during the chain extension reaction, resulting in a lower emission of volatile organic compounds (VOC). Moreover, thanks to the presence of a catalyst, more urethane or urea bonds are formed and less carbonates. Urethanes and ureas exhibit a better hydrolytic stability than carbonates and are therefore preferred.

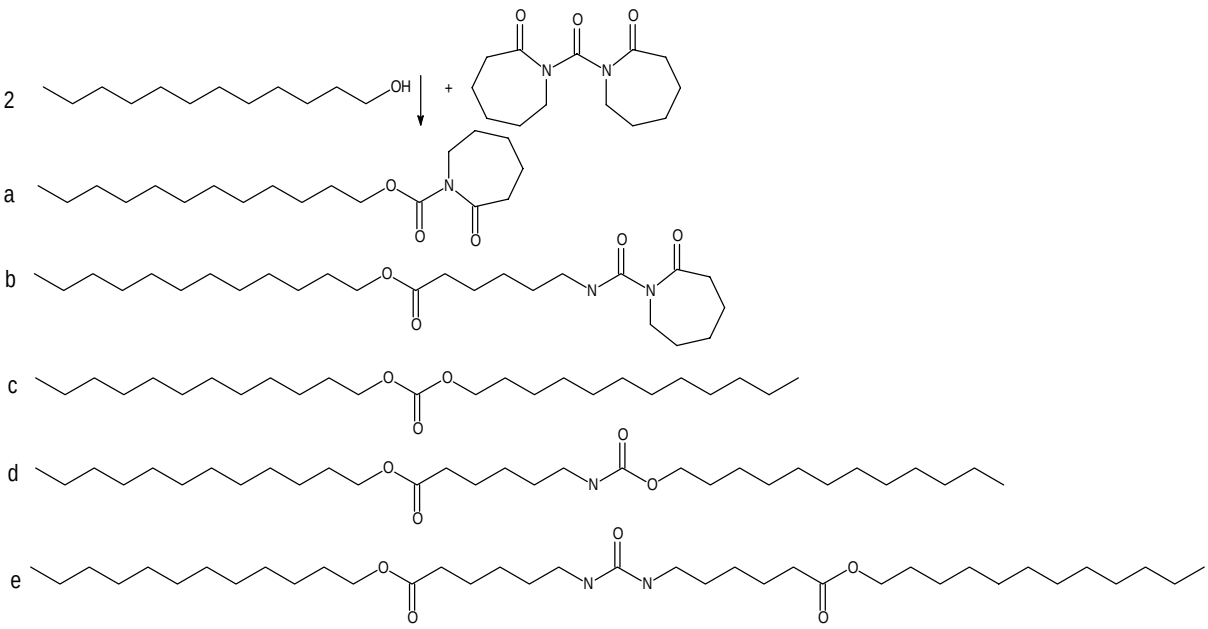
The results of this series of screening experiments, although valuable, are not fully conclusive, since no analysis was made of the actual structure of the reaction products. Therefore a second series of experiments was carried out to get more information on the products.

2.4 Model reactions of n-dodecanol and carbonyl biscaprolactam at 200 ^{o}C

In a second series of experiments reactions were carried out at 200 ^{o}C with CBC and n-dodecanol (mol ratio 1:2) to mimic polyesters. In this case no diluent was used to get a higher concentration of the end products in order to improve the reliability of the analysis. To study the influence of various catalysts, on the conversion of the starting compounds and on the formation of products, the reaction mixtures were analysed by SEC (size exclusion chromatography). The SEC apparatus was equipped with columns that were suitable to detect low molecular weight compounds. To calibrate the SEC equipment one reaction mixture was separated by column chromatography and the major reaction products were identified by ^{1}H-NMR. Two reaction mixtures (one with and one without catalyst) were analysed by LC-MS and the results revealed the compounds (molecular weights) that were present in the mixture. Also this information was used to assign the peaks in the SEC chromatograms. In scheme 2.5 all five expected reaction products are depicted: two reactive intermediate products (activated

carbonate (a) and blocked isocyanates (b)) and the three end products (carbonate (c), urethane (d) and urea (e)). They were all actually detected in the LC-MS.

In a typical experiment n-dodecanol and CBC (in a molar ratio of 2:1) were heated in bulk at 200 ^{o}C for 10 minutes in the presence of one of the catalysts (1 wt% with respect to the total mixture).



Scheme 2.5: The expected products of the reaction of n-dodecanol with CBC (10 min, at 200 ^{o}C in bulk).

In this series 22 catalysts were investigated: LiCl, Li-versatate, NaCl, NaOEt, NaOH, $MgBr_2$, $MgCl_2$, $MgSO_4$, $CaCl_2$, $SrCl_2$, $ScCl_3$, Ti(n-BuO)$_4$, Zr(acac)$_4$, Zr(n-BuO)$_4$, Zr(t-BuO)$_4$, Fe(acac)$_3$, VO(OiPr)$_3$, $ZnCl_2$, Zn(acac)$_2$, $SnCl_4$, DABCO (1,4-diazabicyclo[2,2,2] octane) and p-toluene sulfonic acid. Some of these catalysts were also investigated in the first series and some were new. After the reaction at 200 ^{o}C, the mixture was cooled down quickly and the composition was analysed by SEC. In figure 2.2 a typical SEC chromatogram is shown of the products from the reaction of n-dodecanol and CBC, with and without catalyst. It can be seen that the composition of the products with and without catalyst differs considerably. The carbonate and activated carbonate, both present in the reaction mixture without a catalyst, were practically absent in the presence of a catalyst.

In table 2.2 the analytical data of the reactions with most interesting catalysts are given. Five reaction products, a, b, c, d and e of scheme 2.5, being two intermediates and three end products, may be present. However, the activated carbonate (a in scheme 2.5), was not detected anymore if catalysts were used, because it probably immediately reacts further to

form a carbonate. The concentration of the second reactive intermediate, the blocked isocyanate (b in scheme 2.5), is low as well, but still detectable. Thus, in the presence of catalysts four of the five expected products are determined, meaning that scheme 2.5 looks valid.

Quite a number of these catalysts yield high conversions, giving a lot of freedom to choose the best, taking other properties (colour, stability, etc.) into account as well.

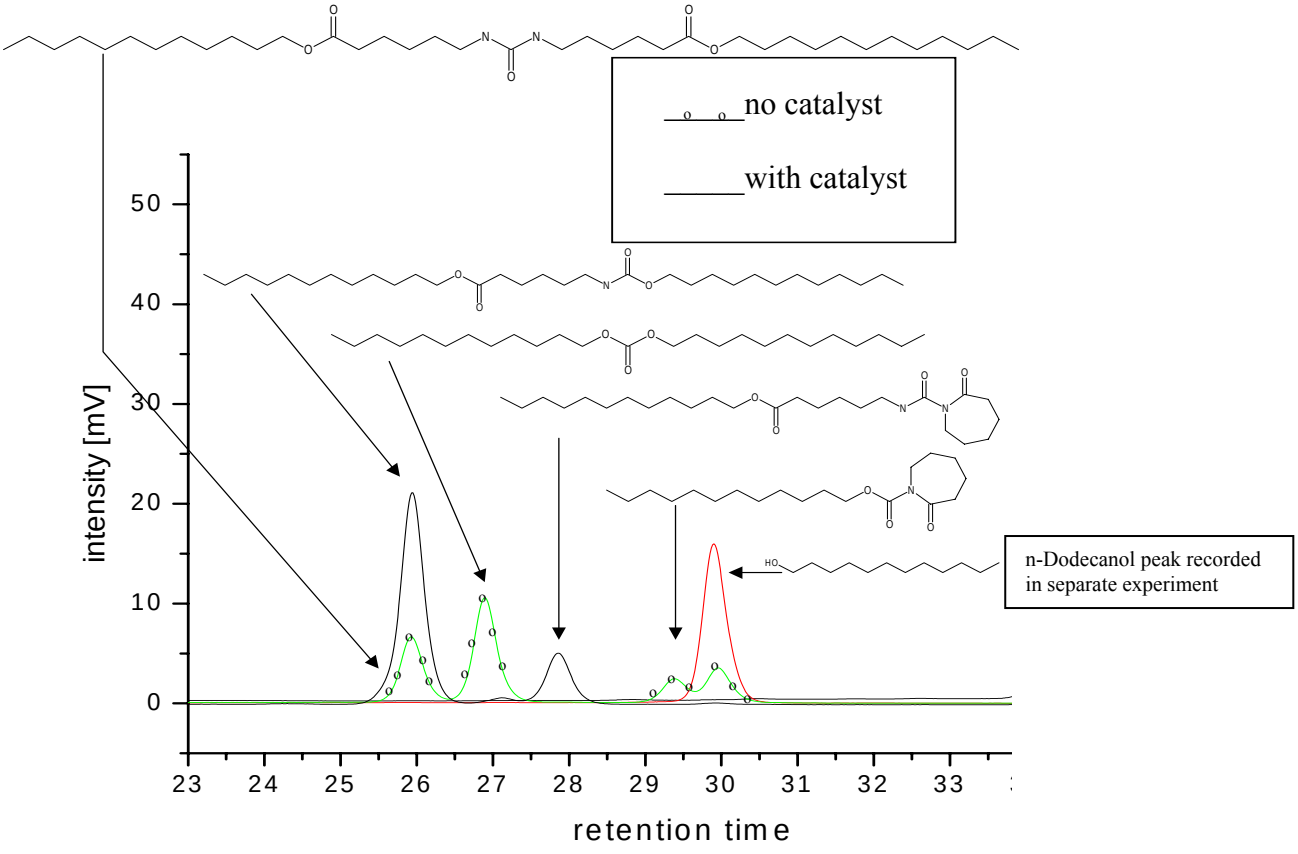


Figure 2.2: Typical SEC chromatogram of the reaction products of n-dodecanol and CBC after 10 min at 200 °C, with and without a catalyst. The urea peak (at 25.3 min) was not present in this sample.

$MgBr_2$, which gives a high conversion combined with a high yield of the desired urethane linkage, is one of the best catalysts tested in this series. The highest conversion is obtained with tetra-n-butoxy zirconate, which on the other hand yields the highest concentration of urea linkages. The compositions of the product mixtures, made with the various catalysts, are quite similar, giving mainly a urethane linkage. p-Toluene sulfonic acid (PTSA) is an exception, giving a very high yield of carbonate linkages. This is not preferred, because aliphatic carbonates have a lower thermal and hydrolytical stability than urethanes or urea's.

Many of the catalysts listed in table 2.2 can be used in polymers, if the linking unit is the section criteria, because the performance of polyesters, with either predominantly urethane linkages or with urethane linkages and small amounts of urea moieties, is expected to be quite similar.

Table 2.2: The relative composition of the products of the reaction between dodecanol and CBC after 10 minutes in bulk at 200 ^{o}C.

Catalyst[1)]	2 x RS [2)] (%) Carbonate	1 x RO + 1 x RS, (%)[2)] Urethane	2 x RO (%)[2)] Urea	1 x RO (%)[2)] BI	Total (%)
p-Toluene sulfonic acid	68	4	0	3	75
Li-versatate	8	71	0	5	84
Zr $(acac)_4$	5	76	7	5	93
$Zr(OBu)_4$	6	64	23	3	97
$Zr(t\text{-}Obu)_4$	6	65	23	3	96
$CaCl_2$	17	70	3	4	94
$Ti(OBu)_4$	6	53	20	4	83
$Zn(acac)_2$	13	72	0	2	87
$MgBr_2$	4	87	0	1	92
$MgCl_2$	2	76	16	1	95
$ScCl_3$	12	77	0	3	92
$SnCl_4$	13	75	0	2	90
Na(OEt)	7	70	8	8	93

[1)] 1 wt% of catalyst with respect to the whole mixture. [2)] RS = ring substitution, RO = ring opening, BI = blocked isocyanate. The % is calculated from the peak area in the SEC chromatogram (UV detection).

It can be concluded that, under the given conditions and in the presence of these catalysts, the reactions are nearly complete in 10 minutes at 200 ^{o}C, because hardly any intermediate product was detected in the reaction mixture. Quite a number of catalysts have a pronounced influence on both the reactivity and the composition of the reaction mixture. The urethane moiety (1xRO + 1xRS) is the main linkage in all these products, and this is in good agreement with the results of the first series, making both series more reliable.

The temperatures applied (175 and 200 ^{o}C) are still far away from extruder conditions (300 ^{o}C). The experimental procedure applied in these first two series could not be used at higher temperatures, since the reactants would evaporate under atmospheric pressure. In order to obtain results at temperatures closer to extruder conditions, some experiments were carried out at 275 ^{o}C in small high-pressure autoclaves.

2.5 Model reactions of ethylene glycol monobenzoate (EGMB) with carbonyl biscaprolactam at 275 °C

In this series of experiments we again took EGMB as model compound in order to simulate the processing of PET. For the same purpose the experiments were now carried out in ethylene glycol dibenzoate to mimic the polyester conditions as well as possible. Closed autoclaves were under these conditions (275 °C) necessary to prevent the evaporation of the reactants. In a typical experiment EGMB, CBC (molar ratio of 2:1) and 1 mol % of catalyst (with respect to CBC) in ethylene glycol dibenzoate as a diluent were added to a five ml autoclave and placed in a sand bath, which was already on a temperature of 275 °C. It took about 9 minutes to reach 275 °C, starting with the metallic autoclaves at room temperature. After that, the autoclave was kept in the sand bath for 4 minutes. The concentration of hydroxy groups in these model experiments was about ten times higher (500 mmol/kg) than in the polymer systems in order to get enough reaction products to analyse them accurately by HPLC. LC-MS measurements were done to assign the reaction products in HPLC chromatograms.

In scheme 2.4 all the possible end products of the reaction of CBC and EGMB are given and they were all detected. The HPLC analysis of the reaction mixtures showed that CBC and the activated carbonate were hardly detectable in the reaction mixture. In table 2.3 the analytical data of the main reaction products are given.

It appeared to be more difficult than expected to carry out good reproducible experiments under these conditions. The most important problem was the reproducibility of the heating profile to reach the final temperature of 275 °C. Moreover this period is long (9 min) compared with the reaction time (4 min) at that temperature. During the heating period the reaction will start already, and that will have an influence on the results. Therefore, only qualitative conclusions can be drawn.

CBC is in all experiments completely converted (even without a catalyst) and thus no information is obtained on the reaction rate. The absence of CBC in the final sample indicates that either it has completely reacted with EGMB or that it is (partly) decomposed under these harsh conditions.

In a separate series of experiments it has been shown that the decomposition of CBC starts within a few minutes when heated up to 250 °C in DSC equipment, without the presence of hydroxy functional compounds. This suggests that some degradation may also be expected if the heating is done in the presence of hydroxy functional compounds.

The main product is again the urethane, which agrees well with the previous series of experiments. Also the presence of only half of the total amount of caprolactam that can maximally be formed points in the same direction. In the presence of a catalyst the formation of carbonate units is much less pronounced (on the average 7 wt%) than without a catalyst (23 wt %), which was also found in the first two series of experiments.

Table 2.3: The composition * of the main reaction product of ethylene glycol monobenzoate with CBC in ethylene glycol dibenzoate after 4 minutes at 275 ^{o}C.

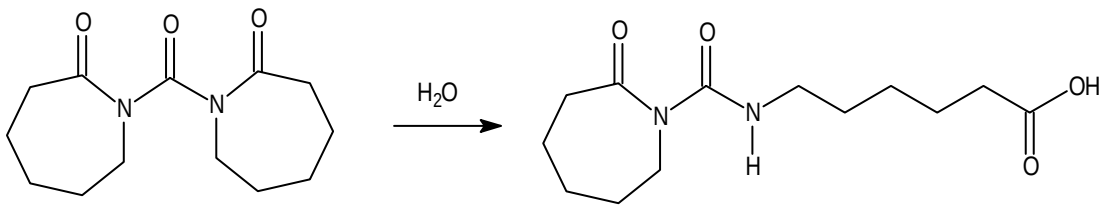
Compound (in scheme 2.2)	Blank	$MgBr_2$	$Zr(OBu)_4$	$Zr(acac)_4$	LiCl
Starting material					
EGMB [1)] (wt%)	17	15	17	12	15
Side product					
Caprolactam [2)] (wt%)	58	54	53	54	56
Products					
2x RS (Carbonate) [3)] (wt%)	23	7	10	7	5
1x RO (BI) [4)] (wt%)	4	4	7	8	4
2x RO (Urea) [5)] (wt%)	7	3	4	4	3
1xRO + 1x RS (Urethane) [6)] (wt%)	36	53	42	42	48

*Only compounds that were found (in HPLC diagram) in major quantities are presented in the table.

1) % Of EGMB present with respect to the starting amount.
2) % Of caprolactam with respect to all the caprolactam present in CBC.
3) % Of two times ring substitution (carbonate) with respect to CBC.
4) % Of one time ring opening (blocked isocyanate) with respect to CBC.
5) % Of two times ring opening (urea) with respect to CBC.
6) % Of ring substitution and ring opening (urethane) with respect to CBC.

CBC is completely consumed, whereas not all the EGMB is converted. This is partly due to the presence of blocked isocyanates that have not yet reacted for a second time with EGMB, and partly to the degradation of CBC.

Next to the expected products (scheme 2.4) a new product is found (scheme 2.6). Meyer[1] had already indicated that the caprolactam ring of N-acyl lactams could be opened by water. Although the starting materials were properly dried, this reaction apparently takes place, meaning that probably some reaction water is formed during this process. This product will hamper the build-up of the molecular weight, since it can behave as a chain stopper.

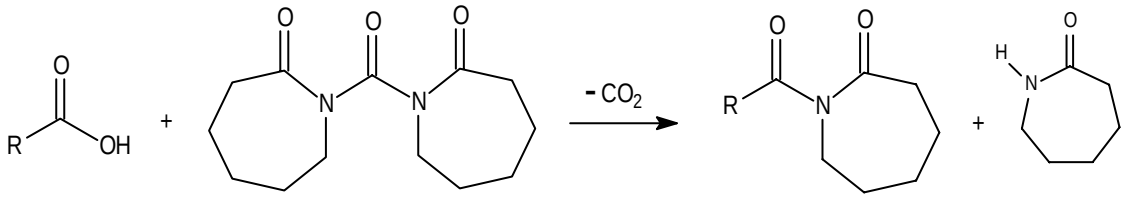


Scheme 2.6: The structure of an unexpected product produced in the reaction of EGMB and CBC, probably formed by the reaction of CBC with water.

Despite the fact that the experimental conditions had certain shortcomings and the mass balance was far from complete, the results are qualitatively in agreement with those of the first two series.

2.6 Model reactions of carboxylic acids with carbonyl biscaprolactam

The concentration of the hydroxy groups decreases considerably during the chain extension reaction of polyesters as expected (*chapter 3*), thanks to the fast reaction with CBC. The concentration of acid groups decreases as well, albeit in a much lesser extent. In model reactions[1)] it was indeed found that CBC reacts with acid groups, forming N-acyl lactams (scheme 2.7). The reaction rate of CBC with acids is lower than with alcohols. Consequently, with polyesters the decrease of the concentration of hydroxy groups will be more pronounced than that of the acid groups.



Scheme 2.7: Reaction of acids with carbonyl biscaprolactam.

N-acyl lactams are activated acids, which are used to make esters under mild conditions. N-acyl lactams can be prepared from acid chlorides and caprolactam. A more common laboratory method to make activated acids is from acids and carbonyl diimidazole[12]. The structure of carbonyl diimidazole (CDI) is very similar to that of CBC. It is proposed that the reaction mechanism of CBC with acids proceeds in the same way as with CDI (scheme 2.7).

[1)] Researchers at Degussa did a number of model experiments in which they showed that the reaction of the monomethyl ester of terephthalic acid with CBC resulted in the corresponding monomethyl ester terephthaloyl lactam in 72 % yield after 13 h at 150 ^{o}C.

2.7 Conclusion

The aim of the model reactions was to find suitable catalysts that are able to shorten the residence time in commercial extruders, during the chain extension process of polyesters. Extruder conditions are characterized by short residence times, excellent mixing processes, very fast rise of the temperature, high temperatures, high viscosities and high pressures. None of the model experiments was really able to fully simulate the extruder conditions and thus the translation of these results to extruder conditions has to be done with care. Nevertheless, these results showed unambiguously a large influence of catalysts on the chemistry of the reaction between hydroxy functional compounds and CBC.

More than sixty catalysts were tested and quite a number of them are able to catalyse the reaction of n-dodecanol or ethylene glycol monobenzoate with CBC considerably. It was found that salts of both transition and non-transition metals performed the best. Actually, magnesium halides, titanium and zirconium alkoxides or acetyl acetonates outperform the rest.

Another conclusion is that urethanes are the main linking moieties that are formed under the conditions applied. Furthermore it was found that catalysts also have a profound influence on the composition of the newly formed linkages. Most of the catalysts substantially increase the concentration of urethane linkages at the expense of the carbonate linkages. The urethane bond is found to be the main linkage, meaning that one caprolactam ring of CBC opens, whereas the other one is substituted.

2.8 Experimental section

Crystal data of CBC: Formula $C_{13}H_{20}N_2O_3$, M = 252.31. Crystal system: orthorhombic, Space group Pbca (no 61), a, b, c = (Å) 10.3749 (1), 10.0965 (1), 24.1681 (3), V = (Å^3) 2531.61 (5), Z = 8, D (calc, g/cm^3) = 1.324, Mu(MoKa, /mm) = 0.094, F(000) = 1088, Crystal size (mm) = 0.18*0.21*0.33. Data collection: Temperature (K) = 125, Radiation (Å) MOKa 0.71073, Theta Min-Max (deg) = 1.7, 27.5, Dataset = -13: 13 ; -13: 12 ; -31: 31, Tot., Uniq.Data, R (int) = 29202, 2897, 0.051, Observed data (I > 2.0 sigma (I)) = 1706.

Refinement: Nref, Npar = 2897, 163, R, wR2, S = 0.0298, 0.0792, 0.75, w = 1/[2^2^(Fo^2^) + (0.0000p)^2^], Max. and Av. Shift/Error = 0.00, 0.00, Min. and Max. Resd. Dens. [e / Å^3] = -0.17, 0.16. Prof. A. Spek, National NO-CW/UU single crystal service facility (a.l.spek@chem.uu.nl).

Materials

CBC (> 99 % pure measured by HPLC) was obtained from DSM New Business Development, ALLINCO and used without any purification.

n-Dodecanol, benzoic acid, ethylene glycol, 2-chloro-ethanol, propylene carbonate and the catalysts were obtained from Aldrich or Acros and used without any purification.

Instrumentation

^{1}H-NMR was done on a Brucker ACF 300, equipped with a 5 mm dual probe head at a frequency of 300 MHz.

HPLC (high performance liquid chromatography) was performed on Nucleosil 120-5-C18 columns and the detection was done with a diode array detection device.

LC-MS was done in the API-150-SCIEC equipment using a Nucleosil 120-5-C18 column with two eluents: A. water + 1 wt % of acetonitrile + 0.02 wt % of formic acid and B. acetonitrile + 0.02 wt% of formic acid. The following elution (1 ml/min) profile was used: from 0 to 35 minutes the ratio between A/B was 95/5, then from 35 to 50 min 0/100 and then from 51 to 60 min 95/5. An electrospray interface (ESI) was used to ionise the molecules.

The SEC (size exclusion chromatography) analyses were done on a system containing two HR 0.5 ($\overline{M}_n$ < 1000), one HR1 (up to $\overline{M}_n$ = 5000) and one HR2 (up to $\overline{M}_n$ = 20,000) columns, and equipped with a Waters 2410 RI detector and a Waters 487 UV detector. The data were collected with a computer and processed with Waters Millenium32 software.

Synthesis

1-[(2-oxo-1-azepanyl)carbonyl]-2-azepanone (1,1-carbonyl bis caprolactam, CBC), according to Okuda [2]

Caprolactam (22.6 g, 0.20 mol) and triethylamine (21.2 g, 0.21 mol) were dissolved in 100 ml benzene, and while the solution was kept at 20 ^{o}C, 50 ml benzene that contained phosgene (11 g, 0.11 mol) was added drop wise, in 30 minutes. Subsequently, the reaction solution was kept at 40 ^{o}C for 2 h, and thereafter cooled to room temperature, and the crystals that had been formed were isolated by filtration. The filtrate was washed with 50 ml of water and the benzene solution was treated with anhydrous $CaCl_2$ to remove the water. After the $CaCl_2$ had been removed by filtration, the benzene solution was evaporated and carbonyl biscaprolactam was obtained as crystals. The yield was 15.0 g, which is 60%. The melting point of the product was 114 ^{o}C.

When N,N-dimethyl or N,N-diethyl aniline was used instead of triethylamine, the yield increased to 80%[10].

Carbonyl biscaprolactam from triphosgene

In a flask of 250 ml 70 ml xylene, caprolactam (9.5 g, 84 mmol) and diethylaniline (11.84 g, 79 mmol) were charged. The mixture was heated to 40 ^{o}C and then triphosgene (3.93 g, 13 mmol) in 30 ml xylene was added drop wise and the mixture was left overnight, while stirring. The reaction mixture was cooled down to room temperature and washed with 100 ml 5wt% $NaHCO_3$ solution and twice with water. The solution was dried on anhydrous sodium sulphate and after removal of the drying agent by filtration the xylene was removed by distillation under reduced pressure. CBC was collected and recrystallized from toluene. The yield was 74.5 g (75 %). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.78 (6H, broad, CH_2 ring), 2.59 (2H, t, CH_2CO), 3.84 (2H, t, CH_2N).

Ethylene glycol monobenzoate

Sodium benzoate (288 g, 2 mol) was added to 2-chloroethanol (600 g, 7.5 mol) in a three-necked flask. After the mixture had been heated at 130 °C for 18 hours it was cooled down to room temperature and 300 ml water was added. Subsequently, the mixture was extracted 3 times with 350 ml of diethyl ether and the organic fractions were combined and dried on anhydrous sodium sulphate. After filtering the sodium sulphate diethyl ether was removed under reduced pressure (rotavapor) and the resulting oil was distilled under vacuum. The ethylene mono benzoate was obtained as colourless oil (1 mbar, top temperature of 125°C).

Yield was 59%: ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 3.33 (1H, s, OH), 3.92 (2H, t, C$\underline{H_2}$OH), 4.42 (2H, t, C (O)OCH_2), 7.39 (2H, q, m-aromatic), 7.50 (H, q, p-aromatic), 8.03 (2H, q, o-aromatic).

Ethylene glycol dibenzoate

Benzoic acid (256.5 g, 2.1 mol), ethylene glycol (62.1 g, 1 mol) and 1 w% of p-toluene sulfonic acid in 500 ml of xylene were refluxed overnight in a 3–necked flask equipped with a Dean-Stark trap. After cooling down the reaction mixture was extracted 3 times with 500 ml of 1N NaOH solution. The xylene solution was dried with anhydrous sodium sulphate and after that the sodium sulphate was filtered off and xylene was removed under reduced pressure (rotavapor). The product was recrystallised from n-isopropanol and was obtained as a white powder. Yield = 56%: ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 4.67 (4H, s, CH_2CH_2), 7.44 (4H, q, m-aromatic), 7.58 (2H, q, p-aromatic), 8.05 (4H, o-aromatic).

Reactions of ethylene glycol monobenzoate and CBC at 175 ^{o}C

CBC (2.52 g, 10 mmol), propylene carbonate (29.7 g) and a catalyst (1 w% with respect to CBC) were placed in a 1-necked flask. After the mixture was heated in an oil bath to 175°C ethyleneglycol monobenzoate (3.32 g, 20 mmol) was added. The reaction mixture was kept at 175°C for 10 min. and then cooled down quickly to room temperature. HPLC measurements were performed to determine the concentrations of CBC, caprolactam and ethylene glycol monobenzoate.

Reactions of dodecanol and CBC at 200 ^{o}C

Dodecanol (3.72 g, 20 mmol), CBC (2.52 g, 10 mmol) and a catalyst (1 wt % with respect to the weight of dodecanol and CBC) were mixed in a glass flask of 25 ml and heated in an oil bath of 200 ^{o}C for 10 minutes. The mixture was cooled down rapidly and analysed by SEC measurements.

Reactions of ethylene glycol monobenzoate and CBC at 275°C

CBC (0.15 g, 0.6 mmol), ethylene glycol monobenzoate (0.20 g, 1.2 mmol), a catalyst (1 mol% with respect to CBC) and 3.24 g (12 mmol) of ethylene glycol dibenzoate were mixed in a cuvet. This cuvet fits accurately in a small autoclave, which was closed tightly. After the autoclave has been buried in a sand bath for 13 min at 275°C it was rapidly cooled down to room temperature. HPLC measurements were used to determine the concentrations of CBC and ethylene glycol monobenzoate and the reaction products.

2.9 References

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[9] Maier,S., PhD Thesis, Freiburg (2003).
[10] See appendix B, list of Patents&publications
[11] The calculations were carried out by B. Coussens at DSM Research. She constructed first CBC with the building facilities of PC Spartan Pro version 1.1, employing the most stable conformation of caprolactam determined in earlier work as a starting point. PC Spartan Pro was also employed to perform a conformational analysis at the semi-empirical AM1 level. In this analysis, only rotation around the central CN bonds was considered, i.e. the conformation of both caprolactam rings was kept fixed. The AMI conformations were subsequently used as input for the Gaussian98 program to perform geometric optimisations at the B3LYP/6-31G* level. In addition, they were used as a starting point to construct the corresponding Mg^{2+} complexes by means of the Cerius2 package. These complexes were also optimised at the B3LYP/6-31G* level. All B3LYP/6-31G* optimisations were carried out using the BFGS algorithm and the set of defaults convergence criteria of 0.00045 Hartree/Bohr for the maximum force, 0.0003 Hartree/Bohr for the RMS force, 0.0018 Bohr for the maximum displacement and 0.0012 Bohr for the RMS displacement. Atomic charges were obtained from a Mulliken population analysis or by a fit to the molecular electrostatic potential.
[12] Staab, H.A., Angew. Chem, **74**, no. 12, 407, (1962).

Appendix 2.1 The HPLC results of the reaction of ethylene glycol mono benzoate (EGMB) with CBC after 10 min at 175 °C.

Catalyst	EGMB	CBC	CBC	Caprolactam	Caprolactam
	Conversion (%)	Measured (%)	Calculated (%)	Measured (%)	Calculated (%)
Zirconium octoate	0	4.5	7.1	0.4	0.0
Lithium sulphate	1	6.1	7.0	0.3	0.1
Tetrabutyl tin	3	5.6	6.7	0.4	0.2
Lithium carbonate	4	7.0	6.5	0.3	0.2
Lithium nitrate	5	5.7	6.4	0.5	0.3
Lithium phosphate	5	5.9	6.4	0.0	0.3
Phosphoric acid	5	5.7	6.4	0.6	0.3
Tributyl tin chloride	5	4.9	6.4	0.3	0.3
Calcium acetate	8	5.8	6.0	0.5	0.5
Tin (II) acetate	8	6.6	6.0	0.4	0.5
Blank	9	5.7	5.8	0.5	0.6
Germanium oxide	9	6.6	5.8	0.4	0.5
Phenylphosphonic acid	9	5.7	5.8	0.5	0.6
Sodium chloride	9	5.5	5.8	0.4	0.6
Tin (II) octoate	9	5.3	5.8	0.5	0.6
Zinc borate	10	5.1	5.7	0.7	0.7
Zinc chloride	11	4.8	5.5	0.8	0.7
Aluminium trichloride	12	3.8	5.4	0.7	0.8
Antimony trioxide	12	6.4	5.4	0.4	0.7
Zinc acetate	13	4.5	5.3	0.7	0.9
Cobalt octoate	15	4.6	5.0	0.8	1.0
p-Toluene sulfonic acid	15	0.4	5.0	4.5	4.7
Tetra butyl ammonium iodide	15	0.7	5.0	0.5	1.0
Potasium lactamate	16	6.7	4.8	0.4	1.0
Zirconium acetyl acetonate	16	5.3	4.8	0.8	1.0
Dibutyl tin acetate	17	6.3	4.7	0.4	1.1
Sodium dodecylbenzene sulfonate	17	0.2	4.7	0.7	1.1
Sodium acetate	20	5.1	4.3	0.7	1.3
Lithium acetyl acetonate	21	4.5	4.1	0.7	1.4
Cobalt acetyl acetonate	22	3.0	4.0	1.1	1.4
Magnesium acetate.hydrate	26	4.1	3.4	1.1	1.7
Maganese (II) acetate	26	4.8	3.4	1.0	1.6
Hypophosphorous acid	27	5.2	3.3	0.7	1.7
Titanium acetyl acetonate	28	3.9	3.1	1.3	1.8
Lithium hydroxide	29	4.0	3.0	1.0	1.9
Zirconium butylate	30	4.8	2.8	1.1	1.9
Dibutyl tin dilaurate	32	4.7	2.6	1.1	2.1
Lantanium trifluormethane sulphonate	32	2.8	2.6	1.2	2.0
Magnesium bromide	32	2.7	2.6	1.6	2.1

Continuation of appendix 2.1					
Catalyst	EGMB	CBC	CBC	Caprolactam	Caprolactam
	Conversion (%)	Measured (wt%)	Calculated (wt%)	Measured (wt%)	Calculated (wt%)
Dimethyl amino pyridine (DMAP)	33	4.0	2.4	0.5	1.1
Lithium isoproxide	35	3.1	2.1	1.4	2.3
Tetra butyl ammonium bromide	40	4.7	1.4	1.2	2.6
Potassium borate	41	2.1	1.3	1.0	2.6
Tetra butyl ammonium hydroxide	43	0.4	1.0	1.7	2.7
Iron (III) acetyl acetonate	49	1.9	0.1	1.9	3.1
Magnesium chloride	59	0.4	0.0	2.1	3.7
Lithium butoxide	66	0.5	0.0	2.3	*4.2*
1,4-diazabicyclo[2,2,2] octane,	75	1.6	0.0	2.1	4.8
1,8-diazabicyclo[5,4,0]undec-7-ene	75	0.7	0.0	2.9	1.8
Titanium (IV) isoproxide	75	0.0	0.0	3.3	4.8
Titanium (III) chloride	77	0.1	0.0	2.5	5.0
Titanium (IV) n-butoxide	84	0.0	0.0	4.1	5.4
Lithium chloride	85	0.0	0.0	2.8	5.4
Lithium methoxide	91	0.0	0.0	3.3	5.9
Sodium ethoxide	95	0.4	0.0	3.4	6.1
Lithium hydride	97	0.0	0.0	3.8	6.2

Chain extension of polycondensates

Abstract

In this chapter the preparation high molecular weight polycondensates is described via chain extension of regular polymers during a reactive processing step, as an alternative route for the solid-state post-condensation (SSP) process. It is shown that carbonyl biscaprolactam (CBC) is a very promising chain extender.

Various polymers, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate (PBT), nylon-6 and nylon-6,6 were tested, and in all cases a strong increase of molecular weight was obtained. The viscosity level is controllable by the amount of CBC.

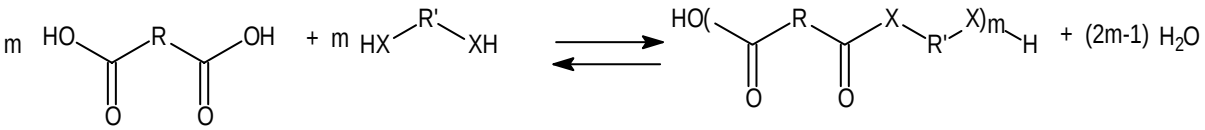
The chain extended polymers are strictly linear, according to SEC and rheology measurements. A strict linear chain extension (no chain branching) is important in many applications.

Most of the reactive extrusion work is done in the DSM micro-compounder, and some experiments are repeated in a ZSK30 extruder to confirm the results, and to improve the reliability of the translation to commercial equipments. The desired increase in molecular weight is obtained in 1 to 3 minutes, which is an acceptable time span for many applications. The resulting polymers are melt stable, since the chain extension reaction is completed within this residence time.

3.1 General introduction

3.1.1 Preparation of polycondensates

Polyesters and polyamides are prepared by a condensation reaction of diacids with diols or diamines, respectively, at temperatures between 240 and 280 °C, while removing volatiles to shift the equilibrium of the reaction in scheme 3.1 to the right.



Scheme 3.1: The preparations of polyesters (X = O) or polyamides (X = NH).

The majority of commercial polyesters and polyamides are prepared in the melt (in bulk) to avoid the costly separation of polymers and solvents and the subsequent recovery of solvents. The viscosity of the melt increases substantially during the course of the polycondensation reaction, which limits the maximally attainable molecular weight.

A second obstacle that hampers the preparation of high molecular weight polycondensates is the occurrence of side reactions that take place during the melt polycondensation step, due to the harsh reaction conditions (T = 240-280 °C and τ = 3-6 h). Longer residence times will give more side products. Consequently, the production of high molecular weight polycondensates is difficult to realize in a melt process.

3.1.2 Solid-state post condensation (SSP)

The relative viscosities of commercial polymers such as poly(ethylene terephthalate) (PET) range from 1.55 dl/g for textile fibres to about 2.05 dl/g for industrial yarns. Low viscous grades are directly prepared in the melt, but high viscosity grades require an additional solid-state post-condensation (SSP) step. Currently, there are two types of SSP processes in use, of which one operates batch-wise and the other one continuously. Although the batch route in tumble dryers (figure 3.1) is more labour-intensive, this technology is still widely in use. In this process step the polycondensation reaction is continued by heating pellets for 20 to 50 hours in the solid state just below the melting point of the polymer, under vacuum, in a nitrogen atmosphere. The required residence time in a SSP process is rather long because of the low polymerisation temperature (about 200 °C), the low diffusion rate of the condensation water out of the pellets and because of the low mobility of end groups in the solid. This method is time and energy consuming, and therefore expensive.

Figure 3.1: Picture of a commercial solid-state post-condensation tumble dryer.

The purpose of this part of the work is to find reactive additives (chain extenders), enabling to replace the SSP process in tumble dryers by a fast chemical coupling reaction of polymer chains in an extruder, in order to make the desired viscosities in a cheaper and more convenient way.

3.1.3. Chain extension, current state

Conceptually, it would be beneficial to have a commercial route in which only a few low molecular weight grades are produced, whereas viscosities of all the other grades are tailored later on by a chemical coupling during the final processing step. To be cost competitive with the SSP process the chain extension step should be carried out in a regular extrusion step, in order to avoid additional investments. Commercial extrusion processes have residence times of 1-3 minutes (at about 300 ^{o}C), and in that short period the mixing and the chain extension reaction have to take place. The selected chemistry should consequently be very fast, not only because of the short residence times, but also because of the low concentration of end groups (about 50 mmol/l).

All considered polycondensates possess reactive end groups (OH, NH_2 or COOH), and quite a number of fast reactions are conceivable with these groups. Many chain extenders are

reported, but most of them gave side reactions (e.g. branching) due to their unavoidably high reactivity. For instance, diphenyl carbonate[1], aliphatic and aromatic bisoxazolines[2], bisepoxides[3], diisocyanates[4], phosphites[5], caprolactam phosphite[6], bisketenimines[7], dianhydrides[8], oxazolinones[9] and dicyanates[10] have been reported, but none of these have successfully been applied in commercial processes. Among all these potential chain extenders bislactams[11] are perhaps the best (no branching), and this was one of the reason to study the simplest member of this family, carbonyl biscaprolactam, in more detail.

3.2 1-[(2-oxo-1-azepanyl)carbonyl]-2-azepanone, (1,1-carbonyl biscaprolactam, CBC)

3.2.1 Bislactams

Bislactams are prepared from lactams and diacid chlorides, and in particular from caprolactam and iso- or terephthaloyl chloride (**2** and **3,** respectively, figure 3.2). Although both aromatic biscaprolactams showed promising results as chain extenders, they did not reach the commercial status so far[11]. Nevertheless, it was our conviction that bislactams were worthwhile for further investigations. The aromatic bislactams yield a strong enhancement of the viscosity of polyesters as well as with polyamides, by reacting exclusively with OH or NH_2 groups of polymers. A further increase in viscosity is obtained if, in addition to bislactams, bisoxazolines were used, which react with the carboxylic end groups[12].

The focus of the present study is on bislactams, and particularly on the non-aromatic member of this family, carbonyl biscaprolactam (**1** in figure 3.2, CBC). This compound attracted so far only little attention in the literature, and has not been described as chain extender[13].

The low raw material cost was an important reason to select CBC. Carbonyl biscaprolactam is prepared from caprolactam and phosgene, which is the cheapest commercially available diacid chloride.

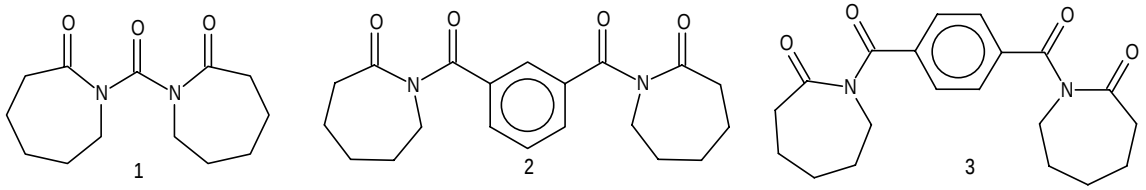


*Figure 3.2: Structure of biscaprolactams of carbonic (**1**, CBC), isophthalic (**2**, IBC) and terephthalic (**3**, TBC) acid.*

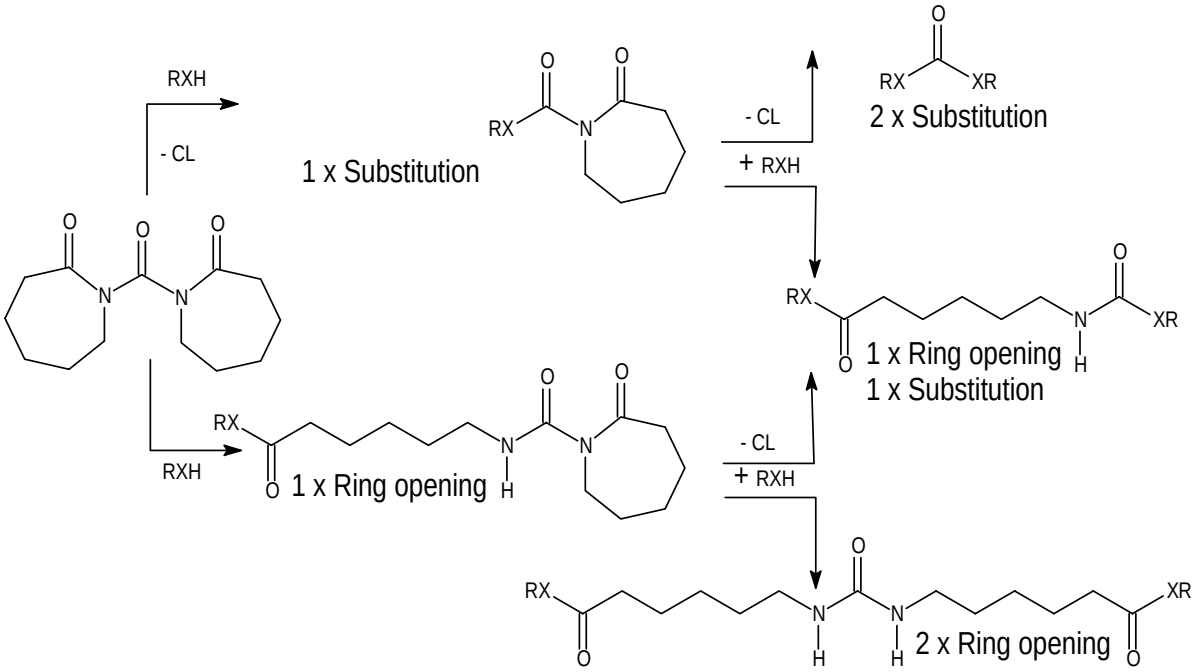
Another advantage of CBC is its low molecular weight compared to the competitive isophthaloyl and terephthaloyl biscaprolactam (IBC, resp. TBC). The molecular weight of

IBC or TBC (M = 356) is 41% higher than that of CBC (M = 252) and thus less CBC is needed when equimolar amounts of chain extender are used.

3.3 Chain extension with carbonyl biscaprolactam

3.3.1 General introduction

Chain extension of polycondensates implies that two consecutive reaction steps have to take place. First, one polymer chain end must react with the chain extender, forming a reactive polymeric intermediate. Subsequently, this reactive intermediate has to react with the end group of another polymer chain. The possible reactions that can take place between CBC and the OH or NH_2 end groups are depicted in scheme 3.2.



Scheme 3.2: The possible reactions between carbonyl biscaprolactam and hydroxy(X = O) or amino (X = NH) functional end groups of polycondensates (CL = ε-caprolactam).

CBC can give ring opening reactions, which has not been reported for other chain extenders. In both reaction steps either a ring opening or a ring substitution can take place, leading to carbonates (2 times ring substitution), urethanes (1 time ring opening, 1 time ring substitution) or ureas (2 times ring opening).

At T > 150 ^{o}C –e.g. during polymer processing- the reactive polymeric intermediates will immediately react further. At lower temperatures these intermediates can be isolated, which will be discussed in the next chapters. In this chapter only the reactions at elevated temperatures are discussed, by which both consecutive reaction steps will take place[14].

3.4 Chain extension of polyesters

3.4.1 Introduction

Most of the chain extension experiments were carried out in a DSM micro-compounder and some experiments were repeated in a ZSK30 extruder (paragraph 3.4.4). For this part of the study poly(ethylene terephthalate) (PET) and poly(butylene terephtalate) (PBT) were chosen, since these are the most important commercial polyesters.

Both, the mixing process (physical process) and the reaction rate (chemical process), determine the overall rate of the chain extension process. In this work the attention is mainly focussed on the chemical part. The mixing depends strongly on the type of extruder, type of screw, temperature, etc., and is, although extremely important, only briefly touched upon in this thesis.

3.4.2 Experimental conditions for chain extension of PET in the DSM micro-compounder

PET is extremely sensitive for hydrolytic degradation at high (processing) temperatures and therefore it is always dried thoroughly (48 h at 140 ^{o}C in a nitrogen atmosphere, under vacuum) before processing, and all handlings were done with great care to exclude moisture. PET pellets were ground to facilitate dosing of the polymer into the micro-compounder. CBC was added to the polymer in the glove box, either as a solid or dissolved in THF. In the latter case THF was evaporated, in a vacuum oven overnight under nitrogen at 50 ^{o}C before use. The PET samples were stored in a glove box in a dry nitrogen atmosphere before use. The samples were transported in a closed vessel and opened just before feeding the polymer to the extruder. The temperature of the extruder was raised to the set point (280 ^{o}C) and the screw speed was set at 60 rpm (revolutions per minute), before the polymer was added. It took about 45 seconds to add the polymer to the extruder and to raise the screw speed to 80 rpm. This point was taken as t_o, the starting time of the experiment. The micro-compounder has an internal closed loop, which allows variations in residence times. The residence times were varied between 4 and 10 minutes, depending on the aim of the experiment. After a chosen residence time the micro-compounder was discharged and the strands were collected for analysis. The equipment (figure 3.3) is provided with an automatic computerized torque measurement system, which is an excellent tool to measure the reaction rate in a qualitative way. The torque data and residence times were directly collected and processed by a computer.

Figure 3.3: Picture of the DSM micro-compounder in which most of the chain extension work has been performed. On the left a view of the complete apparatus and on the right a close-up of the screws.

To verify the reproducibility five successive reactive extrusion experiments were carried out. In figure 3.4 the relative viscosity is plotted versus the residence time in the micro-compounder.

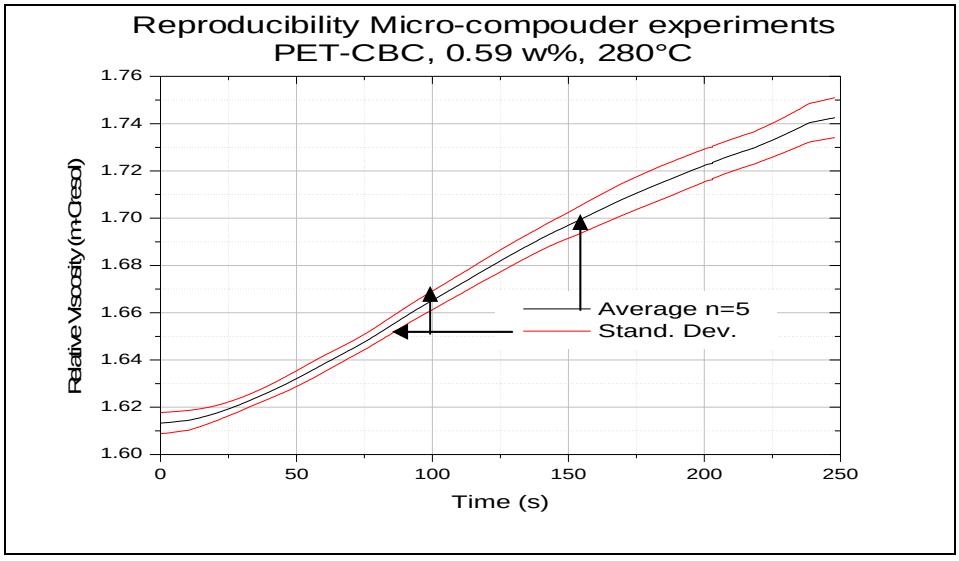


Figure 3.4: Reproducibility of chain extension experiments of PET in micro-compounder.

These relative viscosities are calculated from the empirical relation between the relative viscosity and the torque data (figure 3.5). The middle line in figure 3.4 is the average of the five experiments and the lines beneath and above this line are drawn at a distance of two σ, the standard deviation (enclosing 95.4% of the experimental data). The calculated η_{rel} was 1.74 ± 0.07, after a residence time of 250 seconds.

The torque is a good indicator of the relative viscosity, as is illustrated by the linear relationship between the torque and the relative viscosity (figure 3.5). It was found that: $\eta_{rel} = 1.476 + (1.44*10^{-4}*\text{torque})$, in which the torque is expressed in Nm.

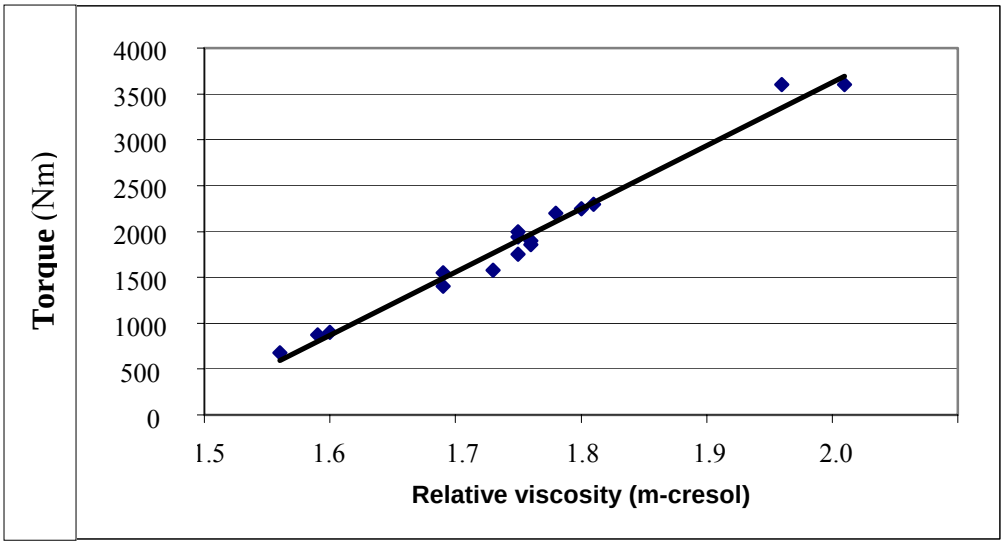


Figure 3.5: The relation between the final torque (in Nm) and the relative viscosity of PET in the micro-compounder, after processing PET with various amounts of CBC.

These results illustrate that the reproducibility of the experiments in the micro-compounder is good. When the equipment is cooled down and restarted, the absolute value of the torque may differ somewhat, but the increase of the torque, due to chain extension, is found to be reproducible.

3.4.3. Chain extension of PET with CBC

The relative viscosity of a general purpose PET grade is about 1.55 (measured in m-cresol), which corresponds with a number average molecular weight ($\overline{M}_n$) of about 20,000 g/mol. The concentration of carboxylic acid end groups is about 30-40 meq/kg and of hydroxy end groups is 60-70 meq/kg. CBC reacts almost exclusively with hydroxy groups, and only to a minor extent with carboxylic groups (see 2.6).

In figure 3.6 the increase of the relative viscosity is given of three commercial PET grades, with different starting viscosities (η_{rel} = 1.56, 1.72 and 1.99 dl/g), after processing with various amounts of CBC. The increase of the viscosity depends on the amount of CBC. Two base grades, with relative viscosities of 1.56 and 1.72 dl/g, would be sufficient to cover most commercial viscosities (in general between 1.55 and 2.05 dl/g) by chain extension. The maximally attainable increase in viscosity of a PET grade is limited, because CBC reacts almost only via the hydroxy groups. The rest of the end groups are carboxylic acid groups, which are hardly reactive under the conditions applied. The relation between the PET viscosity and the amount of added CBC seems to be close to linear (figure 3.6).

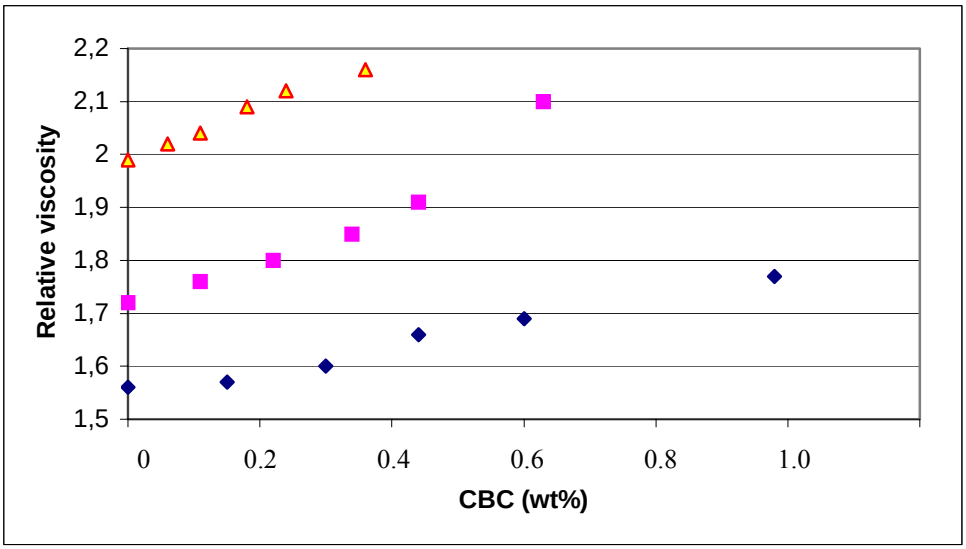


Figure 3.6: The relative viscosity of PET (in dl/g, in m-cresol) as function of the wt % CBC (starting relative viscosity: ◊ = 1.56, □ = 1.72, Δ= 1.99 dl/g; Sample preparation: T = 280 ^{o}C, τ = 6 min.).

However, the relation between molecular weight and solution viscosity is, according to theory, not linear. The Mark-Houwink relation ($[\eta] = KM^{a}$), which gives the relation between the intrinsic viscosity and the molecular weight, is an exponential relation. Thus, a non-linear relation is to be expected if the assumption is made that the molecular weight of PET increases linearly with the amount of CBC. The range of relative viscosities in figure 3.6, however, is by far too small to deviate significantly from linearity, even if a Mark-Houwink type of relation would apply.

Figure 3.7 shows a typical example of the change of the torque of the micro-compounder as function of time in a series of experiments in which PET is processed without CBC and with 0.43 (17.0 mmol/kg) or with 0.59 wt% (23.4 mmol/kg) of CBC. It can be seen that the torque of the virgin PET slightly decreases during processing, which indicates that some degradation

takes place. This is always found with PET, no matter how thoroughly the sample is dried. Similar results are obtained in commercial equipments, even under the very dry conditions as in commercial spinning units. This drop is often attributed to hydrolytic degradation, although we have not found unambiguous proof in the literature for that statement. It is more likely some thermal degradation takes place as well. Figure 3.7 demonstrates the strong increase of viscosity (torque) in time, thanks to the presence of CBC. The increase of the torque levels off after 5 to 6 minutes, indicating that the reaction is nearly completed.

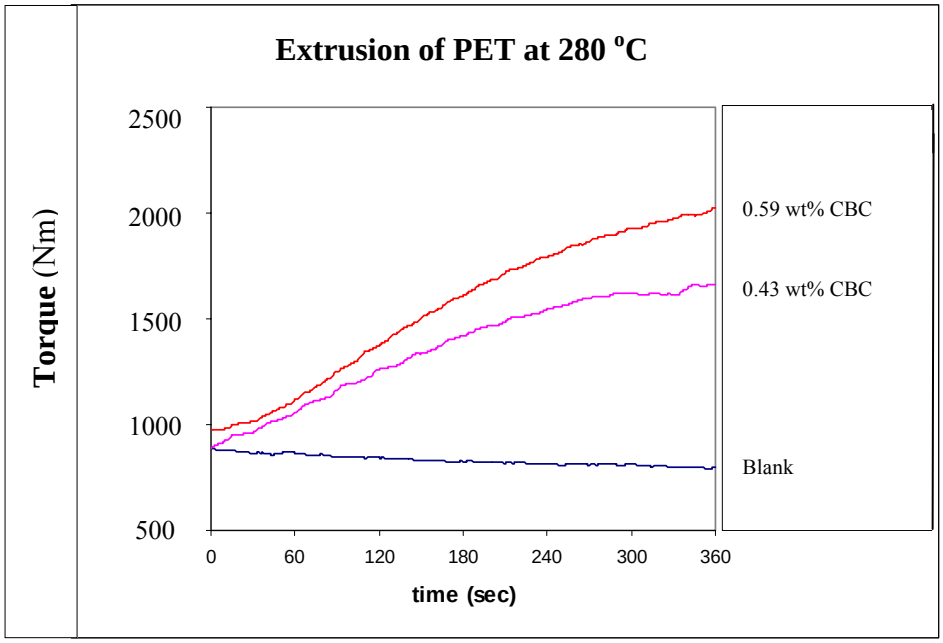


Figure 3.7: The torque during the processing of PET with CBC as function of residence time in the micro-compounder.

A residence time of six minutes is not acceptable for some applications, but the mixing capability of the micro-compounder is less than that of commercial extruders. In paragraph 3.4.4 it will be shown that the maximum viscosity of PET with CBC in a larger twin-screw extruder (ZSK30) is reached within shorter residence times.

After more than six minutes of melt processing the torque decreases slightly, in the same way as observed with virgin PET, suggesting that the newly formed linkage has a similar stability than that of the polyester backbone. This is not always the case with other chain extenders, as in literature many examples are shown, in which the stability of the newly formed linkage is insufficient[15], and that viscosity drops or increases after prolonged heating or repeated extrusions.

With 0.59 wt% of CBC a higher viscosity is obtained than with 0.43 wt%, as expected (figure 3.7). 0.59 wt% (23.4 mmol) CBC is the stoichiometric amount with respect to the number of

hydroxy end groups (47 mmol/kg; notice that one mmol CBC reacts with two mmol hydroxy groups). Theoretically, the stoichiometric amount of CBC should give maximally attainable viscosity. However, as is shown in figure 3.6, the viscosity keeps increasing, even beyond the point of stoichiometry. This conflicts with theory, but it shows that under the experimental conditions the obtained level of the viscosity is an overall result, which is a combination of a viscosity build-up thanks to chain extension and a decrease due to degradation of PET. Furthermore, under these conditions CBC probably degrades to some extent as well.

More quantitative information on the chain extension of PET is given in table 3.1. It can be seen that the viscosity of the virgin PET drops during processing from 1.55 to 1.46. The concentration of the acid and the hydroxy end groups increases during processing of the virgin PET, but not in equal amounts (in mmols), indicating that the viscosity drop is not only due to hydrolysis, but also due to the well-known pyrolysis reaction. In the presence of CBC there is clearly an increase in the viscosity. To get a realistic impression of what the chain extension effect by CBC brings about, it is better to compare column 4 with 3 (virgin PET after processing), rather then 4 with 2 (virgin PET before processing). The final viscosity is the resultant of two processes: the chain extension and chain scission. The final viscosity level obtained by the chain extension process includes the degradation reactions as well.

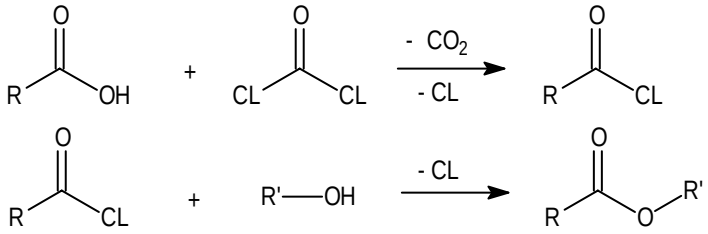
Table 3.1: End group and viscosity data of chain extended PET.

Parameter mmol/kg	Virgin PET Before extrusion	After extrusion	Extrusion with CBC (mmol/kg)
[CBC]	0	0	30
[Acid]	32	45	26
[OH]	61	68	20
η_{rel}	1.55	1.46	1.79

It can be seen that in spite of the use of stoichiometric amounts of CBC the OH concentration does not reach zero. An explanation could be that some degradation of either PET or CBC takes place or that the residence times are too short to complete the reaction.

Nevertheless, the decrease of the hydroxy groups is quite large (from 61 to 20 mmol/kg), indicating that a large part of the OH end groups have reacted. Table 3.1 shows that there is also some decrease in the concentration of acid groups. In model experiments (2.6) it was found that CBC does react with carboxylic acid groups (scheme 3.3), but at a lower rate than with hydroxy groups. In that case probably N-acyl lactams are initially formed. N-acyl lactams are activated acids that react easily with hydroxy groups, forming esters (scheme 3.3).

This reaction can contribute as well to the increase of the viscosity, but only to a limited extent.



Scheme 3.3: The formation of N-acyl lactams from CBC and carboxylic acids, followed by the conversion of N-acyl lactams into esters by the reaction with hydroxy functional compounds (CL = ε-caprolactam).

3.4.4 Chain extension of PET in ZSK30

To gain more information on the chain extension rate in commercial equipments some experiments were done in a ZSK30 extruder. The ZSK30 is a twin-screw extruder, which is, with respect to mixing efficiency, more comparable to commercial extruders than the micro-compounder. Dry PET pellets were mixed with 0.70 wt% of CBC, in the presence of sticking oil, and fed to the hopper of the extruder. Care was taken to exclude moisture as much as possible during these handlings. The residence time was varied by changing the screw speed (figure 3.8).

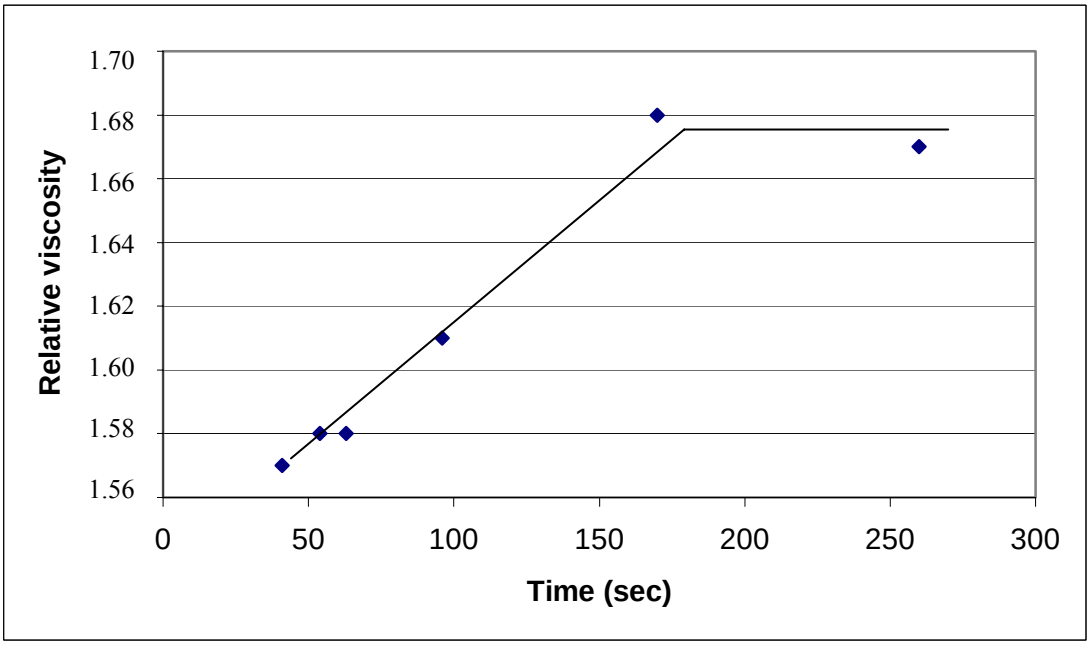


Figure 3.8: The relative viscosity (in dl/g, in m-cresol) of PET as function of residence time with 0.70 wt% of CBC in the ZSK30 extruder (T = 270 °C).

It can be seen that the plateau level of the maximally achievable viscosity is now reached in about 3 minutes, showing that the mixing efficiency of the ZSK30 is much better than that of the micro-compounder. The final viscosity level in the ZSK30 is lower than that obtained in the micro-compounder. A reason might be that it is difficult to work moisture-free (< 100 ppm water) in equipment that is not designed for that purpose[1)], and consequently the reproducibility of these experiments was only modest. The most important information from these experiments is that the maximum viscosity level is reached within much shorter residence times than in the micro-compounder.

A residence time of 3 minutes is still too long for some applications, and therefore the influence of catalysts was studied.

3.4.5 Chain extension of PET with CBC in the presence of catalysts

3.4.5.1 In the micro-compounder

In *chapter 2* a large series of catalysts has been screened using alcohols as model compounds. The results of these model reactions are only indicative for the reaction rate between hydroxy functional polymers and CBC. Therefore, a number of the well-performing catalysts in the model experiments were now tested for the chain extension of PET in the micro-compounder. As discussed before, the starting torque of the micro-compounder is not always exactly the same. In order to eliminate these starting variations, the torque numbers were normalized, by setting the end value on 1 (figure 3.9). The assumption was made that catalysts have only influence on the rate and not on the extent of chain extension. From the non-normalized graphs and also from viscosity measurements it was known that this influence was minor indeed.

In first screening tests $Ti(OR)_4$, $Zr(OR)_4$, $Zr(acac)_4$ and $Al(acac)_3$ performed well (R can be various, e.g. C_3 to C_8 alkyl groups, acac = acetyl acetonate), and amongst these, $Zr(acac)_4$ and $Ti(OCH_2CH(C_2H_5)CH_2CH_2CH_2CH_3)_4$ ($Ti(2\text{-Et-HexO})_4$) were the best. Next a series of experiments was carried out with 0 to 4 mol % of these two catalysts with respect to CBC. From figure 3.9 it can be seen that the reaction rate increases by adding more catalyst. An optimal concentration of the catalyst is about 2 mol % with respect to CBC, meaning about 300 ppm with respect to PET. Adding more than 2 mol% of catalyst gives only a marginal further improvement. With $Ti(2\text{-Et-HexO})_4$ as catalyst the plateau value of the viscosity is obtained in about 100 seconds, which is slightly faster than with $Zr(acac)_4$. Taken the

[1)] In the mean time dozens of companies have tested CBC in PET in single and twin screw extruders and have found similar increases of the relative viscosity as was found in this study in the micro-compounder.

moderate mixing of the micro-compounder into account it can be concluded that a residence time of less than 100 seconds seems feasible, which is acceptable for many commercial applications. Some of the catalysts that performed well in the model reactions were not successful in the extruder experiments with PET. For instance, $MgBr_2$, which proved to be one of the best catalysts in the model reactions, was not useful with PET. This behaviour is attributed to the low solubility of $MgBr_2$ in PET. This shows that model reactions are suitable to screen a large amount of catalysts, but subsequent tests with polymers in extruders are indispensable to make the right choice. Homogeneous model reactions cannot exactly predict the kinetics of the reactions with viscous polymers in the melt.

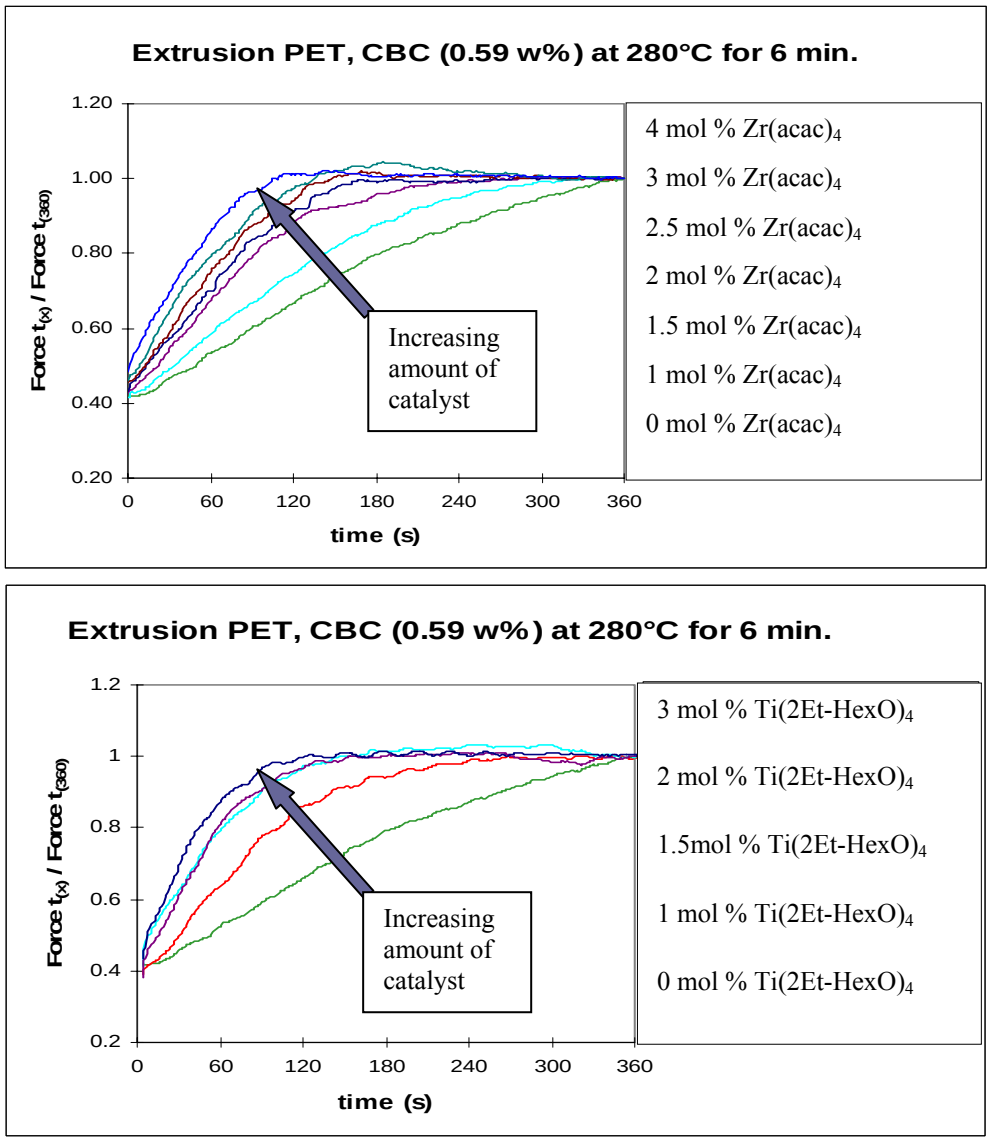


Figure 3.9: The normalized torque of the micro-compounder during the processing of PET with CBC in the presence of various concentrations of $Ti(OCH_2CH(C_2H_5)CH_2CH_2CH_2CH_3)_4$ (bottom) and of $Zr(acac)_4$ (top).

3.4.5.2 In the ZSK30

In order to get a more realistic indication of the reaction rate in commercial equipment, some experiments were done with PET in a ZSK30, in the presence of $Ti(2\text{-Et-HexO})_4$ and $Zr(acac)_4$ as catalyst. A series of experiments was carried out, in which the residence times were varied by changing the screw speed, in the presence of 270 ppm of $Zr(acac)_4$ or 310 ppm of $Ti(2\text{-Et-HexO})_4$ based on PET, which is 2.4 mol% with respect to CBC. From the results, shown in figure 3.10, it can be seen that the plateau level of the viscosity is now reached in about one minute, which is substantially faster than without catalyst (figure 3.8). Also here the titanium catalyst performs slightly better than the zirconium catalyst.

It can be concluded that the reaction rate in the presence of small amounts of catalyst is sufficient to be acceptable for many commercial applications. It is remarkable that the complete process, i.e. the mixing of a low molecular weight chain extender and catalyst in a highly viscous polymer melt, followed by two consecutive chemical reactions, can take place within a time span of only one minute.

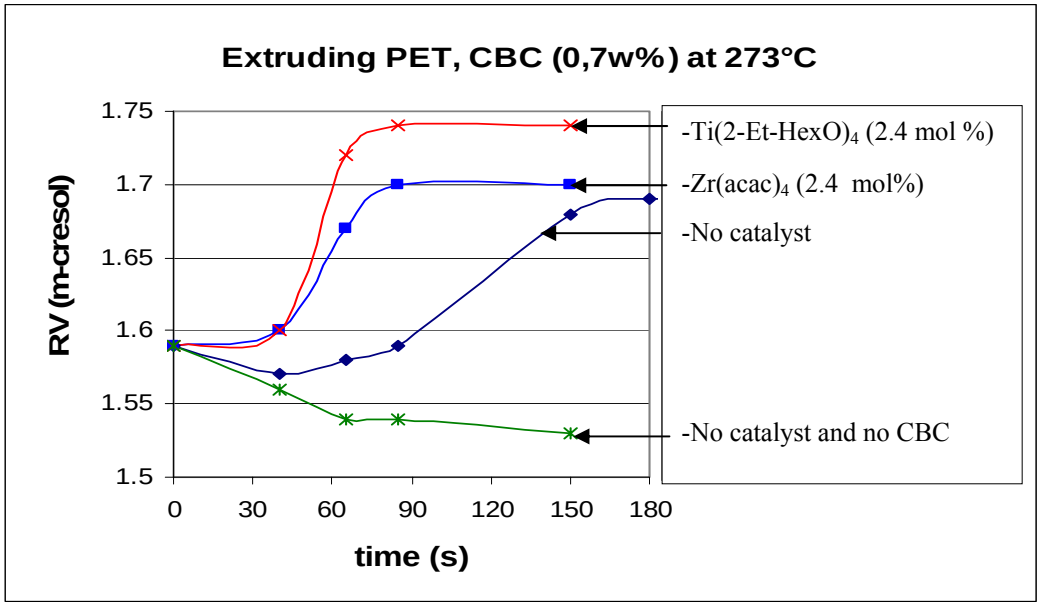


Figure 3.10: The change of the relative viscosity of PET processed with CBC in function of the residence time in the ZSK30 extruder in the presence of $Zr(acac)_4$ or $Ti(OCH_2CH(C_2H_5)CH_2CH_2CH_2CH_3)_4$ (Concentration catalyst, in mol% with respect to CBC).

3.4.6 Properties of chain extended PET

One of the key issues for chain extension is that that the reactions should be fast *and* well-controlled, meaning that no chain branching should take place. In some applications branching is acceptable, sometimes even wanted, but in most applications it is not. The two

most important methods to determine the extent of branching are rheology and SEC (size exclusion chromatography), and both are used here in this work. A series of PET samples was prepared either by chain extension or by SSP, and analyzed by SEC (fig 3.11. and 3.12).

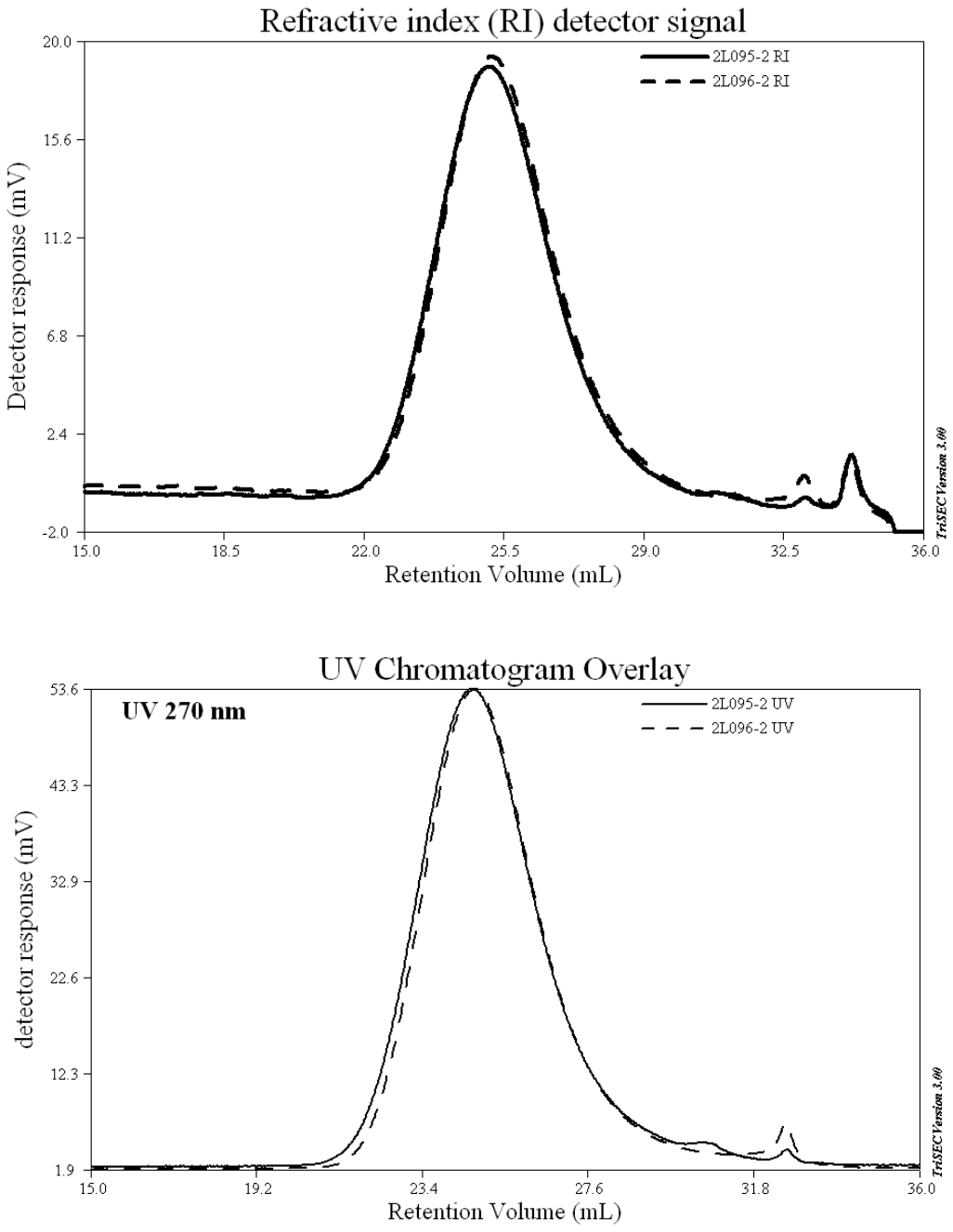


Figure 3.11: The overlays of the SEC curves of PET after chain extension (2L096, dotted line, IV = 0.921 dl/g, η_{rel} = 1.80 dl/g) and after solid-state post-condensation (SSP, 2L095, IV = 0.982 dl/g, η_{rel} = 1.84 dl/g), with UV (bottom) and with RI detection (top).

The relative viscosity of virgin PET was 1.56 dl/g, whereas the η_{rel} of chain extended PET was 1.80 dl/g and of the SSP PET sample 1.84 dl/g. The SEC measurements were carried out with RI (Refractive Index), DV (Differential Viscosity), UV (Ultra Violet light) and with LS (Light Scattering) detection.

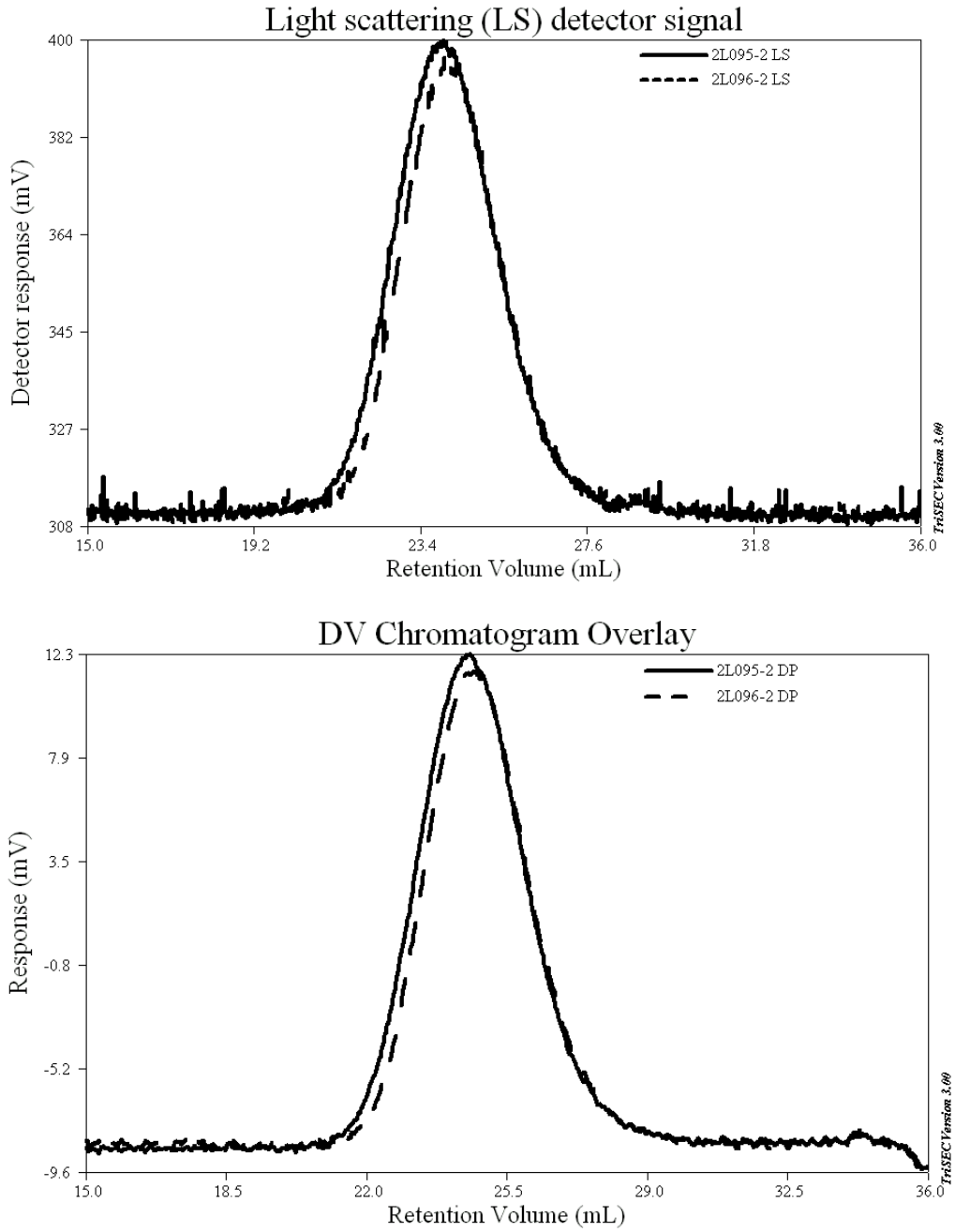


Figure 3.12: The overlays of the SEC curves of PET after chain extension (2L096, dotted line, IV = 0.921 dl/g, η_{rel} = 1.80 dl/g) and after solid-state condensation (2L095, IV = 0.982 dl/g, η_{rel} = 1.84 dl/g), with DV (bottom) and with LS detection (top).

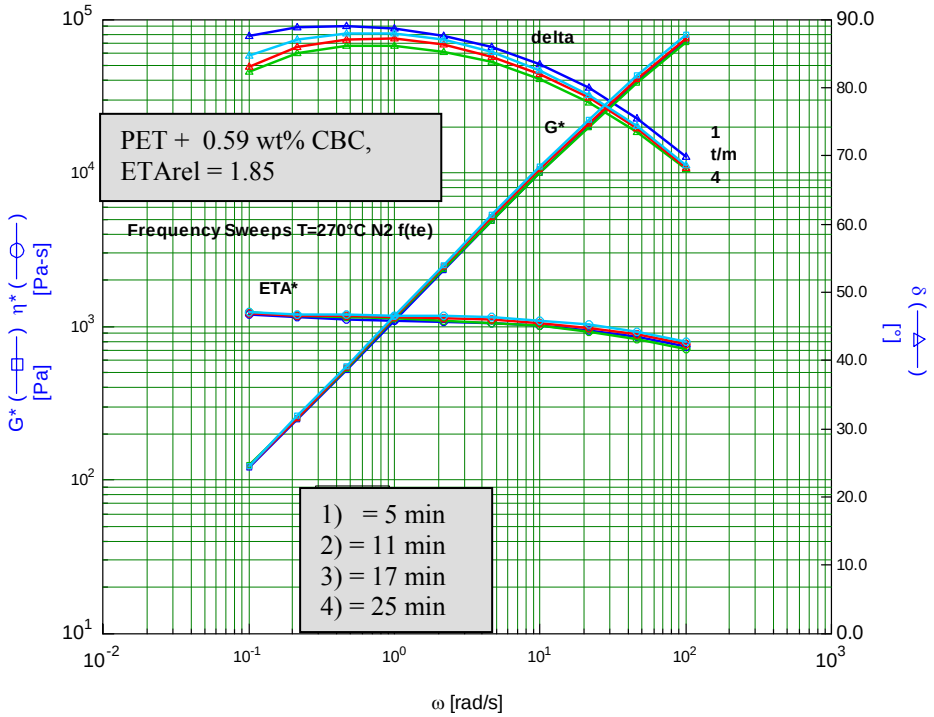
In figure 3.11 and 3.12 curves of the molar masses and the molar mass distributions (MMD) with the various detection techniques are given and in table 3.2 the corresponding numeric values are shown. The overlays of the SEC curves show that the MMDs of SSP PET and chain extended PET are very similar, nearly indistinguishable. From the numeric values (table 3.2) it can be seen that the $\overline{M}_w/\overline{M}_n$ ratio of the chain extended PET and the SSP PET are nearly identical too (2.21 and 2.23, respectively). It is also shown in the table that the $\overline{M}_z/\overline{M}_w$ ratio and the Mark-Houwink exponent a ($[\eta] = KM^a$) are very similar and thus it can be concluded that, according to the SEC data, there is absolutely no indication of branching in the chain extended polymer.

Table 3.2: The molecular structure parameters of chain extended and SSP PET as obtained from multiple detection of SEC separations.

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z/\overline{M}_w$	[η] (dl/g)	Mark-Houwink exponent a
PET 441 SSP (2L095-2)	30,000	67,000	116,000	2.23	1.72	0.982	0.69
PET BAGA + CBC (2L096-2)	28,000	62,000	101,000	2.21	1.63	0.921	0.68

Additional evidence is coming from the rheology measurements. The top graph of figure 3.13 shows the visco-elastic behavior of chain extended PET with a relative viscosity in m-cresol of 1.85 dl/g, and it can be seen that the phase angle δ goes nearly to 90^o, while the slope of the relation between viscosity and frequency (shear rate) only shows a slight shear thinning behaviour, both supporting the conclusion that no detectable chain branching is observable. The visco-elastic properties of a PET sample made by SSP (with a relative viscosity of 1.82 dl/g) are given for comparison (figure 3.13 bottom), and the shape of the curves is quite similar.

More information with respect to the linearity of the chain extended polymers can be extracted from the rheology data and this is discussed in appendix B (see end of this thesis). In short, the ratio between G' (storage modulus) and G'' (loss modulus) is very sensitive for branching and for changes in the molecular mass distribution[16]. The data also clearly show that the chain extension with CBC does not give branching.



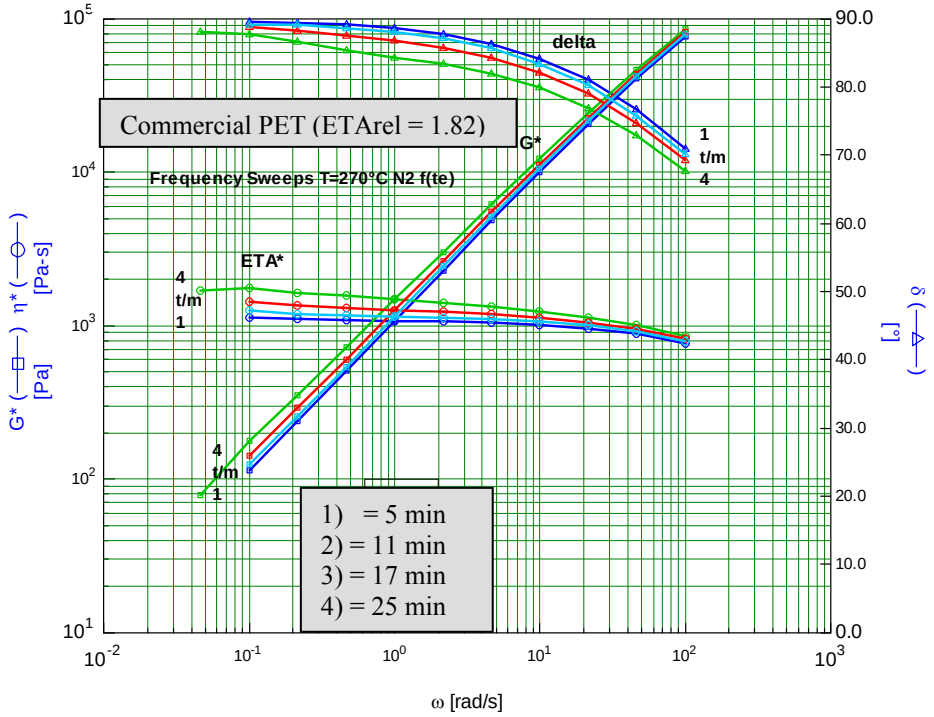


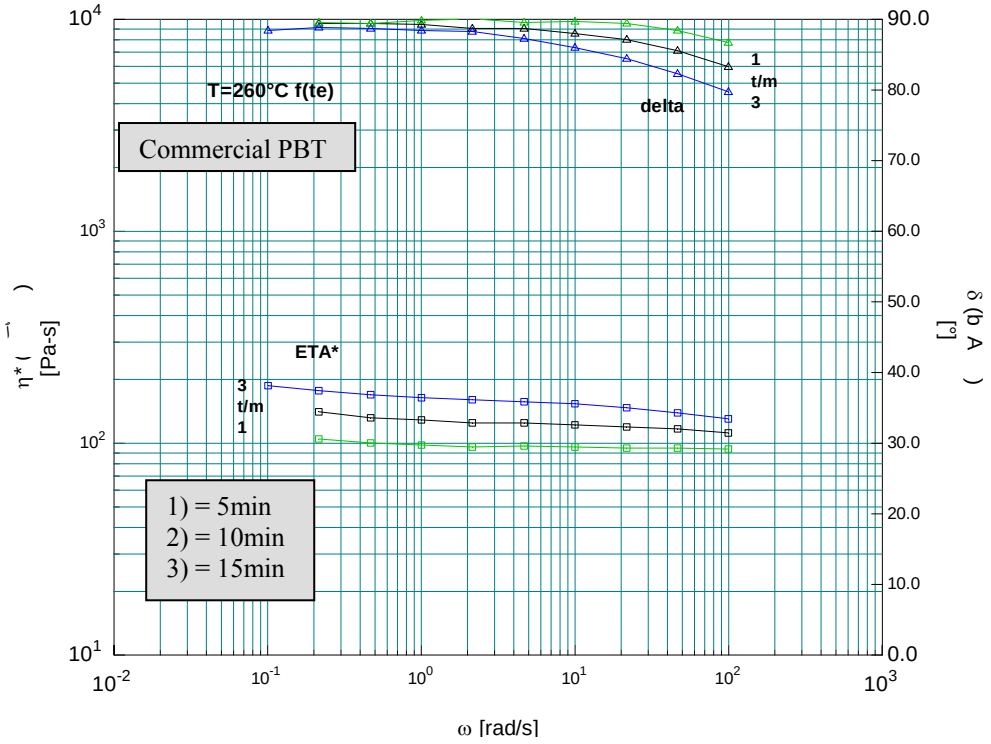
Figure 3.13: The rheology measurements (at 270 °C) of PET prepared by chain extension (top) and with SSP (bottom). In both graphs four viscosity measurements are shown, carried out after 5, 11, 17 and 25 minutes in the melt (The chain extended sample was prepared in 4 min at 280 °C).

During the measurements the viscosity of PET always gradually increases in time due to some post-condensation reactions in the rheometer. The four viscosity curves (and the four δ curves) that are shown in each of the graphs in figure 3.13 were measured after 5, 11, 17 and 25 minutes, respectively. It can be seen that the viscosity of the SSP product (bottom in figure 3.13) increases continuously, whereas the product made by chain extension hardly shows any drift of the viscosity with time, indicating that this product exhibits a higher melt stability. This favorable phenomenon can probably be ascribed to the blocking of the majority of the hydroxy end groups of the polyesters, preventing further polycondensation reactions.
The results of both measurements, SEC and rheology, support the conclusion that there is no indication for any chain branching in the chain extended PET.

3.4.7 Chain extension of poly(butylene terephthalate) (PBT)

The feasibility to increase the viscosity of PBT by chain extension was investigated in the same way as for PET. After PBT was ground and carefully dried (24 hours, 105 ^{o}C, under nitrogen, in vacuum), CBC was added in a glove box. The concentration of hydroxy groups in PBT is higher (88 mmol/kg) than in PET with the same molecular weight, and consequently the concentration of carboxylic acid groups is lower (8 mmol/kg). The higher concentration of hydroxy groups is favourable for chain extension, since CBC reacts mainly with these groups. The experiments were carried out in the micro-compounder (τ = 4 min) at 260 ^{o}C. Also in this case rheology measurements were performed to show the increase of melt viscosity and to confirm the absence of branching. In the top graph figure 3.14 the rheology of the starting virgin PBT is depicted, while at the bottom that of the chain extended PBT is given, showing two different levels of viscosities. It can be seen that the melt viscosity increases substantially from about 150 (top curve) to 400 Pa.s (bottom curve) by adding CBC (0.78 wt %, 31 mmol/kg). The phase angles δ approach nicely in both cases 90^{o} with decreasing frequency (shear rate), indicating that no detectable chain branching has taken place. The slope of the viscosity curve of the chain extended polymers as function of the frequency (shear rate) is flat and not steeper than that of the virgin polymer, again proving that no branching takes place. The linearity of the PBT is unambiguous.
The curves 1, 2 and 3 were measured after 5, 10 and 15 min, respectively. It can be seen that the viscosity of the virgin PBT increases during these measurements, as expected. The chain extended polymer is very stable in the melt and does not increase in viscosity during the measurement. In a commercial production environment it is very important to have melt stable polymers, which consequently give a stable processing behaviour.

PBT T04201 Blank, without CBC



PBT T04201 with CBC

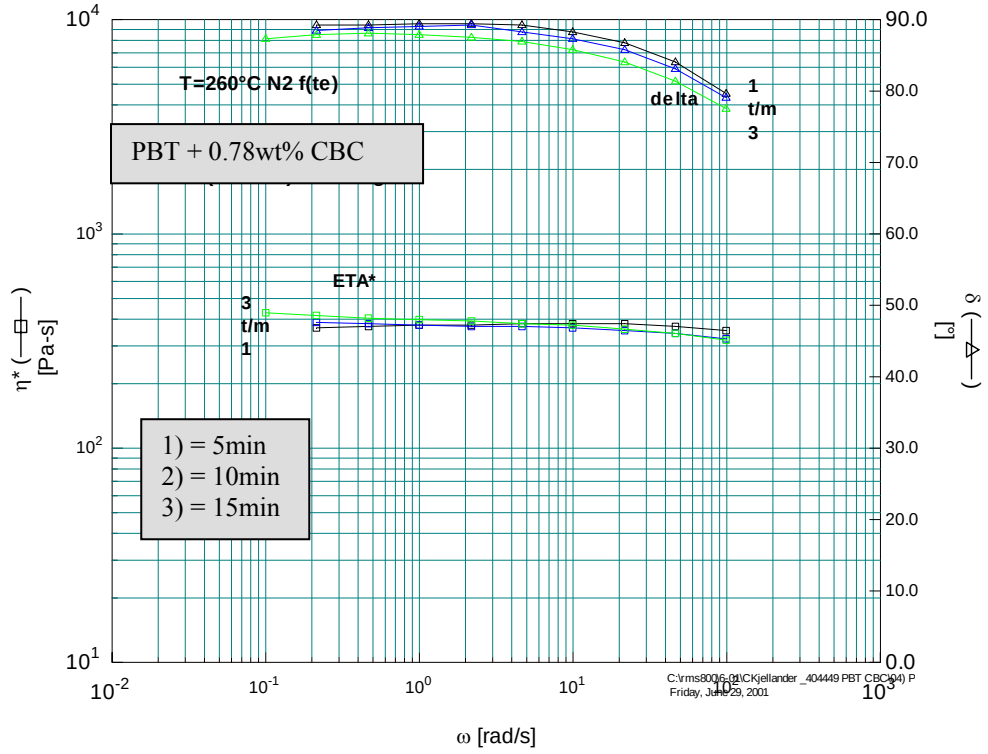


Figure 3.14: Rheology of PBT (at 260 °C) before (top) and after (bottom) chain extension (The chain extended sample was prepared in 4 min at 260°C).

One series of experiments has been done to study the influence of glass fibres on the chain extension process. PBT, with relative viscosity of 1.83 dl/g, was processed with 35 wt% of glass fibres and 1.56 wt% of CBC. After a residence time of 46 sec the relative viscosity increased to 2.34 dl/g, whereas the relative viscosity of the same composition without CBC went down to 1.78 dl/g[17]. These experiments clearly show that chain extension is also applicable in the presence of glass fibres.

3.5 Chain extension with two complementary chain extenders

The focus of this work is to use CBC to react with the hydroxy or amino end groups of polycondensates, whereas the carboxylic acid groups were hardly (2.6) used. But if they would be utilized too, a much more pronounced molecular weight build-up is to be expected. An indispensable condition that has to be fulfilled, to apply successfully two chain extenders simultaneously, is that they do not react with each other. Since one reacts with carboxylic acids and the other one with hydroxy or amino groups, which are complementary groups, it is conceivable, even probable, that some couples of chain extenders will react with each other.

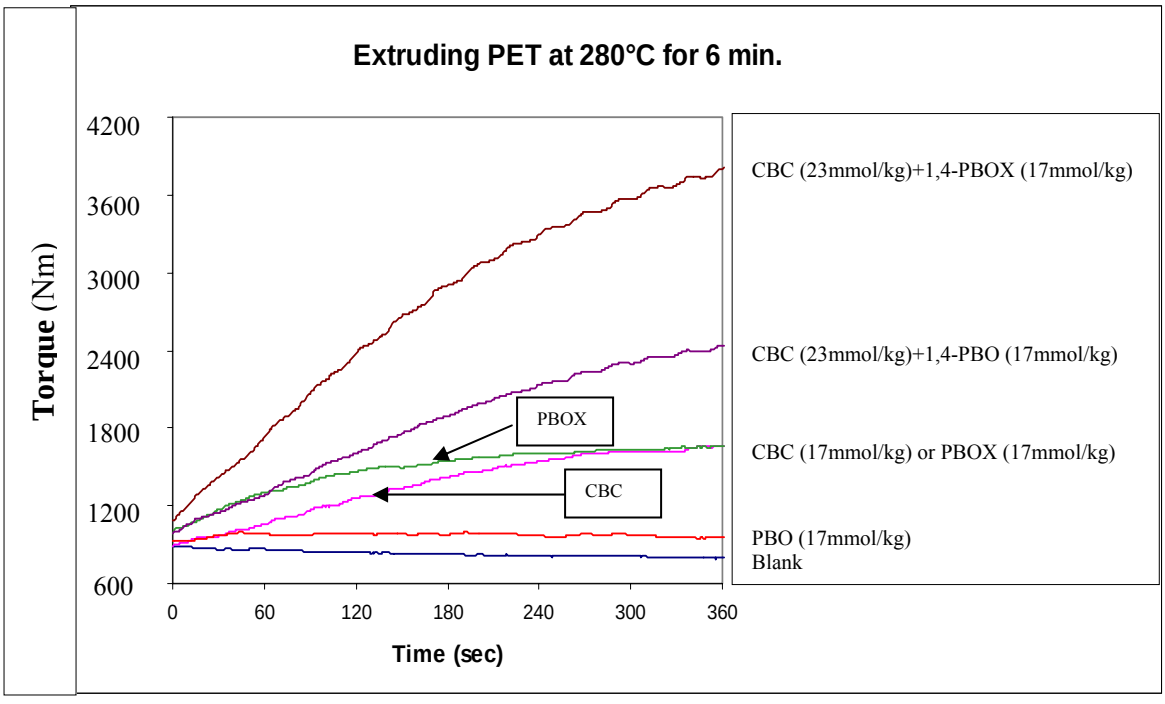


Figure 3.15: The torque of the micro-compounder during the processing of PET in the presence of CBC, 1,4-PBO, 1,4-PBOX, CBC + 1,4-PBO or CBC + 1,4-PBOX.

It was found that Phenylene BisOxazoline (PBO, **1,** fig 3.16) and Phenylene BisOXazine (PBOX, **2**) give the expected additional effect on the increase of the viscosity (figure 3.15).

The efficiency of PBOX[18] is considerably better than that of PBO, which is in contrast with the results of Inata et al.[19]. The results are promising, but this topic is outside the scope of this work. The structures of 1,4-phenylene bisoxazoline (PBO) and 1,4-phenylene bisoxazine (PBOX) are given in figure 3.16.

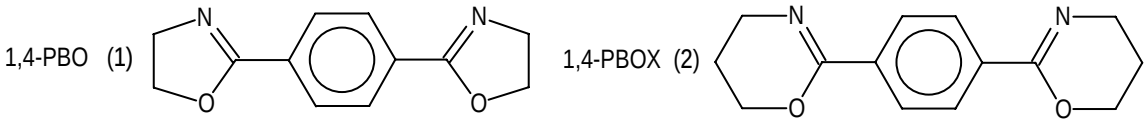


*Figure 3.16: The structure of 1,4-bisphenylene bisoxazoline **1** (PBO) and 1,4-bis phenylene bisoxazine **2** (PBOX).*

3.6 Chain extension of polyamides

3.6.1 Introduction

Polyamides are another important group of polycondensates that are made via a similar production processes as polyesters. Low molecular weight polymers are produced directly in an autoclave, whereas high molecular weight polymers are made in a consecutive step in a solid-state post-condensation process. Nylon-6 and nylon–6,6 are, amongst the nylons, the most important commercial polymers. A number of grades with various viscosities are available on the market to fulfil the needs. The low molecular weight grades are most frequently used, but for high duty applications higher molecular weight polymers are needed. Thus chain extension may be also for nylons an attractive alternative for the laborious SSP process.

3.6.2 Chain extension of nylon-6 with carbonyl biscaprolactam

The enhancement of the viscosity of various polyesters by CBC proceeds via a nucleophilic attack of a hydroxy end group onto one of the carbonyl groups of CBC. Amino groups are more reactive (more nucleophilic) than hydroxy groups, so a faster chain coupling reaction is to be expected with nylons than with polyesters. It is even conceivable that amide groups could react as well with CBC, giving side reactions, possibly forming branched materials.
The experiments were carried out in the micro-compounder and to facilitate dosing the commercial nylon-6 pellets were ground. After that this powder was dried during 18 h at 120 ^{o}C, CBC was added in a glove box, either as a powder or as THF solution. In the latter case THF was removed by drying the samples overnight at 50 ^{o}C in a vacuum oven, in a nitrogen atmosphere. Nylon-6 was processed with CBC for 4 minutes at 265 ^{o}C. The relation between the relative viscosity of nylon-6 (Akulon K123) and the amount of CBC is shown in figure

3.17. It can be seen that CBC is indeed able to increase the viscosity of polyamides, in a comparable way as has been shown with polyesters. The relation between the amount of CBC and the relative viscosity is apparently linear, which enables in a controlled manner the production of materials with selected viscosities.

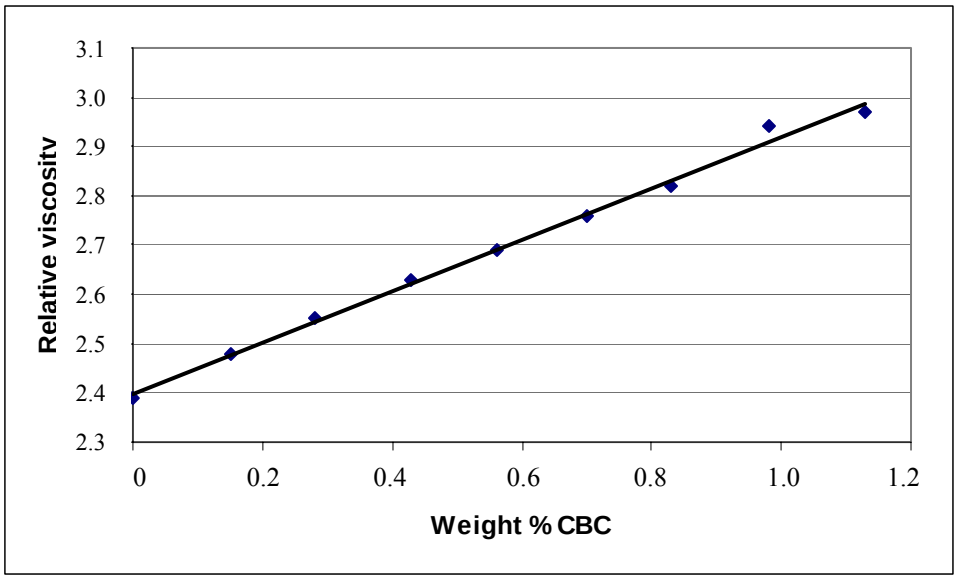


Figure 3.17: The relation between the relative viscosity (in dl/g, in formic acid/water 90/10 wt%/wt%) of nylon-6 (Akulon K123) and the amount of added CBC, after processing (Reaction conditions: τ = 4 min, T = 265 ^{o}C).

The increase of the torque of the micro-compounder, which was an excellent tool to measure the reaction rate between polyesters and CBC, was tested here as well. It takes about 45 seconds to fill the (heated) extruder, close it and to raise the rotation speed of the screws to 80 rpm, before the measurements could be started (point t_o).

However, in this case the torque measurements (figure 3.18) show that the reaction at t_o is already almost complete. Thus, nylon-6 reacts too fast with CBC to measure the reaction rate, yielding the desired viscosity level already in the short pre-compounding step.

Since this reaction is so fast, there was no need to study the influence of catalysts with the objective to increase the rate.

It can be concluded that chain extension is also for nylon-6 a serious alternative for the SSP process, for producing high molecular weight polymers. Starting from two base grades (e.g. η_{rel} of 2.3 dl/g and 2.8 dl/g) the whole range of commercial viscosities (η_{rel} between 2.3 dl/g and 3.6 dl/g) can be covered by chain extension.

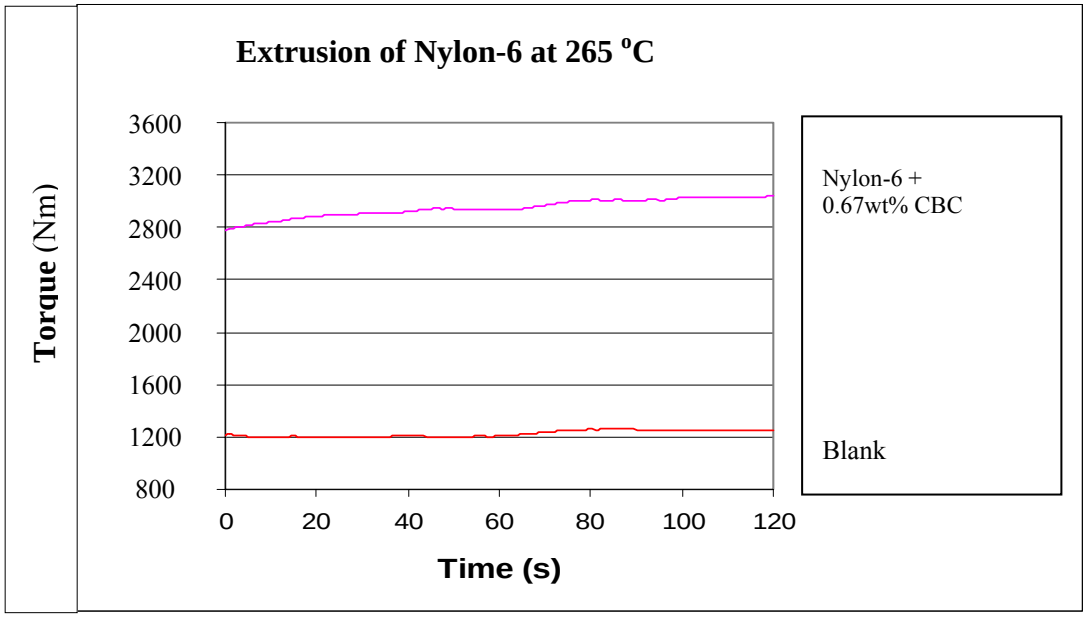


Figure 3.18: The torque of the micro-compounder during processing nylon-6 in the presence of CBC.

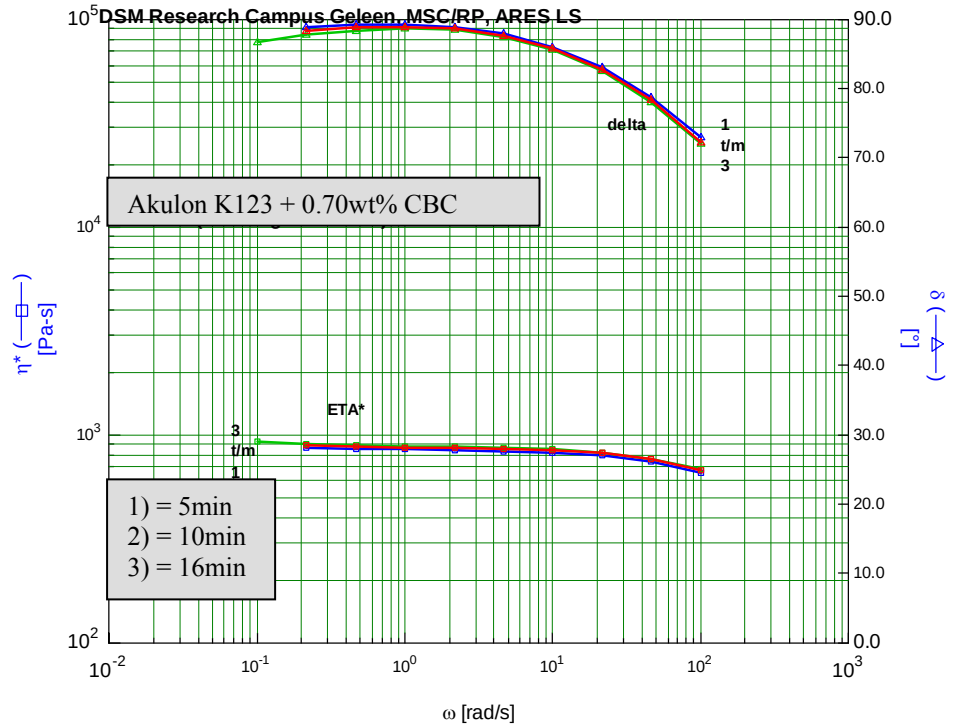
3.6.3 Properties of nylon-6

Rheology measurements were used to study the degree of branching. The bottom graph in figure 3.19 presents the data for the starting nylon-6 (Akulon K123) and the graph at the top is of the chain extended product. It can be seen that the melt viscosity substantially increases (from 400 to 900 Pa.s) by processing nylon-6 with stoichiometric amounts of CBC (0.70 wt%). The phase angle nicely reaches 90°, indicating that the chain extended product is strictly linear. The relation between the viscosity and the frequency (shear rate) has a flat slope, indicating the absence of branching as well. Apparently the amide groups have not reacted with CBC, since that would give branched polymers.

As observed for PET and PBT, the viscosity of the virgin nylon-6 polymer increases during the measurement due to post condensation reactions, whereas the viscosity of the chain extended polymer remains constant.

The most important difference between the SSP and the chain extended polymer is that the latter is actually a “copolymer”, with about 1 wt % of “comonomer”. In order to determine the influence of the “comonomer”, the thermal properties were analyzed. In table 3.3 the thermal properties of some chain extended products is given and, for comparison, also the results with some commercial products with the same range of viscosities are shown. For the preparation of these particular samples two complementary chain extenders were used. It can be seen that the first melting enthalpy of the chain extended polymer is much lower than that of the SSP product.

T = 230 °C



T = 230 °C

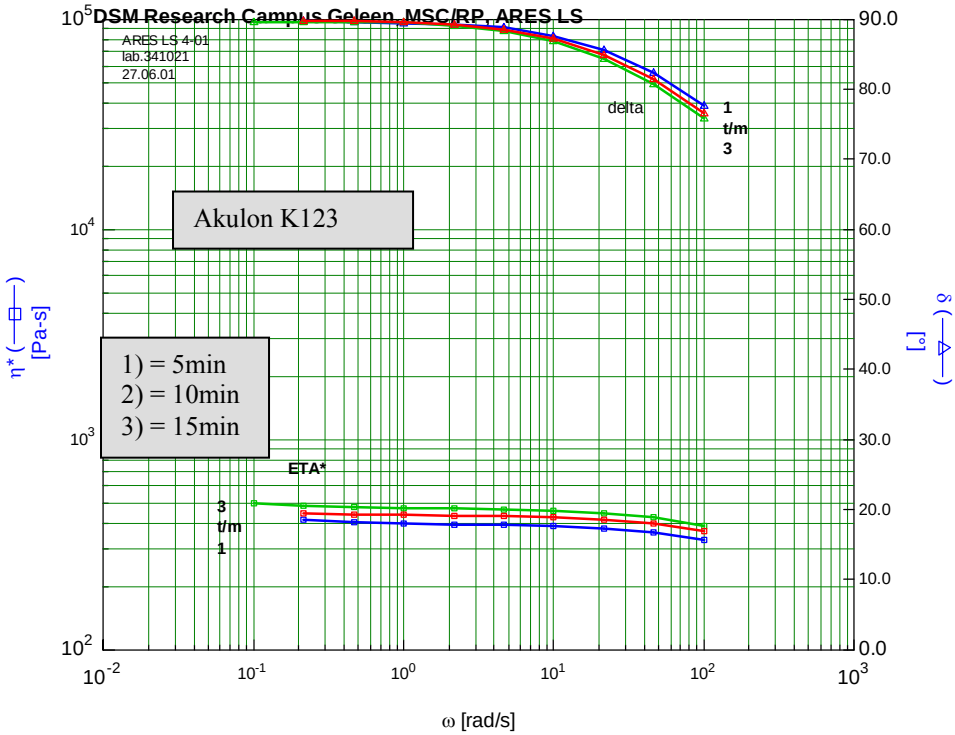


Figure 3.19: Rheology of virgin nylon-6 (bottom; Akulon K123) and a chain extended nylon-6 (top) (The chain extended sample is prepared in 4 min at 265°C).

This is to be expected, since the SSP products are heated for a long time in the solid state, which is actually an annealing procedure, giving products with a higher crystallinity. The crystallisation temperature (T_{cr}) is, in the absence of nucleating agents, strongly dependent on coincidental impurities, which makes in this case a mutual comparison unreliable. The second melting temperatures (T_{m2}) are the most important characteristics. These data show that the melting temperatures of the nylons decrease about 3 ^{o}C, after they have reacted with about 1 wt% of chain extenders. The second melting enthalpy shows that the extent of crystallisation is the same for both types of polymers, and is thus not influenced by chain extension. The decrease of the second melting enthalpy with increasing viscosity is a normal feature that is observed for virgin (post-condensated) as well as for the chain extended polymers.

The conclusion is that the "comonomers", introduced by chain extension, have some influence on the melting temperature, but not on the melting enthalpy. The degree of crystallinity, which determines to considerable extent the mechanical properties, is therefore not affected.

Table 3.3: DSC analysis of chain extended and SSP nylon-6.

Sample	η_{rel} (dl/g)	ΔH_{m1} (J/g)	T_{cr} (^{o}C)	T_{m2} (^{o}C)	ΔH_{m2} (J/g)
K124*	2.52	74	189	224	70
K130*	3.00	98	176	224	64
K136*	3.60	98	176	225	61
F124 + 0.3%PBO+0.35% CBC	3.02	66	187	222	66
F124 + 0.6%PBO+0.70% CBC	3.77	66	185	221	61

*Commercial DSM grades; η_{rel} in formic/water mixture 90wt%/10wt%. ΔH_{m1} and ΔH_{m2} = Melt enthalpy of the first and second heating cycle, respectively; T_{cr} = Crystallization temperature and T_{m2} = melting temperature in second cycle; PBO = phenylene bisoxazoline.

3.6.4 Chain extension of nylon-6,6

3.6.4.1 Chain extension of nylon-6,6 with carbonyl biscaprolactam

The same experimental procedure as for nylon-6 was applied in a limited number of experiments with nylon-6,6, to show the generality of the concept for nylons. Thus, nylon-6,6 pellets were ground and dried at 90 ^{o}C for 18 h, in a nitrogen atmosphere.

CBC powder was mixed with nylon-6,6 powder in the glove box. Nylon-6,6/CBC mixtures were processed in the micro-compounder for 4 minutes at 280 ^{o}C. The increase of the

viscosity as a function of the amount of added CBC is shown in figure 3.20. The same features are observable as with the other polycondensates. A substantial increase in viscosity is obtained and the relation between the relative viscosity and the amount of CBC seems to be linear. Also in this case the relation still applies above stoichiometric amounts ([CBC] = 2[NH_2]) of CBC (0.55 wt%).

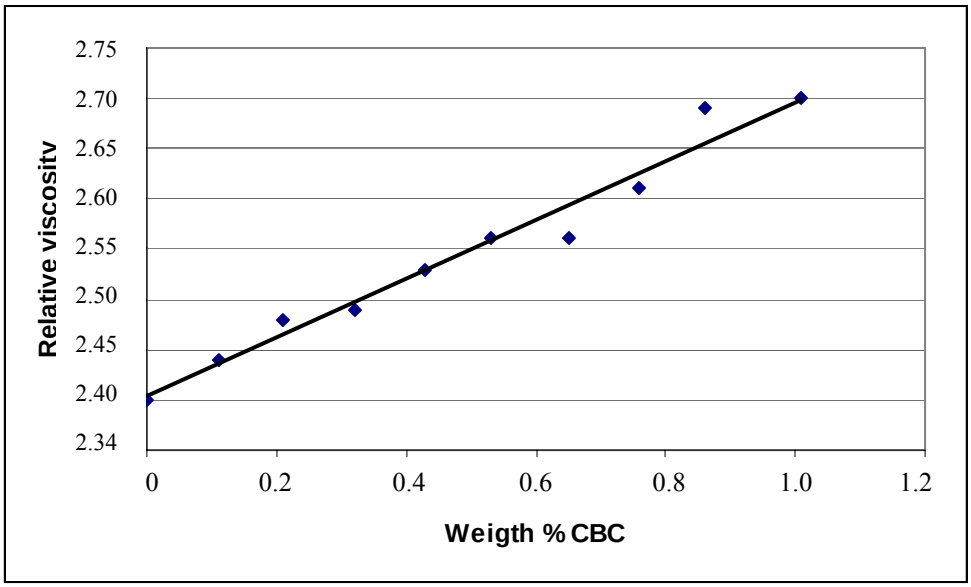


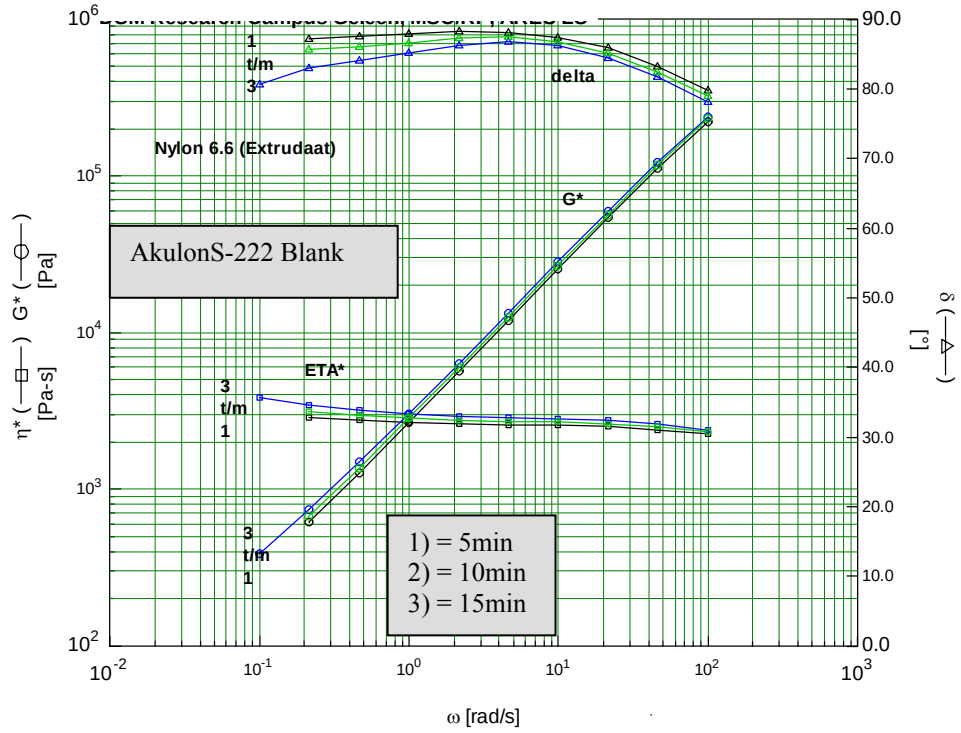
Figure 3.20: Relation between the relative viscosity of nylon-6,6 (in dl/g, in formic acid/water 90/10 wt%/wt%) and the amount of added CBC (Reaction conditions: T = 280 °C, τ = 4 min).

3.6.4.2 Properties of chain extended nylon-6,6

The rheology of virgin nylon-6,6 and of chain extended nylon-6,6 was measured after 5, 10 and 15 minutes of residence time in the rheometer. The phase angle for both samples is now slightly below 90°, indicating that some branching is already present in the virgin material (figure 3.21). The increase of the melt viscosity, from about 300 for the virgin nylon-6,6 to 500 Pa.s for the chain extended polymers, can be seen. The chain extended polymer has more or less the same visco-elastic behaviour as the starting sample, meaning that no additional branches have been formed. Furthermore, it can be seen that also in this case the viscosity of the chain extended polymers is more stable, although the difference is smaller than for the other polycondensates. A preliminary conclusion may be that the results for nylon-6,6 are more or less similar to those of nylon-6.

In general it can be concluded that the results with the nylons are comparable with those obtained with the polyesters. The most important difference is that the reaction rate of nylons with CBC is much higher. Thus, CBC is applicable in both types of polycondensates, in spite of the difference in end groups.

T = 270 °C



T = 270 °C

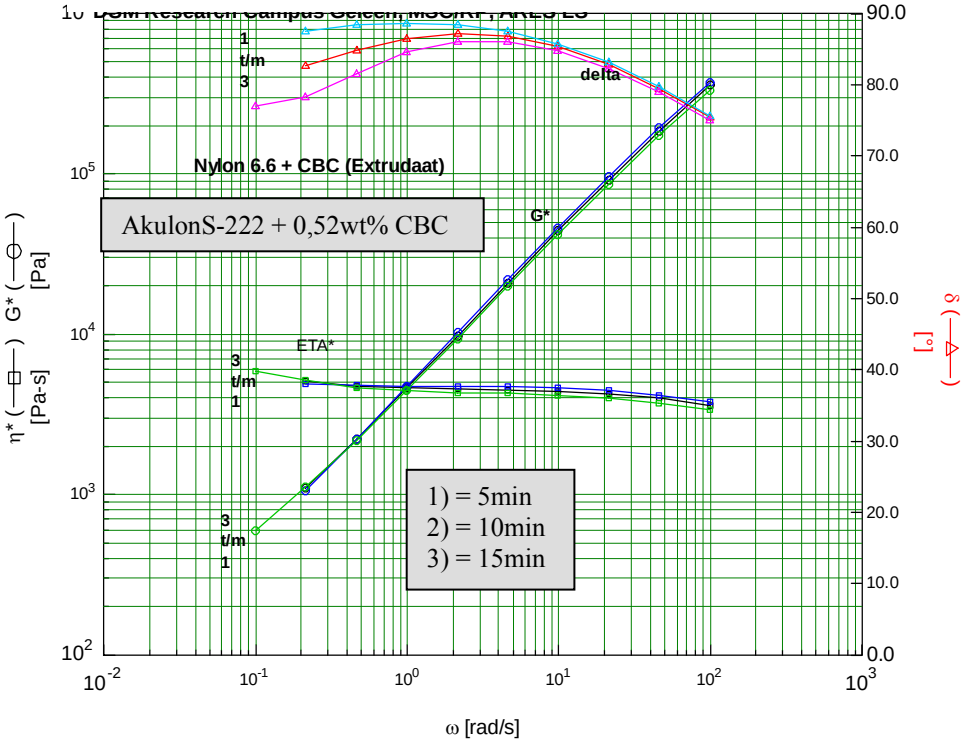


Figure 3.21: The rheology of nylon-6,6 (top) and of the chain extended nylon-6,6 (bottom). (The chain extended sample was prepared in 4 min at 280°C).

3.7 Efficiency of chain extenders

The determination of the efficiency of CBC in the chain extension reactions is difficult. The fact that the viscosity still increases if more than the stoichiometric amount of CBC is added indicates that not all the CBC is used effectively.

It turned out that a quantitative analysis of the chemistry of the polymers is difficult. Furthermore, under the harsh experimental conditions (about 300 ^{o}C) always some degradation will take place, making the reliability of the analysis even more doubtful. This is known for the polymers, but holds probably even more for reactive chain extenders. In spite of these limitations, some efforts have been done to gain insight in the efficiency of the chain extension reaction. For this purpose the concentrations of the amino and carboxylic acid end groups in nylon-6 were analyzed, before and after chain extension. These data were compared with those of a SSP product (table 3.4). The viscosities of the chain extended nylon-6 (Akulon F126) and the SSP product (Akulon F130) are not exactly the same, but close enough to allow some preliminary calculations. The concentration of CBC was matched with the concentration of the amino end groups ([CBC] = 2[NH_2]). In spite of this match and in spite of the fact that the reaction with nylons is expected to go to completion (figure 3.18), the concentration of the amino groups still does not go to zero. Thus even with nylon-6, which is known to be very reactive with CBC, it is not possible to consume all the amino end groups under these conditions. In contrast to PET (table 3.1), there is in this case no indication that the carboxylic acid concentration decreases. A possible explanation could be that the amino groups are much more reactive than hydroxy groups, consuming all the CBC before the less reactive carboxylic acid groups are able to react.

Table 3.4: Analytical data of the end groups and viscosities of nylon-6 (processed at T = 265 ^{o}C, τ = 4 min).

	Blank Akulon F126	Chain extended Akulon F126	SSP product Akulon F130
[CBC] (mmol/kg)	0	29	-
[NH_2] (mmol/kg)	58	16	38
[COOH] (mmol/kg)	52	52	45
η_{rel*} (dl/g)	2.61	3.01	3.12

*In formic acid/water 90/10 wt%/wt%

The end group concentration of the chain extended product (16 + 52 = 68 mmol/kg) is significantly lower than that of the SSP product F130 (38 + 45 = 83 mmol/kg). This is not in

line with the viscosities, which are quite similar, although the end group modification can have some influence on the viscosity[20]. Nevertheless, the difference in the concentration of the end groups is large and a possible explanation could be that part of the CBC has reacted only once, and is still able to react with a second chain. In that case a part of the amino groups (and CBC) is consumed, without having any effect on the viscosity. One can speculate that this difference in end group concentration of the SSP and the chain extended products (83 – 68 = 15 mmol/kg) is due to CBC that has reacted only once, meaning that about 50 % (15 of the 29 mmol) has not yet reacted effectively. Another rough calculation can be made as follows. The decrease in the concentration of the amino end groups (58 – 16 = 42 mmol/kg), due to chain extension, is twice as high as the difference of the amino end groups of F126 and F130 (58 – 38 = 20 mmol/kg). This suggests again that merely about half of the CBC is effective. Although both calculations are far from accurate, both indicate that the efficiency of the chain extension process is still far away from the theoretical value. Nevertheless, the practical results remain very valuable, since the viscosities of the whole range of commercial products can be covered.

3.8 Conclusion

High molecular weight poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), nylon-6 and nylon-6,6 grades have been prepared, by using chain extenders. This procedure offers a technology to circumvent the laborious solid-state post-condensation (SSP) process. A simple compound, CBC (carbonyl biscaprolactam), is found to be suitable to increase molecular weights of polymers having hydroxy or amino end groups. The reaction of CBC with polyesters is completed within 3 minutes, whereas the reaction with nylons is already finished in less than 1 minute. The amino groups of nylons are more reactive than the hydroxy groups of polyesters. The viscosity of all the polycondensates increased linearly with the amount of CBC, enabling a controlled preparation of desired viscosity levels.

The chain extension rate depends on a physical process (mixing) and a chemical process. The reaction rate in the small-scale DSM micro-compounder is about a factor two lower than in a ZSK30 twin-screw extruder. This is completely attributed to the better mixing capabilities of the ZSK30 (physical process).

To increase the reaction rate of CBC with polyesters, the influence of catalysts, selected on the basis of their performance in model reactions (*chapter 2*), was studied. It is found that tetra alkoxy titanates and zirconates and aluminium and zirconium acetyl acetonates are effective in increasing the reaction rate. Amongst these the titanium catalyst,

$Ti(OCH_2CH(C_2H_5)CH_2CH_2CH_2CH_3)_4$, and the zirconium catalyst, $Zr(acac)_4$, are particularly suitable. In the ZSK30 and in the presence of these catalysts the chain extension reaction of polyesters is completed in about one minute. The chain extension concept allows the preparation of almost the whole range of viscosities of the commercial PET, PBT, nylon-6 and nylon-6,6 grades, starting from only two base grades of each polymer.

By performing SEC and rheology measurements it is shown that all the chain extended polycondensates are strictly linear, which is important for many applications, but in particular for fibres.

In conclusion, chain extension of PET, PBT, nylon-6 and nylon-6,6 offers a valuable alternative for the currently used laborious solid-state polymerisation process (SSP).

3.9 Experimental section

Materials

CBC was obtained from DSM, New Business Development, ALLINCO® (purity > 99 %, HPLC) and used as received. PET grades used were: BAGA, PET441, PETA06101 from Acordis and were used as received. ARNA T04201 (PBT) and Akulon K123, F126C, F130C and F136C (nylon-6) and S222 (nylon-6,6) were obtained from DSM. All solvents and catalysts were purchased from Aldrich or Acros and used without any purification.

Instrumentation and methods

The DSM micro-compounder has a volume of 15 ml. A divisible mixing compartment containing two conical screws with a length of 150 mm forms the compounding unit. The mixing time can be varied by a re-circulation loop. The torque data were collected by an automatic data acquisition system (RS232). The set temperature was 280 °C for PET and nylon-6,6, 265 °C for nylon-6 and 260 °C for PBT. A screw speed of 80 rpm was applied.

The ZSK-30 of Werner&Pfleiderer is a double screw extruder with screw diameter of 30 mm, the channel depth is 4.7 mm and the l/d value is 39. The throughput was varied from 3 to 24 kg/h, thereby changing the residence time from 180 to 40 seconds and the barrel temperature was set at 270 °C for PET (figure 3.22).

Company	Proj.Rev	Mach ID	Product	S.L-10	B.Length	Name	Date
dsm	PET-CBC	ZSK30	pet	1324	1320	vv	03/29/2002

Description:

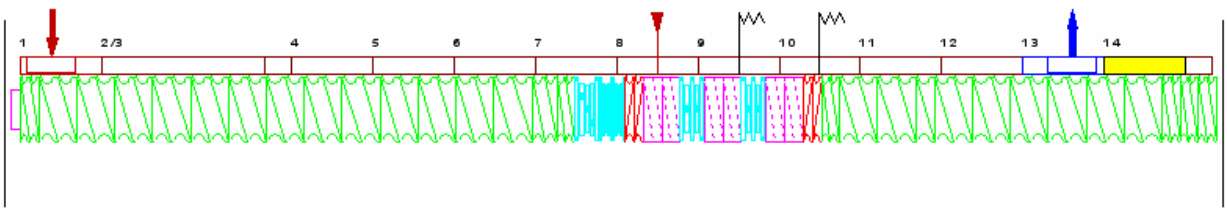


Figure 3.22: Screw design of the ZSK30.

The SEC spectra were recorded with a Hewlett Packard HP 1090 liquid chromatograph, provided with a UV-DAD detector system. The refractive index was measured with a HP 1047A differential refractometer at 35 ^{o}C and the viscosity with a Viscotek H502B at 38 ^{o}C. The Viscotek data manager was DM400. The signal of the light scattering was collected at an angle of 90 ^{o}. The column set (3 PPS PFG linear XL, 7μ8*300 mm) can handle the molecular weight mass ranges from 100 to 1,000,000D. The eluent was hexafluoro isopropanol (T = 35 ^{o}C) with 0.1 wt % potasium trifluoro acetate and the flow rate was 0.4 ml/min.
The computer operating system has three software systems: a) HP chemstation for the operation of the UV data of the chromatograph, b) Astra version 4.73.04 for the operation of the MALLS, c) Viscotek software TriSEC 3.0 or OmniSEC 2.0 to collect the signals and process the data.
The differential scanning calorimetry analysis was carried out on a Perkin Elmer DSC-7. Standard heating rates of 20 ^{o}C/minute were used, with samples of 5-20 mg in a dry nitrogen atmosphere.
Low frequency DMS measurements: Dynamic Mechanical Measurements were performed with a Rheometric Scientific ARES-LS dynamic analyzer equipped with ϕ25 mm Invar parallel plate geometry. The plate-plate distance was set at 1.8 mm. Isothermal frequency scans (from 100 rad/s to 0.1 rad/s) were performed (in shear) at the appropriate temperature in a dry nitrogen atmosphere.
The DMTA measurements probe the complex dynamic modulus (G*) and phase angle (δ) at the appropriate temperature, as function of the angular frequency (ω).
^{1}H-NMR was done on a Brucker ACF 300, equipped with a 5 mm dual probe head at a frequency of 300 MHz.
The relative viscosities (η_{rel}) of solutions of PET in m-cresol at concentration c = 0.5 g/dl were measured using an Ubbelohde viscosimeter at 25 ^{o}C. The relative viscosities (η_{rel}) of solutions of nylon-6 and nylon-6,6 in formic acid (90 wt% formic acid/10 wt% water) at concentration c = 0.5 g/dl were measured using an Ubbelohde viscosimeter at 25 ^{o}C.
Determination of the end groups of polyesters and nylons was performed as follows. Polyesters were dissolved in 1,1,1,3,3,3,-hexafluoro-2-isopropanol (HFIP) together with 1-hexadecanol as internal standard. The hydroxy groups were esterified with antracenoyl chloride and the analysis was done by HPLC with UV detection. The concentration of the amino groups in polyamides was determined by dissolving the nylons in m-cresol and by titration of the amino groups with ethanolic HCl solution. The titration was followed by means of potentiometric detection electrodes.
Carboxylic acid groups of polyesters were determined by dissolving the polyesters in o-cresol/2-t-butylphenol, after diluting the solution with chloroform the mixture was titrated potentiometrically with tetrabutyl ammonium hydroxide in 2-propanol. Carboxylic groups in polyamides are determined by dissolving the samples in 2-t-butylphenol. After diluting the solution with chloroform the mixture was titrated potentiometrically with tetrabutyl ammonium hydroxide in 2-propanol.

Synthesis

Sample preparation of PET (drying, grinding, CBC addition)
Pellets of PET were ground in a SPEX 6750 Freezer mill. Then this polymer was dried at 140 ^{o}C for 48h under vacuum (< 200 mbar) in a nitrogen atmosphere. CBC was added as a powder or dissolved in THF (1 wt% CBC in THF) and then an appropriate amount of the powder or THF solution was added to the ground PET in a glove box under a nitrogen atmosphere. The

samples prepared via the solution route were subsequently dried at 50 ^{o}C for18 h under vacuum (< 200 mbar) in a nitrogen atmosphere, and stored in the glove box until use.

Sample preparation of PET with catalysts
For the preparation of samples with catalyst the same procedure was followed as described above. The catalyst was added to the same THF solution in which CBC was dissolved.

Sample preparation of PBT
PBT pellets were ground in a SPEX 6750 Freezer mill. Then this polymer was dried for 24 hours at 105 ^{o}C, in vacuum (< 200 mbar) in a nitrogen atmosphere. CBC powder was added in an appropriate amount to the ground PBT in a glove box under a nitrogen atmosphere. The samples were stored in the glove box until use.

Sample preparation of nyon-6
Pellets of Akulon K123, Akulon F126C, Akulon K130C and Akulon F136C were ground in a SPEX 6750 Freezer mill. Then this polymer was dried at 120 ^{o}C for 18h under vacuum (< 200 mbar) in a nitrogen atmosphere. CBC was added as a powder or dissolved in THF (1wt% of CBC in THF) and then an appropriate amount of this solution was added to the ground nylon-6 in a glove box under a nitrogen atmosphere. The samples prepared via the solution route were dried at 50 ^{o}C for 18 h under vacuum (< 200 mbar) in a nitrogen atmosphere, and stored in the glove box until use.

Sample preparation of nylon-6,6
Pellets of Akulon S-222 were ground in a SPEX 6750 Freezer mill. Then this polymer was dried at 120 ^{o}C for 18h under vacuum (< 200 mbar) in a nitrogen atmosphere. CBC was added as a powder or dissolved in THF (1wt% of CBC in THF) and then an appropriate amount of the powder or of the THF solution was added to the ground nylon-6,6 in a glove box under a nitrogen atmosphere. The samples prepared via the solution route were dried at 50 ^{o}C for 18 h under vacuum (< 200 mbar) in a nitrogen atmosphere, and stored in the glove box until use.

Handling of the micro-compounder
The DSM micro-compounder was heated to the appropriate temperature (280 ^{o}C for PET and nylon-6,6, 265 ^{o}C for nylon-6 and 260 ^{o}C for PBT). While dosing the polymer powder the screw speed was set to 60 rpm (revolutions per minute). After dosing had been completed (about 45 sec) the screw speed was increased to 80 rpm and that point was taken as the start of the experiment t_o. During the compounding step the torque on the screws was measured continuously and the data were collected and processed by a computer. The micro-compounder was discharged after the appropriate compounding time (mostly between 4 and 6 minutes) and the strands were collected for further analysis.

Handling of the ZSK30 extruder
PET pellets were dried in a tumble dryer (12h at 140 °C in a dry nitrogen atmosphere) and packed in sealed bags to prevent the up-take of moisture. Next, the pellets were tumbled in a drum roller under dry nitrogen and CBC was stuck onto the pellets by using 0.1 wt % of Primol 352 oil. If catalysts were used, they were mixed with CBC in a glove box under dry nitrogen. The feeder and the inlet of the ZSK30 were flushed with dry nitrogen, while a plastic foil covered the hopper. The barrel temperature was set at 270 ^{o}C, and the temperature of the polymer melt was 273 °C. The screw speed was set at 100 rpm and the throughput was between 2 and 24 kg/h, resulting in different residence times. In these experiments a standard screw design was used as depicted in figure 3.22.

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A one step process to prepare blocked isocyanates

Abstract

A new method to prepare blocked isocyanates, in a one step process from carbonyl biscaprolactam (CBC) and amines or alcohols, is developed. CBC has been showed to be useful as chain extender for polyesters and nylons, in which it couples two polymer end groups. After the first reaction step reactive intermediates are formed, and it was investigated whether this reaction could be stopped halfway through to isolate these useful intermediates.

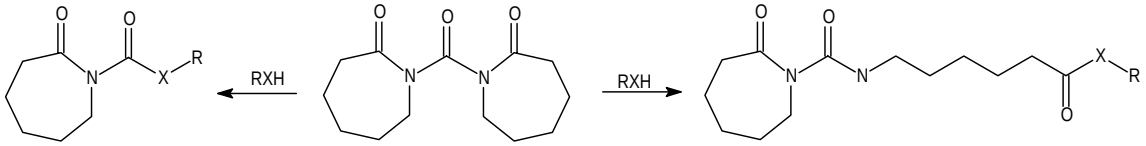
Amines substitute very selectively one of the caprolactam rings of CBC, giving blocked isocyanates (BIs, caprolactam carbamates) in nearly quantitative yield. The reaction mixture contains only the corresponding blocked isocyanate and caprolactam, if stoichiometric amounts of the starting compounds are used. Caprolactam is quite well water-soluble and can easily be removed by an aqueous extraction. A number of mono-, di- and triamines were used and they all rendered similar good results. It appears to be a general method to make a wide variety of blocked isocyanates.

The reaction of CBC with primary alcohols gives BIs as well, but only if suitable catalysts are used, such as $MgBr_2$, $Ti(OR)_4$ or $Zr(OR)_4$. In that case one of the caprolactam rings of CBC opens selectively. The yield is somewhat lower than with amines, but still about 90%.

4.1 Introduction

The aim of previous chapters was to find suitable chemicals that were able to increase the viscosity of polymers by means of a coupling reaction during the extrusion step. This chain extension process implies that two successive reactions take place, as depicted in scheme 3.2. Carbonyl biscaprolactam (CBC) is a special kind of chain extender since the proposed intermediates are either activated carbonates or blocked isocyanates (caprolactam carbamates) as depicted in scheme 4.1. After substitution of the first caprolactam ring the chemical nature of the central carbonyl group is changed, so it was anticipated that the reactivity of this intermediate product would be different than that of CBC.

In scheme 4.1 two possibilities are given for the first reaction step. If the reaction goes to the left side the product is either an activated carbonate (if X = O) or a blocked isocyanate (if X = NH). Since the caprolactam ring can be opened the reaction can go to the right as well and then the product is always a blocked isocyanate, independent of the nature of X. The existence of these two fundamentally different reaction paths, both leading to possible interesting products, makes CBC a unique chemical. So, if we are able to find conditions to stop the reaction halfway through, for instance by lowering the temperature, this method could lead to a new route to make blocked isocyanates or activated carbonates.



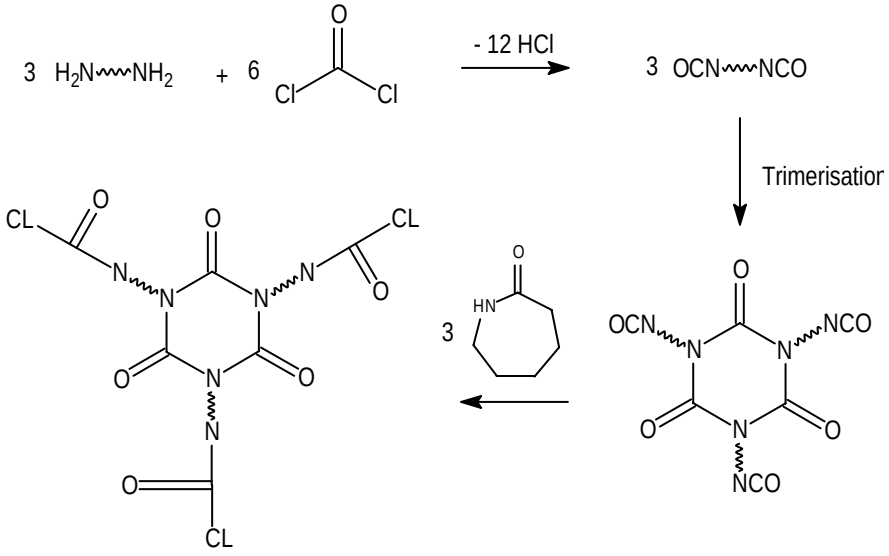
Scheme 4.1: The first possible steps of the reaction of amines (X = NH) or alcohols (X = O) with CBC at temperatures below 150 °C.

Meyer has indicated in his publication[1] (in 1956) that hexamethylene diamine yields blocked isocyanates with CBC, but unfortunately without giving experimental conditions, yields or analytical data.

4.2 Commercial blocked isocyanates

Blocked isocyanates are interesting products, since they have proved to be valuable crosslinkers for hydroxy functional coating resins[2]. Furthermore, they could, in principle, react with hydroxy or amino groups of respectively polyester or polyamide thermoplastic polymers at elevated temperatures (> 150 °C). Quite a number of commercial crosslinkers are available, for instance from Bayer, Degussa, Nippon Polyurethane, Creanova, Takeda and Asahi. The vast majority of the BIs crosslinkers are tri-functional, made by the trimerization

of diisocyanates. Difunctional BIs are, to the best of our knowledge, hardly used in coatings because of the too low functionality and the too high volatility. As a result, commercial difunctional BIs are hardly available. Hexamethylene diisocyanate (HDI) or isophoron diisocyanate (IPDI) are the most commonly employed compounds for making trimers. These difunctional isocyanates are prepared from the corresponding diamines and phosgene. During the trimerization reaction of diisocyanates one of the isocyanate groups is built-in in the isocyanurate ring, whereas the second group is still free (scheme 4.2). The trimerization reaction produces, besides trimers, also oligomers of the trimers that are difficult to separate from the trimers, and consequently commercial products are always mixtures [3].



Scheme 4.2: The current preparation of blocked isocyanates (CL = ε-caprolactam).

Isocyanates are often "blocked" to reduce their reactivity and toxicity temporarily. Blocking of the isocyanates enables the mixing of the crosslinker with a coating resin without the risk of premature gelation. The blocking reaction is reversed on heating, yielding thereby the free isocyanate again, which can subsequently react with amino or hydroxy groups of coating resins. Caprolactam is most frequently used as a blocking agent because it is cheap and non-toxic and the deblocking temperature (> 150 ^{o}C) is in a good range for practical use.

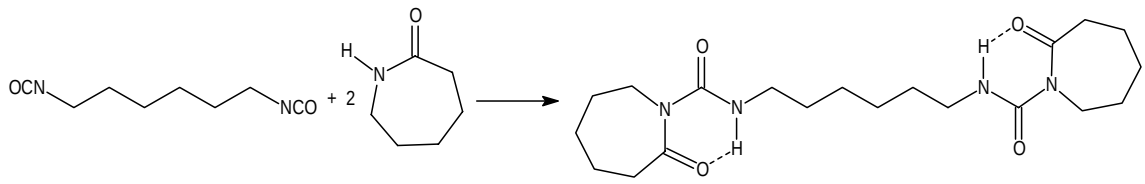
The blocking reaction is not quantitative, if stoichiometric amounts of the reactants are used, and consequently commercial products are therefore often contaminated with small amounts of -undesirable- free isocyanates or with an excess of free blocking agent[4].

The number of (commercial) diisocyanates and BIs is limited and BIs containing additionally functional groups hardly exist. So there is a need for a general method to make a wide variety of (functional) BIs, starting from non-toxic chemicals.

4.3 Blocked isocyanates as chain extenders

Trifunctional blocked isocyanates, which are commonly used as coating crosslinkers, are not applicable as chain extenders in polyesters or nylons, since this would lead to branched or even crosslinked products. Commercially difunctional blocked isocyanates, to be used as chain extenders in thermoplastic materials, are hardly available. Brüggemann, a German company, gave some indication on such a product (Bruggolen M510) on their website, but there was no detailed information on the chemical structure, composition or on the chemistry of this product. Quite recently the information has been removed from their website, which may suggest that the product is withdrawn from the market.

One of the targets of this work is to produce performance materials with enhanced properties by using functional chain extenders. It was anticipated that BIs might be very useful for that purpose, since they easily react with hydroxy or amino end groups of polyesters and nylons, respectively, while they are not toxic and easy to handle. Consequently, it was very important to prove first that difunctional blocked isocyanates could be used as controllable chain extenders. To test their applicability, the caprolactam blocked hexamethylene diisocyanate (HMDC), produced from caprolactam and hexamethylene diisocyanate (HMDI), was used (scheme 4.3).



Scheme 4.3: The preparation of the caprolactam blocked hexamethylene diisocyanate (HMDC).

HMDC was tested in nylon-6 (Akulon K123 of DSM) in equimolar amounts with respect to the reactive groups (1 mol chain extender per 2 mol $-NH_2$) and with twice the equimolar amounts (thus in excess). The reactivity was compared with CBC under the same conditions. An excess of chain extender should in principle lead to less chain extension. However, due to various reasons this is not found in practice (paragraph 3.7).

From table 4.1 it can be seen that the increase of the viscosity of nylon-6 for both chain extenders is comparable, and that viscosity still increases beyond the point of stoichiometry (which is a molar ratio CBC/NH_2 of 0.5). At lower concentrations, CBC looks slightly more

effective than HMDC on a molar basis, while at higher concentrations it is the other way around.

The molecular weight of HMDC (= 364) is higher than that of CBC (= 252) and consequently more of that additive (costs) is needed to get the same effect, assuming the same efficiency. From figure 4.1 it can be seen that on weight basis CBC is somewhat more efficient, but the difference is not that large. Thus, with respect to the efficiency for increasing viscosity, both products behave quite similar.

Table 4.1: Relative viscosities (in formic acid/water 90/10, wt%/wt%) of nylon-6 before and after chain extension.

Sample	Blank	CBC	CBC	HMDC	HMDC
Ratio CE/NH_2*	0	1	2	1	2
Weight %	0	0.7	1.4	1.1	2.2
η_{rel} (dl/g)	2.34	2.98	3.12	2.93	3.38

*Ratio = 1 means 0.5 mol of chain extender per mol NH_2 end group.

The rheology of these samples was measured to get information on the presence (or absence) of branching. The rheology data of the two chain-extended nylon-6 samples, with one or two equivalents of CBC or HMDC with respect to the number of NH_2 end groups, are shown in figure 4.2.

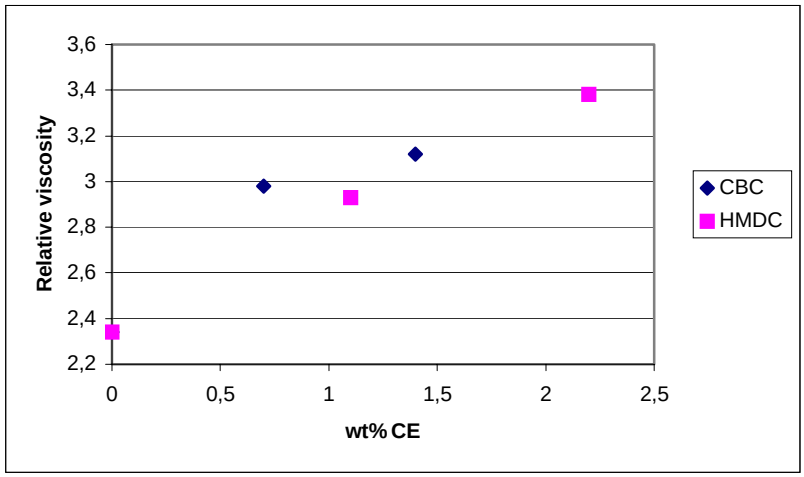


Figure 4.1: Relation of the relative viscosity (in dl/g, in formic/water 90/10 wt%/wt%) of nylon-6 and the wt % of CBC or HMDC (Sample preparation: T = 240 °C and τ = 4 min).

The similarity in rheology upon using both chain extenders is remarkable. By adding one equivalent of chain extender (so that every amino group can react) the rheology of both polymers is similar to that of linear starting polymers.

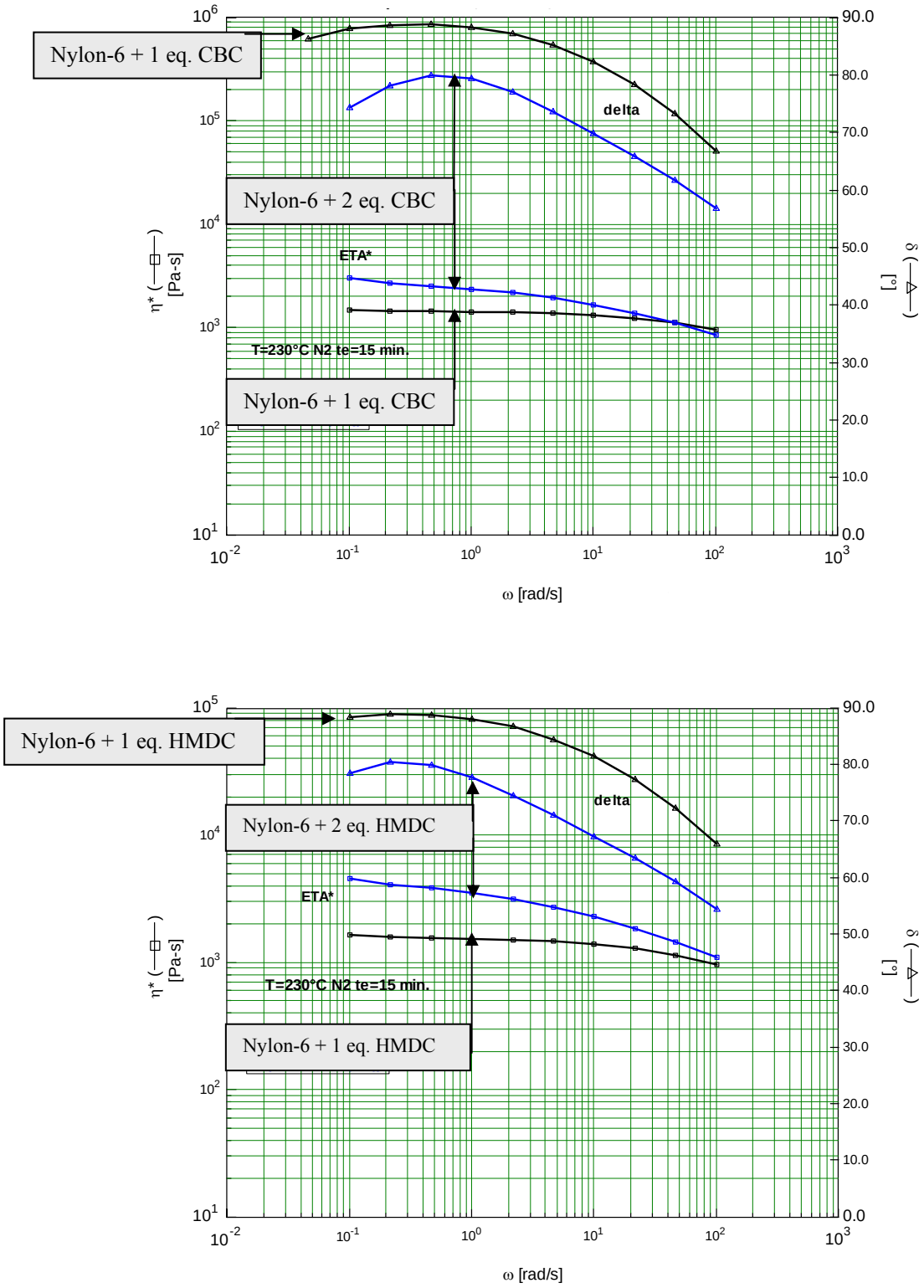


Figure 4.2: Rheology at 230 °C of chain extended nylon-6 with 1 and 2 eq CBC (top) and with 1 and 2 eq HMDC (bottom). The two lower curves are viscosities and the two upper curves phase angles. (Sample preparation: 4 min. at 265 °C).

By adding two equivalents, thus with a large excess of chain extender with respect to the amino end groups, a further increase in viscosity is observed, as already was found before (see figure 3.6 and 3.17 and paragraph 3.7). With an excess of chain extender the rheology of both polymers shows that some branching can be observed, whereas the extent of branching looks the same. Thus, it can be concluded that both chain extenders behave quite similarly.

Blocked isocyanates can de-block and eliminate caprolactam on heating, giving the free isocyanates. Free isocyanates are toxic and could give side reactions, such as dimerization, trimerization, etc., before they perform the desired chain extension reaction. Furthermore, isocyanates can also react with the NH of the amide bond, yielding branched polymers. CBC on the other hand, becomes also a blocked isocyanate, but only after the first reaction has taken place. So in that case there will never be a free low molecular weight isocyanate present in the polymer. Thus, in principle the probability of side reactions is larger with BIs than with CBC, but according to rheology, this does not take place. Since isocyanates can give all kinds of side reactions it is likely that some branching can take place if an excess of chain extender is used, particularly with polyamides. This probably causes the (small extent of) branching, as is evidenced by the deviation of the phase angle from 90^{o}.

It can be concluded that the results so far indicate that difunctional blocked isocyanates yield polymers with higher viscosities in a controlled manner, similarly as with CBC.

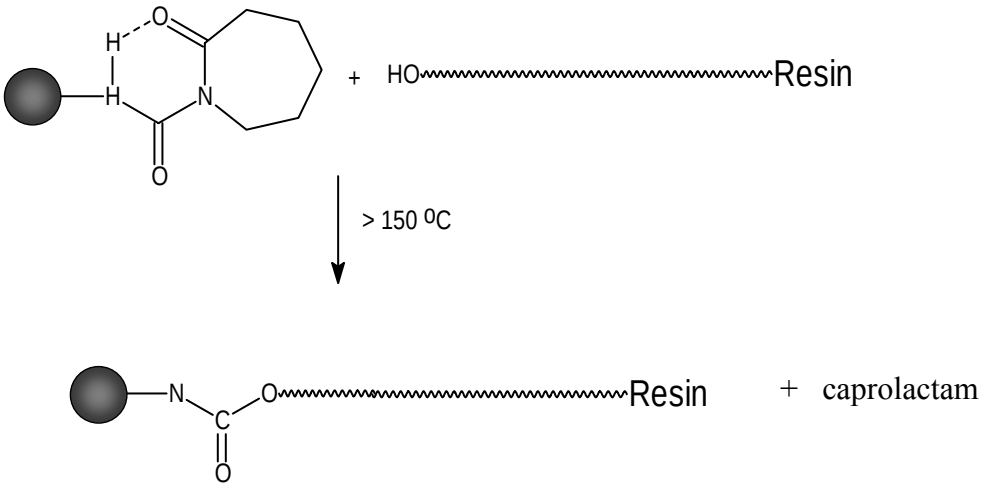
4.4 Blocked isocyanates from a retro synthetic point of view

BIs are used in coating resins, with as only purpose to make 3D polymer networks. Since these crosslinkers are an integral part of the final product, the crosslinkers could also be used to introduce special properties in coatings. But, as far as we are aware, there are hardly any studies on introducing specialty groups in polymers or coatings via a crosslinker/chain extender. It may well be that there are no suitable methods to make functional BIs.

The term functional BIs needs some clarification. A functional BI is a compounds that contains additional functional groups, next to the blocked isocyanate groups, which are also functional groups. Thus these compounds possess at least two functionalities.

If a versatile method for preparing functional BIs would be available, offering a wide variety of functional linking additives, they could be used to couple “functionality” covalently onto polyesters or nylons, as depicted in scheme 4.4.

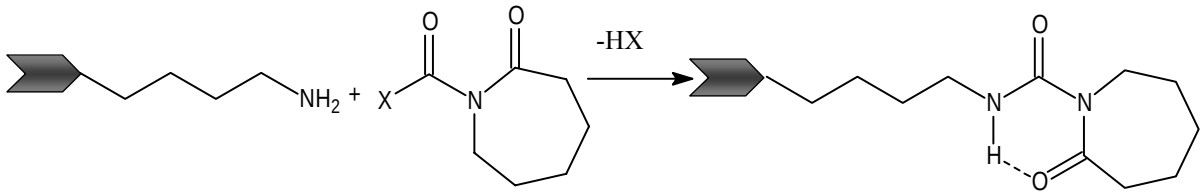
The present method (scheme 4.2) to make blocked isocyanates, by starting from highly reactive isocyanates, is not very suitable for introducing functional groups into (blocked) isocyanates.



Scheme 4.4: Introduction of functional groups ● by blocked isocyanates in polyesters (or nylons).

When looking at the synthesis of BIs from a retro synthetic point of view, it is conceivable to start from a blocked isocyanate *precursor* and fix this onto amines. In this case every primary amine could be converted into a BI. Moreover, amines containing additional functional groups could be used as well (scheme 4.5).

The key issue of this concept, as depicted in scheme 4.5, is that the substitution of X of the blocked isocyanate precursor should be much faster than the substitution of the caprolactam ring (high selectivity). Furthermore, the formed BI should not react with the amines that are present in the reaction mixture during the synthesis.



Scheme 4.5: The one-step synthesis of functional blocked isocyanates from blocked isocyanate precursors and functional ➤ amines (X = leaving group).

Asymmetrical compounds in which X is chlorine are not uncommon. But the emission of HCl, during the reaction is serious limitation. Symmetrical compounds are thought to have hardly any selectivity. Although CBC is a symmetrical molecule it was anticipated that the substitution of the first caprolactam ring would be much faster than the second one, since the intermediate products, caprolactam blocked isocyanates, are known to be stable up to 150 ^{o}C.

So if the substitution of the first caprolactam ring takes place below 150 ^{o}C, than substitution rate of the second caprolactam ring will be much lower than that of the first one. This selectivity may offer the possibility to make a wide variety of BIs[5].

One explanation for the possible difference in the substitution rate of both (identical) caprolactam rings of CBC is the change of the electron density on the central carbonyl, after the nitrogen of caprolactam is replaced by nitrogen of an amine. The carbonyl group, next to the nitrogen in the caprolactam ring is an electron-withdrawing group and will decrease the electron density on the central carbonyl group, thereby making this carbonyl group more reactive towards nucleophiles. After the substitution of the first caprolactam by an amine the electron density on the central carbonyl carbon atom will increase. This qualitative view is supported by calculations with a Spartan molecular modeling program[6] (student edition). The positive charge of the carbon atom of the central carbonyl group in CBC is +1.196, whereas the positive charge of the same carbon atom in the blocked isocyanate is +1.055 (figure 4.3), which quantitatively supports a possible difference in reactivity.

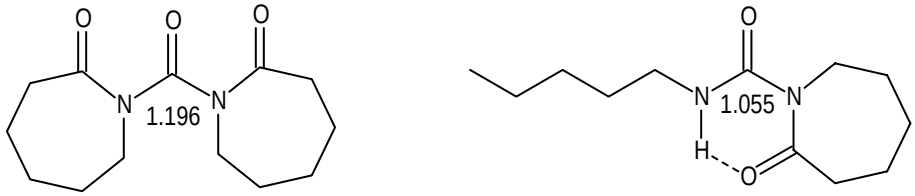


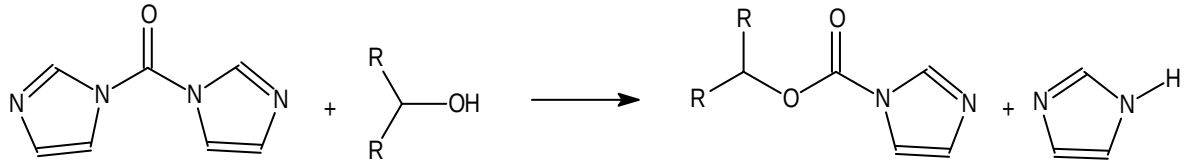
Figure 4.3: Charge of CBC and blocked isocyanates calculated with Spartan.

A second important stabilization effect, which is due to the particular caprolactam structure, is intra-molecular hydrogen bonding (fig 4.3), which is not possible with CBC and often not with other symmetrical carbonic acid derivatives. So it is quite reasonable to expect that CBC will react with amines in a selective way (paragraph 4.5).

Carbonyl diimidazole (CDI), which is often used in this kind of reactions, has some structural similarities with CBC (scheme 4.6), but is much more reactive. For instance, CDI decomposes violently in water at room temperature in seconds[7], whereas CBC can be washed with water without any sign of decomposition. The selectivity of CDI is consequently much lower than that of CBC, due to its higher reactivity. Nevertheless, CDI still reacts in a selective way with sterically hindered secondary and tertiary alcohols, forming imidazole carboxylic esters by substituting only one of the imidazole groups[8] (scheme 4.6).

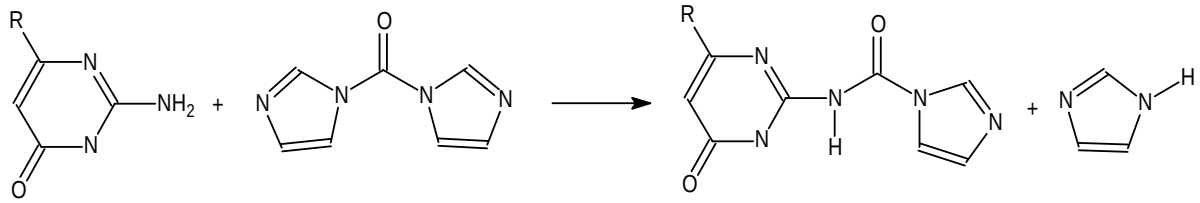
After a secondary (or tertiary) alcohol has substituted the first imidazole group of CDI, a primary alcohol (or amine) can substitute the second imidazole group in a consecutive

reaction, yielding unsymmetrical carbonates. If a mixture of primary and secondary alcohols (or amines) is offered to the reactive intermediate only the primary alcohol (or amine) reacts selectively.



Scheme 4.6: The reaction of a secondary alcohol with CDI.

Recently, Keizer et al.[9] showed that isocytosines, which have amino groups with a strongly reduced nucleophilicity, give substitutions of only one of the imidazole groups, resulting in blocked isocyanates (scheme 4.7).



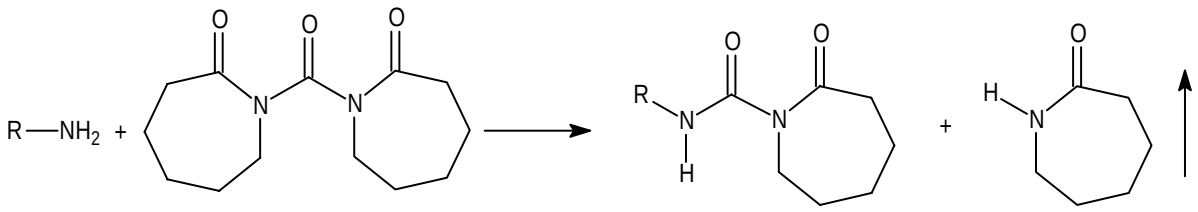
Scheme 4.7: Synthesis of blocked isocyanate from CDI and isocytosines.

Thus, CDI offers a route to make imidazole carboxylic esters (with secondary and tertiary alcohols, scheme 4.6) and to prepare blocked isocyanates with some amines (with low nucleophilicity, scheme 4.7), but the number of possibilities is limited.

Toxicity is an important issue in the commercial acceptance of products by the market. The low toxicity of CBC (and caprolactam) is not only a big advantage, but it is even a prerequisite for commercialising such a product.

4.5 Blocked isocyanates from amines and CBC

The preparation of BIs from primary amines with CBC was studied below 150 ^{o}C to prevent the second reaction step (scheme 4.8). In a typical example stoichiometric amounts of n-hexyl amine and CBC were heated in toluene at 80 ^{o}C overnight. These reactions are usually rather fast and are mostly completed within a couple of hours (2 to 4h). Nevertheless these experiments were done overnight to be completely sure to get complete conversion.



Scheme 4.8: The reaction of an amine with CBC at 80 ^{o}C in toluene as solvent.

The reaction appears to be very selective and only gives (according to ^{1}H-NMR analysis) the corresponding BI in nearly quantitative yield, since no side products were detectable. In figure 4.4 the ^{1}H-NMR spectrum of the crude reaction product of this experiment (with stoichiometric amounts of CBC and amine) is given and it can be seen that the expected products are present, whereas no side products are visible. The signals of CBC (e.g. at 3.85 ppm) and of hexyl amine (e.g. the $C\underline{H}_2NH_2$ peak at 2.15 ppm) have completely disappeared, whereas the presence of caprolactam is observable (e.g. at 2.4 ppm).

This high selectivity, which is shown here for hexyl amine, appears to be a unique property of CBC. It enables the preparation of BIs without any or hardly any side products, in a one-step reaction starting from the non-toxic chemical CBC.

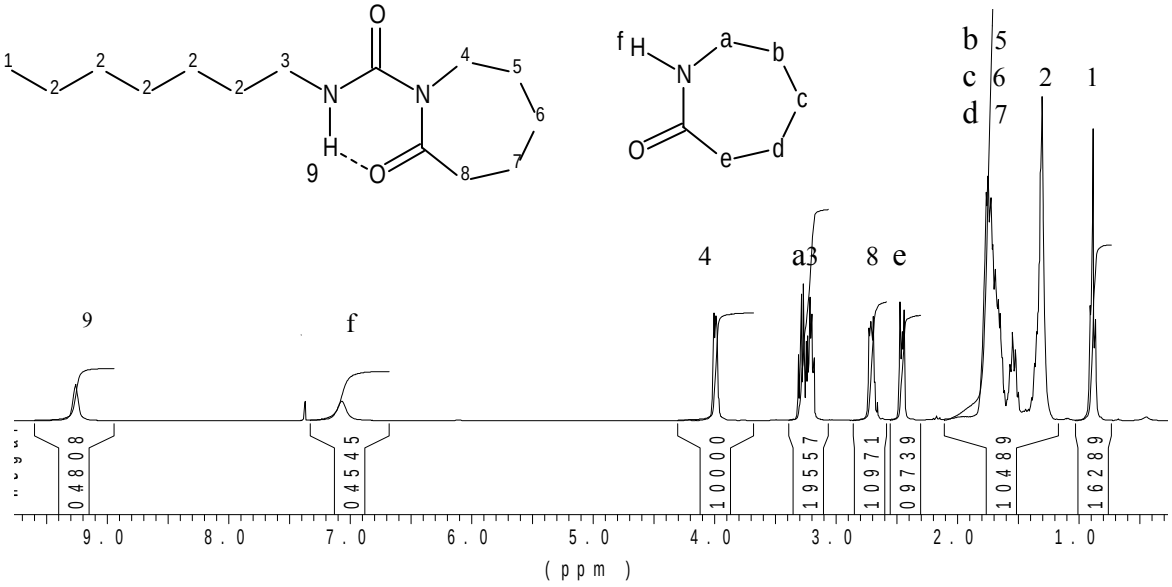


Figure 4.4: ^{1}H-NMR of the crude reaction mixture of hexyl amine and CBC in toluene.

The reaction can be carried out in (various) solvents as well as in bulk. There is a preference for solvents such as toluene, because the reactants and the reaction products are mostly soluble in this solvent. Moreover, caprolactam is readily water soluble, while in most cases the products are not. In that case a simple aqueous extraction is sufficient to separate

caprolactam from reaction product. The addition of $CaCl_2$ or HCl increases the solubility of caprolactam in water, thereby improving the purification procedure. If the products are water-soluble too a consecutive reaction with the intermediate BIs can be carried out (*chapter 5*), making that product less water-soluble. It is also possible to remove caprolactam by film evaporation under high vacuum, but this is more laborious.

Many other amines (more than fifteen) have been tested and so far all primary amines yielded similar excellent results under these conditions. These results suggest that a general method is now available to make blocked isocyanates in high yields from primary amines and CBC. The applicability of this method with amines, containing groups with special properties, is studied as well and described in *chapter 5, 6 and 7*. In figure 4.5 some representative examples of the products that have been made with this method are shown. This new route to caprolactam-blocked isocyanates seems to be broadly applicable[4].

It is noteworthy that during the preparation both BIs and amines are present in the reaction mixture, and although they are able to react with each other they don't do so at 100 ^{o}C.

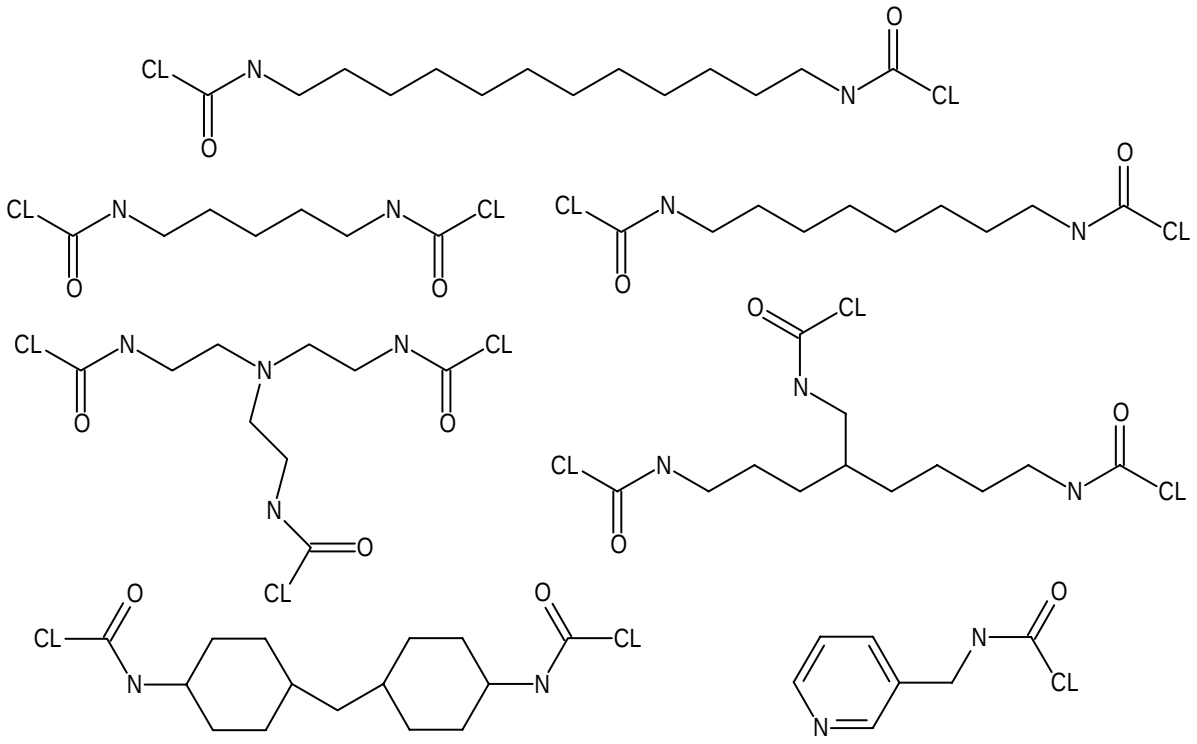


Figure 4.5: Structure of various blocked isocyanates prepared in high yields from the corresponding amines and CBC (ε-CL = caprolactam).

The reaction rate of aromatic or secondary amines with CBC is much lower than of primary amines. Interestingly, if blocked isocyanates could be made from secondary amines via this route, blocked isocyanates could be prepared of which the corresponding isocyanates do not

exist. Some experiments were carried out with dibutyl amine and it was found that blocked isocyanates were formed, but only at higher temperature (160-180 ^{o}C). Under these conditions the reaction is less selective than with primary amines at lower temperatures. Nevertheless, the BIs were assigned in the reaction mixture, but not (yet) isolated. The large difference in reactivity between primary and secondary amines was the inspiration to study the reaction between CBC and compounds that contain both primary and secondary amines more in detail (*chapter 5*).

The reaction between primary amines and CBC always results in a complete substitution of one caprolactam ring (left side of scheme 4.1). So far it was not possible to detect any ring opening reaction with amines.

4.6 Blocked isocyanates from alcohols and CBC

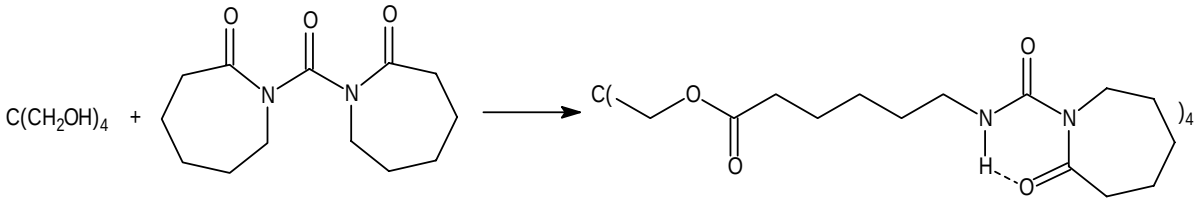
A concept to make (blocked) isocyanates in a one-step reaction starting from alcohols looks unfeasible at first glance. But, the right pathway of scheme 4.1 suggests that BIs could be made if one of the caprolactam rings opens. In that case the necessary nitrogen atom for the isocyanate group, which is obviously not present in alcohols, will come from caprolactam.

In *chapter 3* it is discussed that catalysts increase the reaction rate of CBC with alcohols (at T > 150 ^{o}C) and, more importantly here in this context, that they change the composition of the reaction mixture, giving more urethane linkages. This indicates that, in the presence of catalysts, probably BIs are formed as intermediates by opening the first caprolactam ring. The reversed order, in which first a substitution takes place and then ring opening reaction, giving also a urethane linkage, is less probable. BIs were indeed found as intermediates, whereas hardly any caprolactam carbonates were detected. So, series of experiments were done to find the conditions (temperatures and catalysts) to stop the reaction stops halfway through, giving hopefully BIs in good yields.

At first some reactions were done with alcohols and CBC in the same way as with the amines, thus without catalysts and in toluene as solvent, but these reactions gave complex reaction mixtures. Then the best catalysts out of the chain extension investigation (*chapters 2 and 3*), $MgBr_2$, $Zr(OR)_4$ and $Ti(OR)_4$, were used to study the influence of catalysts on the composition of the reaction mixture of an alcohol with CBC at 125 ^{o}C.

Initially some reactions were carried out with dodecanol in toluene, but under these conditions the reaction rate was quite low. When the reactions were carried out in bulk the conversion of CBC was completed within about two to four hours, which looked promising. Next pentaerytritol (scheme 4.9) was selected to react with CBC, since this would give four-

functional blocked isocyanates, which could be used in coating applications. The reaction of pentaerytritol with CBC in the presence of $Zr(OBu)_4$, however, gave initially the same ill-defined mixture as without catalysts, which was an unexpected result. However, it was noticed that at the start of the reaction the mixture became turbid and the zirconium catalyst may have formed an insoluble complex, with pentaerytritol. In a second series of experiments $MgBr_2$ was used as a catalyst, and now the reaction as depicted in scheme 4.9 proceeded as expected.



Scheme 4.9: Reaction between pentaerytritol and CBC

The progress of this reaction can nicely be followed by ^{13}C-NMR (figure 4.6).

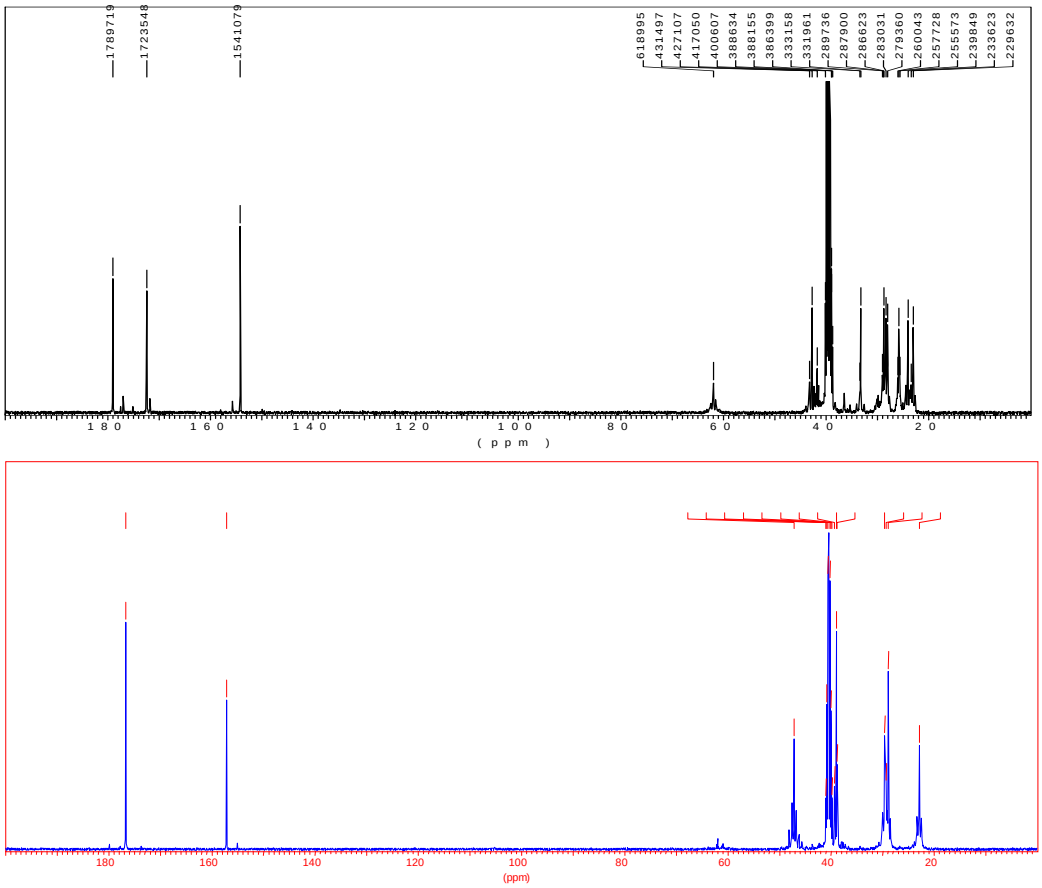


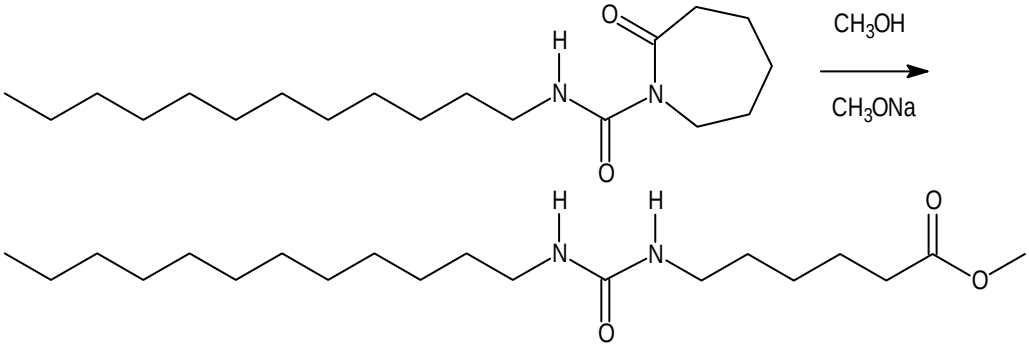
Figure 4.6: ^{13}C-NMR spectrum of the crude reaction mixture of pentaerytritol and CBC in the presence of $MgBr_2$ as catalyst at the start (bottom) and after 2 hours at 125 ^{o}C (top).

CBC has two different types of carbonyl groups, whereas the formed BI has three different carbonyl groups (an ester, a (blocked) isocyanate and the caprolactam ring). It can be seen that at the start there are two carbonyl groups (157 and 176 ppm) that have almost completely disappeared (in the crude reaction mixture) after two hours, whereas at that point in time three carbonyl groups (154, 172 and 179 ppm) are visible of the end product. The yield of the tetra functional blocked isocyanate is about 90% (before purification). For most of the coating applications this purity may be enough to use this material without further purification. In *chapter 6* a successful preparation (and application) of a BI from an alcohol containing a special group is described, showing the broader applicability of this method.
The preparation of blocked isocyanates in a one step reaction from an alcohol (and CBC) is unprecedented[5].
Although we have tested so far only a limited number of alcohols, it is expected that a variety of blocked isocyanates can be made from alcohols and CBC, which enlarges the scope of this methodology, since alcohols are more available than amines and moreover they are cheaper.

4.7 Ring opening of caprolactam carbamate (caprolactam blocked isocyanate)

So far we have demonstrated that, depending on the conditions, one caprolactam ring of CBC can either be substituted or opened, giving blocked isocyanates. It is well known that the reaction of hydroxy or amino functional compounds with BIs always proceeds via the substitution of caprolactam blocking group, resulting in the emission of volatile organic compounds. It would be of great value if this second caprolactam ring could be opened as well to suppress the emission of volatiles.
From the results of table 2.2 and 2.3 (and the work of S. Maier [5]) it can be seen that, by using basic catalysts, some double ring opening (= formation of urea) occurs and that the extent of double ring opening depends on temperature. The lower the temperature, the higher the concentration of urea groups is (double ring opening). Thus it was conceivable that under well-defined conditions the second ring could open in substantial amounts. To test this a blocked isocyanate of dodecyl amine was prepared by the reaction with CBC and the formed caprolactam was removed by an aqueous extraction. Caprolactam BI (caprolactam dodecyl carbamate) was added to an excess of methanol that was pre-treated with a catalytic amount of NaH, and stirred at room temperature overnight. NaH yields in methanol CH_3ONa, which is the basic catalyst that was expected to be suitable to catalyze for the ring opening reaction. Indeed, under these conditions, the blocked isocyanate was completely converted in the

corresponding ester-urea by a complete ring opening of the caprolactam ring. The ^{1}H-NMR spectrum showed hardly any detectable amount of side products.



Scheme 4.10: Ring opening reaction of the caprolactam ring of a caprolactam blocked isocyanate.

This result may be very useful in commercial coating applications, since this reaction proceeds at low temperature, which is an advantage in coating applications. Maybe even more importantly, no volatile organic compounds (VOC) are emitted during this reaction.

4.8 Conclusion

Two novel routes are found to prepare caprolactam-blocked isocyanates. In the first method blocked isocyanates were prepared starting from primary amines and carbonyl biscaprolactam. In this method amines substitute quantitatively one of the caprolactam rings of CBC. This is a reversed procedure, in which first the blocked isocyanate precursor group (CBC) is prepared, which is subsequently fixed onto amines in a one-step process, offering a new route to produce blocked isocyanates.

So far more than fifteen primary (di- and tri-) amines have been tested. They all yield blocked isocyanates by reacting them with CBC in a 1 to 1 molar ratio in toluene at 80 to 100 ^{o}C. CBC shows a unique selectivity, in which the reaction proceeds in high yields with hardly any side reaction.

In a second method BIs are prepared from CBC and alcohols in a one step reaction, and in high yields (about 90 %). In this case the first caprolactam ring of CBC has to open, whereas with amines always a complete substitution of the first caprolactam ring takes place. It is remarkable to make (blocked) isocyanates in a one step reaction from alcohols, since they do not contain the required nitrogen atom. The necessary nitrogen atom for the isocyanate group comes in this case from the caprolactam.

Thus, a wide range of caprolactam-blocked isocyanates is prepared starting from a blocked isocyanate precursor (carbonyl biscaprolactam) and amines or alcohols, without making a detour by using toxic amines or isocyanates as intermediates.

4.9 Experimental section

Materials

CBC was obtained from DSM New Business Development, ALLINCO (> 99 % pure, HPLC) and used without purification.
Amines, alcohols, catalysts and toluene were purchased from Aldrich or from Acros. Trisamino nonane is obtained from Monsanto and used as received.

Instrumentation

NMR spectra were recorded on a Brucker ACF 300 MHz in various solvents.
A Spartan molecular modeling program (student edition 2.0) was used for the calculation of the electron density of the carbonyl groups of the blocked isocyanates and CBC.

Thin Layer Chromatography (TLC)

The progress of the reactions was often followed by measuring the conversion of CBC with TLC (SiO_2 on glass). With ethylacetate-hexane (4:1) as eluent a clear separation of the reaction components was obtained.

Synthesis

Hexylamine + CBC

n-hexyl amine (10,0 g, 99 mmol) and CBC (24.6 g, 98 mmol) were heated overnight in toluene (40 ml) at 80 ^oC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.89 (3H, t, CH_3), 1.30 (10H, m, CH_2 hexyl chain), 1.75 (12H, CH_2 rings), 2.42 (2H, t, $COCH_2$ caprolactam), 2.70 (2H, t, $COCH_2$ blocked caprolactam), 3.25 (4H, t, $C\underline{H_2}NH$ BI + $C\underline{H_2}NH$ caprolactam), 3.97 (2H, t, CH_2N), 7.03 (1H, s, NH caprolactam), 9.22 (1H, s, NH BI).

1,4-Diaminobutane + CBC

To a solution of carbonyl biscaprolactam (54.4 gram, 0.2 mol) in 100 ml of ethyl acetate at 78 °C a solution of 1,4-diaminobutane (8.8 gram, 0.1 mol) in 30 ml of ethyl acetate was added slowly (30 min). A white precipitate was visible. After 4 hours the reaction was completed. The reaction mixture was cooled to 50 °C and filtered. Caprolactam blocked 1,4-diaminobutane was isolated as a white powder. Yield = 70%: ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.56 to 1.65 (10 H, $CH_2CH_2CH_2$ ring + $CH_2C\underline{H_2}C\underline{H_2}CH_2$), 2.59 (4H, t, CH_2CO), 3.20 (4H, q, $NHC\underline{H_2}$), 3.90 (4H, t, NCH_2), 9.20 (2H, broad, NH).

1,6-Diaminohexane + CBC

To a solution of carbonyl biscaprolactam (151.2 gram, 0.6 mol) in 400 ml of ethyl acetate at 78 °C a solution of 1,6-diaminohexane (34.9 gram, 0.3 mol) in 50 ml of ethyl acetate was added (in 20 min). The reaction mixture was stirred for 2 hours and then cooled down to room temperature. The mixture was extracted three times with 250 ml of water containing 2 wt% of calcium chloride and once with 250 ml of demineralised water. The ethyl acetate layer was dried with anhydrous sodium sulphate. After the sodium sulphate had been removed by filtration ethyl acetate was distilled under reduced pressure (rotavapor). The product was a white powder. Yield 96%: ^{1}H-NMR (300 MHz, d6-DSMO) δ = 1.26 to 1.63 (14 H, $CH_2C\underline{H_2}C\underline{H_2}C\underline{H_2}C\underline{H_2}CH_2$ + $CH_2CH_2CH_2$ ring), 2.68 (4H, t, CH_2CO), 3.15 (4H, q, $NHC\underline{H_2}$), 3.90 (4H, t, NCH_2), 9.15 (2H, broad, NH).

1,8-Octylamine + CBC

To a solution of carbonyl biscaprolactam (252 gram, 1 mol) in 400 ml of ethyl acetate at 78 °C a solution of 1,8-diaminooctane (72 gram, 0.5 mol) in 150 ml of ethyl acetate was added slowly (30 min). The mixture was stirred for 2 hours and then it was cooled to room temperature. The solution was extracted three times with 500 ml of water containing 2 wt% of calcium chloride and once with 250 ml of demineralised water. The ethyl acetate layer was dried with anhydrous sodium sulphate. After the sodium sulphate had been removed by filtration the ethyl acetate layer was concentrated to 100 ml and cooled to 5°C. A white product precipitated and was isolated by filtration. Yield = 66%: ^{1}H-NMR (300 MHz, d6-DSMO) δ = 1.26 to 1.63 (18 H, $CH_2CH_2CH_2$ ring + $CH_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_2$), 2.68 (4H, t, CH_2CO), 3.15 (4H, q, $NHC\underline{H}_2$), 3.90 (4H, t, NCH_2), 9.15 (2H, broad, NH).

1,12-Diamino dodecane

To a solution of carbonyl biscaprolactam (1001 gram, 4 mol) in 1500 ml of ethyl acetate at 78 °C a suspension of 1,12-diaminododecane (401 gram, 2 mol) in 500 ml of ethyl acetate was added. After stirring the mixture for 2 hours the hot solution was filtered and cooled down to room temperature and poured into 1000 ml of water. The suspension was filtered with a P-2 glass filter. The product was a white powder. Yield = 80%: ^{1}H NMR ($CDCl_3$): δ = 1,5 (m, 32H, $CH_2CH_2CH_2$ ring + $CH_2(C\underline{H}_2)_{10}CH_2$), 2,7 (t, 4H, CH_2), 3,3 (t, 4H, $NHC\underline{H}_2$), 4,0 (t, 4H, NCH_2), 9,3 (s, 2H, NH).

1,7-Diamino-3-(2-amino ethyl) heptane (trisamino nonane) + CBC

To a solution of carbonyl biscaprolactam (302.4 gram, 1.2 mol) in 400 ml of ethyl acetate at 78 °C a solution of tris-aminononane (69.3 gram, 0.4 mol) in 100 ml of ethyl acetate was added drop wise (60 min). After stirring the mixture for 3 hours the solution was cooled down to room temperature. The ethyl acetate layer was extracted three times with 500 ml of water containing 2 wt % of calcium chloride and once with demineralised water (250 ml). The ethyl acetate layer was dried with anhydrous sodium sulphate. After the sodium sulphate was removed through filtration ethyl acetate had been removed by distillation under reduced pressure (rotavapor). The product was isolated as a yellow oil. Yield = 92%: ^{1}H NMR (300 MHz, d6-DSMO) δ = 1.44 to 1.64 (28H, broad, $CH_2CH_2CH_2$ ring + $NCH_2CH(C\underline{H}_2\ CH_2N)$ $C\underline{H}_2C\underline{H}_2C\underline{H}_2\ C\underline{H}_2CH_2N$), 1.99 (1H, m, CH), 2.69 (6H, t, CH_2CO), 3.15 (6H, t, $C\underline{H}_2NH$), 3.90 (6H, t, CH_2N), 9.16 (3H, broad, NH).

4,4'-Diamino cyclohexane

To a solution of carbonyl biscaprolactam (225 gram, 0.89 mol) in 400 ml of ethyl acetate at 78 °C a solution of 4,4-diaminodicyclohexane methane (94 gram, 0.45 mol) in 100 ml of ethyl acetate was added (30 min). After stirring the solution for 2 hours the reaction mixture was cooled down to room temperature and extracted three times with 500 ml of water containing 2 wt% of calcium chloride and once with 250 ml of demineralised water. The ethyl acetate layer had been dried with anhydrous sodium sulfate. After the sodium sulfate was removed through filtration the ethyl acetate layer was concentrated to 200 ml and cooled down to 5°C. A white product was isolated by filtration. Yield = 70%: ^{1}H NMR ($CDCl_3$) δ = 0.8 to 1.21 (12H, broad, $CH_2CH_2CH_2$ caprolactam ring), 1.66 (16H, broad, CH_2 cyclohexyl ring), 1.95 (4H, m, CH_2), 2.60 (4H, t, $C(O)CH_2$), 3.50 (2H, m, CH), 4.00(4H, t, NCH_2), 9.09 (2H, broad, NH).

Trisaminoethylamine + CBC

To a solution of carbonyl biscaprolactam (75.6 gram, 0.3 mol) in 200 ml of ethyl acetate at 78 °C a solution of trisamino ethylamine (14.6 gram, 0.1 mol) in 20 ml of ethyl acetate was

added in 20 min and the reaction mixture was stirred for another 4 hours. Then the mixture was cooled to room temperature and extracted twice with 250 ml of water containing 2 wt% of calcium chloride and once with 250 ml of demineralised water. The ethyl acetate layer was dried with anhydrous sodium sulfate. After the sodium sulfate had been removed through filtration the ethyl acetate was distilled off under reduced pressure (rotavapor). The product was a clear yellow oil. Yield 99%: ^{1}H-NMR in $CDCl_3$: δ = 1.73 (18H, broad, ring), 2.69 (12H, m, $COCH_2$, NCH_2), 3.35 (6H, q, $C\underline{H}_2NHCO$), 3.97 (6H, t, $C\underline{H}_2N$), 9.33 (3H, s, NH).

N,N-dimethylamino ethyl amine + CBC

A solution of N,N-dimethylamino ethyl amine (5 g, 56.8 mmol) and CBC (14.5 g, 57.5 mmol) was stirred for 18 h in toluene (50 ml) at 80 ^{o}C. The solvent was removed under reduced pressure, yielding yellow oil. Vacuum distillation of this oil was carried out in a Büchi Kugelrohr apparatus at 130 ^{o}C and 5 mbar. ^{1}H-NMR in $CDCl_3$: δ = 1.75 (6H, m, ring), 2.26 (6H, s, CH_3), 2.45 (2H, t, NCH_2), 2.71 (2H, m, $NCOCH_2$), 3.40 (2H, t, CH_2NH), 4.00 (2H, m, CH_2NCO), 9.38 (1H, broad, NH).

3-Methylamino-pyridine + CBC

A solution of 3-methylamino-pyridine (10 g, 92.6 mmol) and CBC (23.8 g, 94.4 mmol) in toluene (100 ml) was stirred at 80 ^{o}C for 18 h. About half of the solvent had been removed under reduced pressure. After the solution was cooled down to room temperature the organic phase was washed 6 times with water. The solution was dried with anhydrous magnesium sulphate, filtered and the toluene was distilled off under reduced pressure. ^{1}H-NMR in $CDCl_3$: δ = 1.75 (6H, m, ring), 2.72 (2H, t, $NCOCH_2$), 4.01 (2H, t, $CONCH_2$), 4.50 (2H, d, $CONHC\underline{H}_2$), 7.25 (1H, q, Ar-H), 7.64 (1H, d, Ar-H), 8.50 (1H, d, Ar-H), 8.57 (1H, d, Ar-H), 9.73 (1H, broad, NH).

N-Dodecyl (N-methoxycarbonyl pentyl) urea

Dodecyl amine (3.7 g, 20 mmol) and CBC (5.04 g, 20 mmol) were dissolved in toluene (25 ml) and heated overnight at 80 ^{o}C. The reaction mixture was cooled down and extracted 3 times with 50 ml of water containing 2 wt% of $CaCl_2$. The organic layer was dried with anhydrous Na_2SO_4, and after filtration the solvent was removed under reduced pressure (rotavapor). To 6 ml of methanol NaH (18 mg, 0.75 mmol) was added and the mixture was stirred at room temperature for 2 hours. After subsequent addition of caprolactam dodecyl carbamate (5.35 g, 16.5 mmol) the mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure, giving the ester-urea in quantitative yield. ^{1}H-NMR in $CDCl_3$: δ = 0.88 (3H, t, $CH_2C\underline{H}_3$), 1.26 to 1.62 (28H, broad, CH_2), 2.30 (2H, t, CH2C(O)O), 3.17 (4H, m, $C\underline{H}_2NH$), 3.67 (3H, s, OCH_3), 4.25 (2H, broad, NH).

Pentaerytritol + CBC

After CBC (5.04 g, 20 mmol) had been heated to 125 ^{o}C pentaerytritol (0.73 g, 5 mmol) and $MgBr_2$ (50 mg) were added to the melt and the mixture was stirred for 3 hours. The mixture was cooled down to room temperature. The product is a slightly yellow solid. ^{13}C-NMR (MHz, $CDCl_3$) : δ = 20 to 30 (16C, CH_2 middle of chain), 39 (14C, CH_2 next to N or CO), 42 (4C, CH_2O), 62 (1C, $\underline{C}(CH_2\text{-})_4$, 154 (4C, OCO), 172 (4C, NCO), 179 (4C, N(CO)N).

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Hydroxy and amine functional blocked isocyanates, enabled by a double selectivity

Abstract

A methodology is developed to prepare in a one step reaction blocked isocyanates, still containing free hydroxy or amino groups that can be used to be functionalized. Primary amines react fast and quantitatively with carbonyl biscaprolactam (CBC), yielding blocked isocyanates, whereas secondary amines need much higher temperatures. This large difference in reactivity is explored by studying reactions of CBC with polyamines, containing primary as well as secondary amino groups. CBC reacts, in these cases, in a selective manner with only the primary amino groups, while leaving the secondary amino groups completely unaffected. The free secondary amino group enables the preparation of functional blocked isocyanates. That procedure demonstrates the unique double selectivity of CBC, because only one of the caprolactam rings is substituted and only primary amines are reactive, whereas both reactions proceed in high yields.

Similarly, the selectivity of CBC with amino alcohols was studied, because primary amines are more reactive than alcohols. Under well-chosen conditions, only the primary amino groups of amino alcohols react in a selective way with CBC, while leaving the hydroxy groups unaffected, giving the hydroxy functional blocked isocyanate in high yields. Also with amino alcohols the unique double selectivity of CBC is demonstrated.

5.1 Introduction

In the synthesis of complex organic structures, and particularly in the peptide chemistry, protecting groups are frequently used, to render temporarily amino groups inert. Due to their beneficial use in organic synthetic procedures the proliferation of the protecting groups became widespread. To fulfil the various needs in a broad area of the organic chemistry, many new protecting groups were introduced[1].

An important family of protecting groups are carbonic acid derivatives, and particularly chloroformate derivatives. Amines are converted into carbamates (BIs) by the substitution of only chlorine of the chloroformate. This selective substitution takes place because of the non-symmetrical structure of the chloroformate, in which chlorine is much more prone to be substituted than the hydroxy functional compound. The formation of a strong acid (HCl) during this reaction step is a disadvantage. HCl has to be removed as salt by adding a tertiary amine.

Another favourite protecting group for amines is the t-Boc group. This is one of the few examples in which a *symmetrical* compound (t-butoxy-dicarbonate) reacts with amines, and stops after the first substitution step, yielding carbamates, similarly as has been shown with carbonyl biscaprolactam (CBC).

Little information is available on selective reactions of *symmetrical* carbonic acid derivatives with compounds containing, next to a primary amino group, hydroxy or secondary amino groups[2]. In that case a double selectivity is needed: only one of the (same) leaving groups has to be substituted and only one of the nucleophilic groups should be active.

Chapter 4 describes the preparation of blocked isocyanates (BIs; caprolactam carbamates) from amines and CBC. It was mentioned that secondary amines react much slower with CBC than primary amines. This difference in reactivity could offer an opportunity for a selective reaction, in which only primary amines react with CBC, while only one caprolactam ring is substituted. It was also shown (*chapter 4*) that the reaction rate of alcohols with CBC, without using catalysts, is much slower than that of primary amines. Here too there is a remarkable difference in reaction rate, which could lead to a selective reaction of CBC with compounds containing both primary amino and primary alcohol groups.

So, if CBC would react selectively with only the primary amino groups, leaving the hydroxy or secondary amino groups in tact, then the free hydroxy and (secondary) amino could be used to link them onto groups with special properties, yielding functional blocked isocyanates.

5.2. Reaction of CBC with polyamines, containing both primary and secondary amino groups.

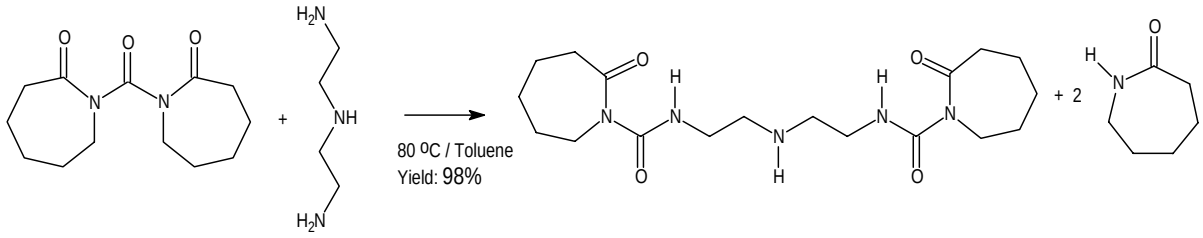
Attempts to make BIs from dibutyl amine and CBC at 100 ^{o}C failed. The starting products were recovered completely after 4 hours reaction time. The fact that secondary amines do not react at temperatures up to 100 ^{o}C prompted us to study the reaction of CBC with compounds containing both primary and secondary amines.

The first polyamine that was tested was bishexamethylene triamine (BHTA). BHTA has two primary amino groups at the end of the chain and one secondary amino group in the middle of this molecule. The reaction of BHTA and CBC was done under similar conditions as with compounds having only primary amino groups (*chapter 4*). Thus, in a typical experiment 1 mol of BHTA and 2 mols of CBC were mixed in toluene and heated overnight at 80 ^{o}C. A molar ratio between CBC and BHTA of two was taken, assuming that only the primary amino group would react and the secondary amine not at all. TLC (thin layer chromatography) revealed that after a few hours most of the BHTA and CBC had disappeared. After the reaction mixture has been stirred overnight, the mixture was cooled to room temperature. Caprolactam that is formed during this reaction was removed by an aqueous extraction. The product was isolated by evaporation of toluene under reduced pressure and obtained in nearly quantitative yield. According to ^{1}H-NMR (figure 5.1) the resulting product is pure, and thus the reaction proceeds in a controlled manner.

Figure 5.1: The ^{1}H-NMR spectrum of the reaction product of bis-(hexamethylene triamine) and CBC.

Primary amines (and CBC) are completely converted into BIs, whereas the secondary amine remains unaffected. CBC appears to have the right balance in reactivity, high enough towards primary amines so that the reactions proceeds is an acceptable time, and low enough to prevent reactions with secondary amines. This interesting product contains two blocked isocyanate groups and still has a free secondary amino group. This secondary amino group can be used subsequently to link all kinds of functional groups to it, and this possibility will be demonstrated later on (in *chapter 7*).

To test the generality of this procedure the reaction was repeated with bisethylene triamine (scheme 5.1). The chain length between the primary and secondary amino groups is now shorter, making the reactivity of the amino groups different. But the reaction with CBC proceeds basically in the same way. According to TLC the reaction is almost completed after about 2 hours at 80 ^{o}C, giving the desired product, with caprolactam as the only side product.



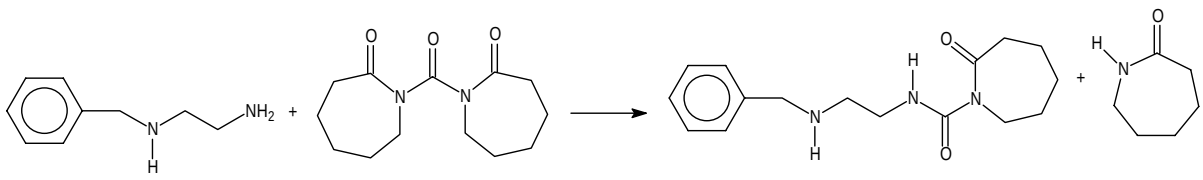
Scheme 5.1: The reaction of bis ethylene triamine and CBC in toluene at 80 ^{o}C.

The removal of caprolactam by an aqueous extraction is very convenient if the water solubility of the product is low. However, if the solubility, as in this case, is rather high, this method is not applicable due to the high losses during the extraction. For instance in this case, after 6 aqueous extractions of the toluene solution, the yield of this product was only 15 %, whereas still some traces of caprolactam were present (^{1}H-NMR result). Most of the product ended apparently in the aqueous phase.

One option to circumvent these losses is to continue with the "crude" mixture, containing only the product and caprolactam, and functionalise the free secondary amino group, provided that caprolactam does not interfere with this consecutive reaction. If the solubility of the subsequently formed product in water is low, caprolactam can be extracted after that step. If this approach is impossible then caprolactam has to be removed under vacuum, by for example a film evaporator.

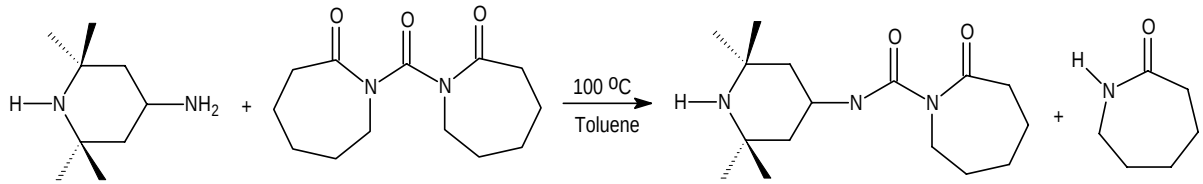
Next this new method was tested with aromatic compounds, containing a primary and a secondary amine and for that purpose N-aminoethyl-N-benzylamine was used (scheme 5.2).

Thus, N-aminoethyl-N-benzylamine and CBC were mixed in equimolar amounts in toluene as solvent and the conversion of CBC and of the primary amino groups proved to be complete after 18 h at 60 ^{o}C. The solubility of the formed product in water was low enough to remove caprolactam by an aqueous extraction. After 6 extractions the product was free from caprolactam and the yield was still over 90 %. There was no indication in the ^{1}H-NMR spectrum that the secondary amino group had reacted.



Scheme 5.2: Blocked isocyanate prepared from N-aminoethyl-N- benzylamine and CBC.

Next the reactivity of CBC was tested with a compound containing a primary amine, fixed onto a secondary carbon atom, and a secondary amine. For that purpose trisacetone diamine (TAD; scheme 5.3) was used, which is a useful product that can be used to introduce a second functionality.



Scheme 5.3: The reaction of trisacetone diamine with CBC

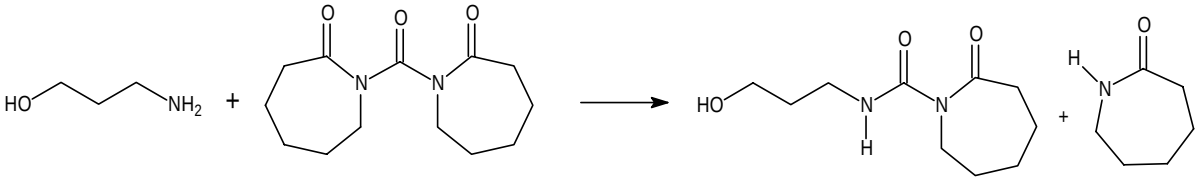
This compound contains a primary amine on a secondary carbon atom, which in general is less reactive than a primary amine on a primary carbon. In this case the secondary amine is less reactive as well due to steric hindrance. So, there was a fair chance that again high selectivities could be obtained. It was found indeed that the reaction proceeded indeed in high yields (88% after purification), whereas only the primary amino group had reacted.

This compound can be used in several interesting applications, e.g. to link it onto polyesters or nylons, possibly giving polymers with a long lasting UV stability because of the presence of a non-leachable hindered amine light stabiliser (HALS). Another option is to oxidize it, making TEMPO (2,2,6,6-tetramethyl-1-piperidyloxy) functional polycondensates, which can be used as macro-initiator for the radical polymerisation of olefins.

The double selective reactions, in which only one of the caprolactam rings is substituted and only the primary amine groups reacts, proceed always in nearly quantitative yields, but the purification step to remove caprolactam determines mostly the final yield.
In conclusion, the very high selectivity of CBC provides a methodology to make blocked isocyanates that still have free secondary amino groups for further elaborations.

5.3 Reactions of carbonyl biscaprolactam with amino alcohols

The large difference in the reaction rate of an alcohol and an amine with CBC was used to explore the preparation of hydroxy functional BIs. It was anticipated that this difference in reaction rate, in the absence of catalysts, might be high enough to transform predominantly only the amino group of amino alcohols into blocked isocyanates. The hydroxy group would remain available for further modifications.
To verify this hypothesis the reaction of propanol amine with CBC was studied, under similar conditions as with amines (see scheme 5.4).



Scheme 5.4: The reaction of propanol amine with CBC.

In a typical experiment 50 mmol of CBC and 50 mmol of propanol amine were dissolved in 40 ml of toluene and heated for four hours at 120 ^{o}C. Also in this case it was found that the reaction proceeds with a high conversion, but the reaction rate is somewhat slower than with common primary amines. An explanation for this behaviour could be that this amino group is less nucleophile due to the electron withdrawing inductive effect of the hydroxy group. Another explanation is that propanol amine forms intramolecular hydrogen bonds, making the amino group less nucleophilic. Nevertheless, by choosing a higher temperature (120 ^{o}C) the reaction is complete within three to four hours. The product (caprolactam 3-hydroxy-propyl carbamate) is rather well soluble in water, and therefore caprolactam cannot be removed by an aqueous extraction. In that case the mixture was used in the next reaction step, and after that it appeared to be possible to remove caprolactam by an aqueous extraction (*chapter 6*).
The high selectivity, as was found with polyamines, is also seen here. According to the ^{1}H-NMR spectrum only the amino group reacts and there is no indication that the hydroxy group

is modified nor that the formed BI has reacted with the hydroxy or amino groups. Thus one caprolactam group is selectively substituted by the amino group only.
To verify the general suitability of this method, similar reactions were carried out with ethanolamine, 6-amino-1-hexanol and (2-hydroxyethoxy)-ethyl amine and CBC (figure 5.2).

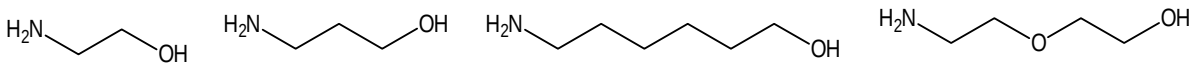
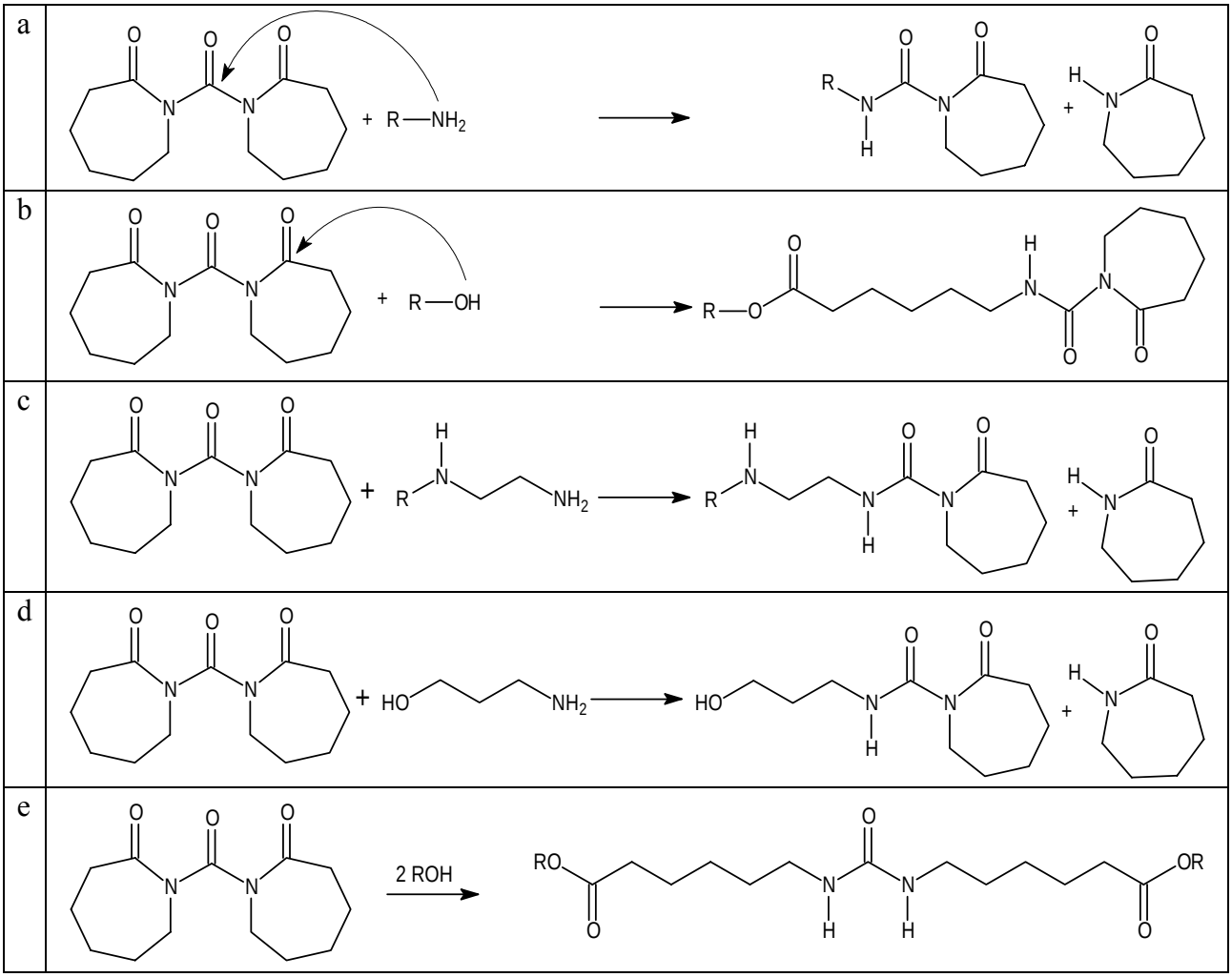


Figure 5.2: Amino alcohols used in the reaction with CBC giving the corresponding BIs.

Here the same experimental conditions were applied and it was shown that these reactions give in all cases the corresponding blocked isocyanates in a nearly quantitative yield. Thanks to the longer alkyl spacer in e.g. 6-amino-1-hexanol, the corresponding blocked isocyanate is much less water-soluble and in that case caprolactam can be removed from the reaction mixture by an aqueous extraction. Since all four amino alcohols showed the same results it seems that this reaction is generally applicable for amino alcohols.
In conclusion, due to the right balance between reactivity and selectivity of CBC, it is possible to make BIs containing free amino and hydroxy groups.

5.4 Summary of the selectivities of CBC

In the previous part of this work a number of different pathways of the reaction of amino or hydroxy containing compounds with CBC have been described. In this paragraph an overview is given of all these different types of selectivities that have been discussed so far and the reactions are depicted in scheme 5.5. Primary amines substitute only one of the caprolactam rings (scheme 5.5a). The second caprolactam ring can be substituted by amines too, but only at higher temperatures. With primary alcohols and in the presence of catalyst an opening of the first ring of CBC takes place (scheme 5.5.b). Polyamines containing primary and secondary amino groups react only via the primary amino group (scheme 5.5c). Amino alcohols react through a double selectivity, in which only one caprolactam of CBC is substituted and only the amino group is active (scheme 5.5d). Finally, with basic catalysts a double ring opening can be obtained (scheme 5.5e).
The number op options with CBC to make reactive additives is larger than with other carbonic acid derivatives, thanks to the possibility of the ring opening of the caprolactam ring.



Scheme 5.5: A summary of the selective reactions of CBC with amines and alcohols. In reactions b and e catalysts are needed.

5.5 Conclusion

The selective preparation of blocked isocyanates from amines, containing primary and secondary amino groups, and CBC has been shown. Only the primary amino groups of these compounds react, whereas the secondary amino groups remain totally unaffected. The secondary amino groups are still available and can be used to couple them to compounds with special properties. During the course of the synthesis primary amines are present next to the already formed blocked isocyanates, but there is no indication that these primary amines react with these blocked isocyanate under the applied reaction conditions (100 ^{o}C). The pure products are obtained in high yields.

Reactions of the amino group of amino alcohols with CBC in toluene give also blocked isocyanates in high yields. The reaction rate is slightly lower than that of common primary

amines, but the corresponding hydroxy functional blocked isocyanates are formed in a nearly quantitative yield, within a few hours. Although the hydroxy group can react with CBC, this does not take place in any detectable amount.

The balance of the reactivity of CBC is remarkable, since in fact two types of selectivity are involved: 1. only one of both caprolactam rings is substituted and 2. only the primary amine is active. Moreover, both selective reactions proceed in high yields.

The most convenient method to separate the blocked isocyanate from the formed caprolactam is by an aqueous extraction, since caprolactam is well water-soluble. The addition of $CaCl_2$ or of HCl to the water phase further improves the solubility of caprolactam. If the water solubility of the product is too high, caprolactam has to be removed by means of a vacuum distillation.

5.6 Experimental section

Instrumentation

NMR spectra were recorded on a Brucker ACF 300 MHz in chloroform.

Materials

CBC was obtained from DSM New Business Development, ALLINCO, (> 99 % pure according to HPLC) and used without purification.

2-Hydroxy ethylamine, 3-hydroxy propyl amine, 6-hydroxy hexyl amine, 2-(2-aminoethoxy)-1-ethanol, bishexamethylene triamine, bisethylene triamine, trisacetone diamine, N-aminoethyl-N-benzylamine, $CaCl_2$, $MgSO_4$ and toluene were purchased either from Aldrich or Acros, and were all used as received.

Synthesis

Reaction of bishexamethylene triamine (BHTA) with CBC

To a solution of bis-(hexamethylene)triamine (100.00 g, 0.466 mol) in dry toluene (400 ml) CBC (246.84 g, 0.980 mol) was added and the resulting mixture was stirred at 80°C for 18 hours. The reaction mixture was then cooled down to room temperature, concentrated under reduced pressure to half its original volume and washed with a saturated aqueous calcium chloride solution (5 x 250 ml) followed with distilled water (8 x 250 ml). Drying of the organic layer with anhydrous magnesium sulphate was followed by filtering off the salt and by the complete removal of the solvent under reduced pressure, yielding the desired product as a brown waxy solid. Yield: 198.32 g, 0.439 mol, 94 %; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.35 (8H, m, C$\underline{H}_2$), 1.56 (8H, m, C$\underline{H}_2$), 1.73 (12H, m C$\underline{H}_2$, ring), 2.57 (4H, t, C$\underline{H}_2$NH), 2.68 (4H, m, NCOC$\underline{H}_2$), 3.26 (4H, m, CONHC$\underline{H}_2$), 3.98 (4H, m, C$\underline{H}_2$N), 9.26 (2H, bt, CON$\underline{H}$).

Reaction of bisethylene triamine (BETA) with CBC

To a solution of bis-(ethylene)triamine (2.0 g, 19.4 mmol) in toluene (20 ml) CBC (10 g, 39.6 mmol) was added and the resultant mixture was stirred at 80°C for 18 hours. The reaction mixture was then cooled to room temperature, concentrated under reduced pressure to half its original volume and washed with distilled water (6 x 15 ml). Drying the organic layer with anhydrous magnesium sulphate was followed by filtering off the salt and by the complete

removal of the solvent under reduced pressure, yielding the desired product as a brown waxy solid. Yield: 1 g, 15 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 to1.74 (24H, broad, ring + chain), 2.70 (4H, t, HNC<u>H</u>$_2$), 2.81 (4H, t, NCOC<u>H</u>$_2$), 3.41 (4H, q, C<u>H</u>$_2$NHCO), 3.99 (4H, t, C<u>H</u>$_2$NCO), 9.38 (2H, s, NHCO).

Reaction of trisacetone diamine with CBC

Trisacetone diamine (5.0 g, 32.1 mmol) and CBC (7.3 g, 29.0 mmol) were dissolved in toluene and stirred overnight at 100°C. According to TLC (alumina, ethyl acetate) all the CBC had reacted. The colourless solution was extracted three times with 30 ml of a 2 wt% aqueous $CaCl_2$ solution. The organic layer was dried on anhydrous Na_2SO_4, filtered and the toluene was removed under reduced pressure. Yield: 11 g, 88%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (2H, q, CHC<u>H</u>$_2$C, 2 x equat.), 1.1 –1.3 (12H, CH_3), 1.75 (6H, ring), 2.0 (2H, q, CHC<u>H</u>$_2$C, 2 x axial), 2.7 (2H, NC(O)C<u>H</u>$_2$), 4.0 (2H, C(O)NC<u>H</u>$_2$), 4.2 (1H, CH), 9.2 (1H, NH). ^{13}C-NMR (300 MHz, $CDCl_3$): δ =23.4, 28.2, 28.4, 29.0, 34.9, 39.7, 43.6, 43.9, 45.2, 50.9, 154.0, 179.3.

Reaction of N-aminoethyl-N-benzyl amine with CBC

CBC (8.39 g, 33.3 mmol) was added to a stirred solution of N-aminoethyl-N-benzyl amine (5.00 g, 33.3 mmol) in dry toluene (100 ml) at 60 °C. The reaction mixture was stirred for a further 18 hours at 60 °C before cooling down to room temperature. The organic mixture was subsequently washed with a saturated aqueous calcium chloride solution (2 x 200 mL) followed by distilled water (4 x 200 ml). Drying of the organic layer with anhydrous magnesium sulphate and filtration was followed by removing of the solvent under reduced pressure, yielding the desired product as pale yellow oil. Yield: 9.23 g, 30.6 mmol, 92%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.74 (6H, bs, CH_2), 2.71 (2H, bm, C<u>H</u>$_2$NCONH), 2.81 (2H, t, C<u>H</u>$_2$NH), 3.35 (2H, q, C<u>H</u>$_2$NHCO), 3.81 (2H, s, C<u>H</u>$_2$Ar), 3.97 (2H, bm, C<u>H</u>$_2$CON), 7.27 (5H, m, ArC<u>H</u>), 9.45 (1H, bt, CON<u>H</u>).

Reaction of 3-amino propanol with CBC

To a solution of CBC (12.61 g, 50 mmol) in toluene (40 ml) 3-amino propanol (3.76 g, 50 mmol) was added and the mixture was heated in a nitrogen atmosphere for 4 hours at 120°C. According to TLC measurements CBC was completely converted. The reaction product was a mixture of caprolactam 3-hydroxy propyl carbamate and caprolactam, and this was used in chapter 6 in the next step without purification. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.48 (6H, m, $CH_2CH_2CH_2$ ring) 1.58 (2H, m, CH_2C<u>H</u>$_2CH_2OH$), 2.69 (2H, t, $CH_2C(O)$), 3.46 (2H, m, C<u>H</u>$_2$OH), 3.90 (2H, t, CH_2N), 4.50 (1H, broad, OH), 9.19 (1H, broad, NH).

Reaction of 6-amino-hexanol with CBC

To a solution of CBC (25.3 g, 100 mmol) in toluene (100 ml) 6-amino hexanol (11.76 g, 100 mmol) was added and the mixture was heated under nitrogen atmosphere for 4 hours at 120°C. According to TLC measurements CBC was completely converted. The organic mixture was subsequently washed with a saturated aqueous calcium chloride solution (2 x 200 mL) followed by distilled water (4 x 200 ml). The organic layer was dried with anhydrous magnesium sulphate, the salt was removed by filtration and the solvent was distilled off under reduced pressure. ^{1}H-NMR (300 MHz, d6-DMSO) δ = 1.26 to 1.66 (14H, broad, $CH_2CH_2CH_2$ ring and $CH_2CH_2CH_2CH_2$ chain), 2.68 (2H, t, CH2C(O)), 3.15 (2H, t, NHC<u>H</u>$_2$), 3.38 (2H, m, C<u>H</u>$_2$OH), 3.90 (2H, t, NCH_2), 4.33 (1H, broad, OH), 9.15 (1H, broad, NH).

Reaction of 2-(2-aminoethoxy)-1-ethanol with CBC

To a solution of CBC (12.61 g, 50 mmol) in toluene (40 ml) 3-amino propanol (3.76 g, 50 mmol) was added and the mixture was heated under nitrogen atmosphere for 4 hours at

120°C. According to TLC measurements CBC was completely converted. The organic mixture was subsequently washed with a saturated aqueous calcium chloride solution (2 x 200 mL) followed by distilled water (4 x 200 ml). The organic layer was dried with anhydrous magnesium sulphate, the salt was removed by filtration and the solvent was distilled off under reduced pressure. ^{1}H-NMR (300 MHz, d6-DMSO) δ = 1.60 (6H, m, $CH_2CH_2CH_2$ ring), 2.29 (2H, t, $CH_2C(O)$), 2.69 (2H, t, CH_2N), 3.36 (2H, t, $NHC\underline{H}_2$), 3.51 (2H, t, $NHCH_2C\underline{H}_2O$), 3.66 (2H, t, $OC\underline{H}_2CH_2O$), 3.92 (2H, t, $OCH_2C\underline{H}_2O$), 4.22 (2H, t, NCH_2), 9.30 (1H, broad, NH).

5.7 References

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Chapter 6

Functional coatings

Abstract

The novel methodology that has been developed to make blocked isocyanates is explored for making coatings with special properties.

The technology to convert functional compounds with hydroxy groups directly into blocked isocyanates is used to make functional BIs from perfluorine alcohols and CBC. Coatings, containing only small amounts of this fluorine compound, possess very hydrophobic surfaces with exceptionally low surface tension, thanks to a self-stratification process.

The unique selectivity of CBC towards amino alcohols is used to make hydroxy functional BIs, which are subsequently converted into acrylate monomers, by reacting the free hydroxy groups with acryloyl chloride. Polymethacrylate copolymers, comprising these functional BIs, hydroxyethyl methacrylate and methyl methacrylate, are prepared by a radical polymerization at 120 ^{o}C, without any sign of crosslinking. If these self-crosslinkable resins are applied on metal substrates and cured at 180 ^{o}C, transparent crosslinked coatings are obtained, with good mechanical properties.

6.1. Introduction

Due to the negative impact of solvent borne coatings on the environment and for economic motives, there is worldwide a strong interest in powder coatings. Although powder coatings are widely used in industrial applications, the market share is still low compared with solvent and water borne systems, because this technology is relatively young. The market share is rapidly growing, thanks to the technical and economical advantages. The advantages of powder coatings are the high utilization of the paint (hardly any waste), absence of solvents, low fire risk, no disposal problems, no air pollution and reduced health risks[1].

The main organic constituents of powder coatings are resins and crosslinkers. The resins are mainly polyesters, acrylics and epoxies. In principle polyester resins may contain many different monomers, but in practice only a few acids and diols are used. Terephthalic and isophthalic acid are the favourite acids and neopentyl glycol, propylene glycol and ethylene glycol are the preferred diols. The same considerations hold for the acrylic resins. Many compositions are possible, but only a limited amount of monomers are available on a large scale and used in commercial systems. Two epoxy resins, diglycidyl ether of bisphenol-A and Novolac based resins, are commercially most widely used, and since these resins are also prepared in quite large quantities they are readily available and relatively cheap[2].

Although the number of monomers is limited, the number of coating resins is still quite substantial. In contrary, the number of commercial crosslinkers for powder coatings is low. In polyesters triglycidyl isocyanurate, blocked isocyanates and β-hydroxyalkylamides are preferred. In acrylic resins blocked isocyanates and dodecane dicarboxylic acid are mainly in use, while in epoxy resins dicyandiamides, amines and anhydrides (as crosslinker/catalysts) are frequently applied.

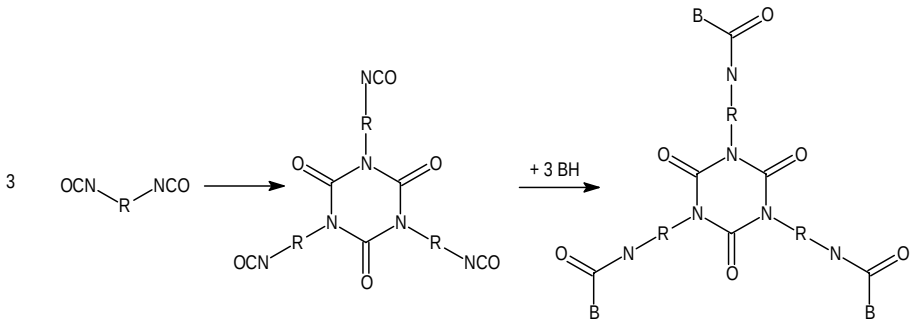
Up till now these crosslinkers are solely applied to make in a fast way chemical networks, in high conversions, but seldom to influence the properties of the coating by their chemical nature. Adapting and improving of properties of the coating are so far only done by modifying the resins, and not by adjusting the crosslinker. This is due to the lack of crosslinkers with functional groups.

A major class of crosslinkers is isocyanates, giving high quality polyurethane coatings. Isocyanates are highly reactive and can only be used in two-component coating systems by adding them to a polyol just before applying the coating. If a long shelf-life is required the isocyanate is blocked temporarily by means of a blocking agent, giving blocked isocyanates (BIs) as a result. This blocking reaction is reversible and on heating the isocyanate becomes free again and can react with the hydroxy groups of coating resins. Actually, only two types of BIs are commercially available and only a limited amount of specialized companies are able to prepare them because of health issues. Tailoring properties of the coatings by the structure of the crosslinker has therefore been difficult so far.

So, there is a need for a safe and simple method to make a wide variety of BIs, which can be used to tailor the coating properties by the nature of the crosslinker. This will expand the possibilities to tune the coating properties. Moreover, it is particularly important to prepare BIs from non-toxic chemicals, because this widens the applicability as well. The impact on improving the surface properties of products by using functional coatings is very large, because the surface of a product determines to a large extent the overall properties of the product.

6.2. Commercial blocked isocyanates

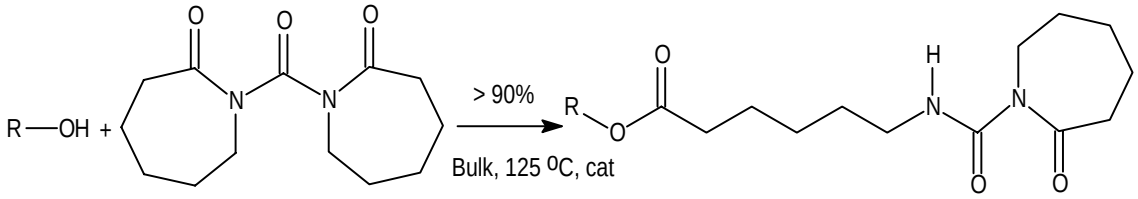
Before going into the details of the new compounds, a short description is given of the present route to make BIs. Blocked isocyanates are prepared by the addition reaction of a blocking agent to isocyanates (*chapter 4*). Caprolactam is the most frequently used blocking agent, because it is cheap and not toxic. Hexamethylene diisocyanate (HDI) and isophoron diisocyanate (IPDI) are commercially the most important isocyanates and always used in their trimerized form, to reduce the volatility (toxicity) and to increase functionality. The synthetic procedure is shown in scheme 6.1. In general crosslinkers need to have functionalities higher than 2 to ensure good crosslink densities, necessary to get highly durable and chemically resistant coatings. In commercial coating systems BIs are combined with hydroxy functional polyester or acrylate resins.



Scheme 6.1: The commercial route to make blocked isocyanates starting from isocyanates (BH is a blocking agent).

6.3 Coatings with fluorine functional blocked isocyanates

The direct preparation of blocked isocyanates from ordinary alcohols and CBC is described in *chapter 4* (scheme 6.2). The use of catalysts, like $MgBr_2$, $Ti(OR)_4$ or $Zr(OR)_4$, is indispensable to get good yields of the ring opening reactions.



Scheme 6.2: The direct preparation of BIs from alcohols with CBC in the presence of a catalyst.

Here the preparation of *functional* BIs is studied, starting from functional alcohols and CBC, in a one step procedure. This concept is explored with fluorine containing alcohols. The functionality in this case is the highly hydrophobic perfluorine group. It is to be expected that these fluorinated blocked isocyanates may give coatings with hydrophobic properties.

There are two possibilities conceivable to apply linkable additives in hydroxy functional coating resins[3]. One approach is to replace the usual (trifunctional) crosslinkers completely by new ones that have special properties. Another approach is to add additionally functional additives with the same reactive groups as the regular crosslinkers have. The latter case is more flexible and less of the new product is needed. Moreover, in that case the number of blocked isocyanate groups of the new compound does not play a role (one is enough) since the usual crosslinker is added too, to ensure the necessarily

crosslink density. Here the latter methodology has been adopted, to prepare polyester coatings with a low surface energy.

Materials with low surface tension are very well appreciated in many applications for their special properties such as biocompatibility, anti-fouling and low friction. Although most of the fluorine containing materials is highly appreciated for their properties, their use is still limited due to the high costs. The most important characteristics of these materials are basically achieved by their surface properties and there is no need to have the majority of the expensive fluorine in the bulk of the coating. Self-stratification may offer the solution to improve the balance between costs and performance.

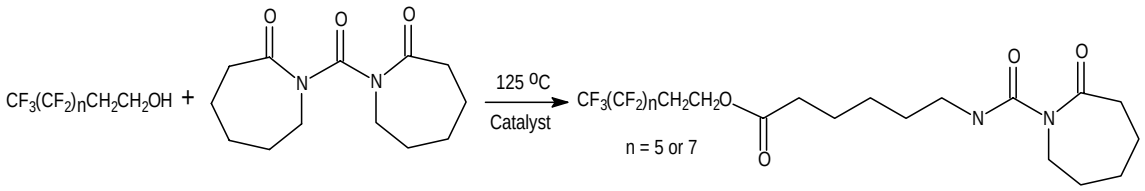
Self-stratification is a physical process by which the compound with the lowest surface tension migrates to the coating-air interface. The surface tension of air is much lower than that of polyester coating resins. The total free energy of the system minimizes if the low surface tension compound migrates to the air-resin interface. This behaviour offers an excellent opportunity to add small amounts of a fluorine compound that migrates to the surface, giving a fluorine enriched top layer. The diffusion rate of fluorine containing compounds depends on a number of parameters such as the fluorine content, the molecular weight, the reactivity, the temperature and the viscosity of the system. The lower the molecular weight, the higher the diffusion rate. Ming et al.[4] have shown that the effect of mixtures of fluorinated and non-fluorinated resins on surface tension was modest, whereas their results with the lower molecular weight fluorinated crosslinkers were much better. Unfortunately, their fluorinated crosslinkers were statistical mixtures and therefore ill-defined. The motivation of this work is to make well-defined low molecular weight fluorine containing reactive additives based on the unique CBC chemistry.

In order to ensure durability it is indispensable that the additives are chemically fixed in the cured coating, in particular in the surface layer. Non-covalently bonded additives can easily be wiped away and are therefore not durable and bad for the environment. Furthermore, the enriched surface layer should not be too thin to prevent loss of quality in case of small surface damages. A chemical coupling between the additive and the coating resins is therefore absolutely necessary.

Powder coatings consist of resins with a number average molecular weight of 3,000 to 5,000 g/mol, crosslinkers, pigments and some additives, but no (organic, volatile) diluents. One important group of these coating systems comprises hydroxy functional polyesters and caprolactam blocked isocyanates as crosslinkers.

These systems are particularly well suited to study the influence of the addition of various (small) amounts of fluorine functional blocked isocyanates, since they can react in the same manner as the regular blocked isocyanate crosslinker.

Thus well-defined perfluorine compounds containing BI groups were made by the CBC methodology. Two pure perfluorine alcohols, $CF_3(CF_2)_nCH_2CH_2OH$ with n = 5 and n = 7, and a commercial mixture with n = 5 to 7 (Zylon BA-L) were tested in making the corresponding BIs (scheme 6.3).



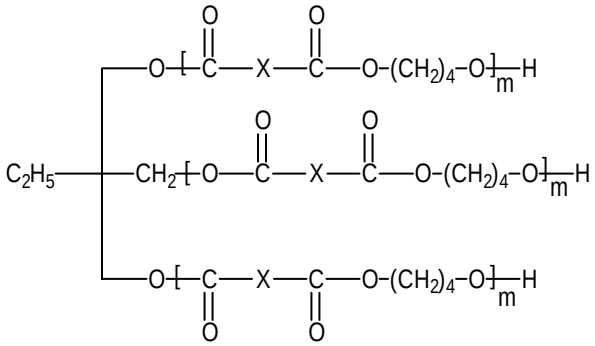
Scheme 6.3: Preparation of fluorinated BIs from perfluorine alcohols with CBC.

The perfluorine alcohol that is used in these experiments has a $–CH_2CH_2-$ spacer between the perfluoralkyl groups and the hydroxy group. It might well be that perfluorinated alcohols with a completely fluorinated alkyl group behaves differently, because the perfluorine groups is a strong electron withdrawing group.

The synthesis was done in the same way as with ordinary aliphatic alcohols, thus by heating the perfluorine alcohol and CBC during three hours at 125 ^oC, in the bulk and in the presence of a catalyst (2-ethyl-hexyloxy titanate). The suspension of CBC (melting temperature 115 ^oC) and the perfluorine alcohol became a clear mixture after a few minutes of heating. The reaction was followed via TLC, and is finished after 3 to 4 hours. Thus it is shown that the reaction of CBC with the perfluorine alcohols proceeds similarly as with aliphatic alcohols. The yield was quite high (> 95 wt%), but the product was slightly yellow, which is not acceptable in coating applications. The coloured impurity was easily removed by dissolving the reaction product in toluene and treating the solution with active carbon black. After removal of the carbon black by filtration a colourless

solution was obtained, which gave a colourless product after removing toluene (rotor evaporator). This product can be used without any further purification. If a high purity is needed and additional crystallisation step (from ethyl acetate) is necessary.

The coating system tested consisted of a hydroxy functional polyester (depicted in figure 6.1), a crosslinker and the perfluorine additive with n = 5 and 7 (scheme 6.3). The hydroxy functional polyester was prepared according to Ming et al.[4] by heating an equimolar mixture of glutaric acid, adipic acid and azelaic acid (0.1 mol each) and trimethylol propane (0.1 mol) and 1,4 butane diol (0.3 mol), in the presence of a catalyst (Fascat 4101, 0.1 % with respect to the total amount of monomers) until 95 % of the theoretical amount of water was collected.



X = equimolar mixture of $(CH_2)_3$, $(CH_2)_4$ and $(CH_2)_7$; m = 1-2

Figure 6.1: Schematic presentation of an average structure of the hydroxy functional polyester resin.

Desmodur BL-3272, a commercial trifunctional caprolactam blocked isocyanate from Bayer -based on hexamethylene diisocyanate- was used as a crosslinker. Several fluorine-containing coatings were prepared by adding small amounts of the fluorine containing blocked isocyanate (the compound of scheme 6.3 with n = 7 contains 46 % F). Six coating formulations were made with increasing fluorine concentrations with both additives, varying between 0 to 3.8 wt % F. The curing reactions were done at two different temperatures, 150 and 200 ^oC, to study the rate of self-stratification, which is the resultant of the diffusion rate (physics) and the rate of coupling of the fluorine additive (chemistry) onto the polyester. The cure time at 150 ^oC is about 3 hours, whereas the reaction needs only 15 minutes at 200 ^oC. The kinetic data of the cure rate were obtained from IR, which monitored the decrease of the –OH concentration.

To measure the surface properties contact angle measurements were carried out. The value of the contact angle of two liquids (water and hexadecane) on the coating allows the estimation of the surface tension of coatings. These measurements revealed that at both curing temperatures (150 and 200 ^{o}C) the contact angles increase substantially with increasing fluorine content, meaning that the surface tensions decrease considerably. In figure 6.2 the advancing contact angles of water and the static contact angles of hexadecane are plotted in relation to the overall fluorine content of the coatings.

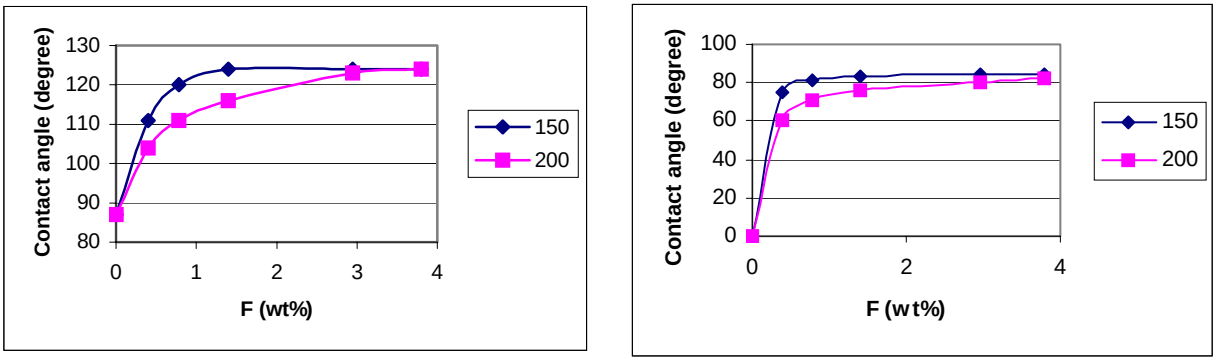


Figure 6.2: Contact angles of water (left) and hexadecane (right) as function of the total amount of added fluorine (n = 7; scheme 6.3) to the resin, cured at 150 and 200 ^{o}C.

The relation between the fluorine content of the coating and the contact angle depends on the curing temperature (150 ^{o}C or 200 ^{o}C), which is, as mentioned before, a result of the competition between chemistry and physics. When the coatings are cured at 200 ^{o}C, the water contact angles increase steadily from 87 to 124^{o} and the hexadecane contact angles increase from 0 to 80^{o}, as the added overall fluorine content of the coating increase from 0 to 3.8 wt %. From the shape of the curves in figure 6.2 it can be seen that the maximum value for the contact angles is reached at about 3 to 4 wt % of fluorine, but at lower concentrations already quite high contact angles are obtained.

When the resin is cured at 150 ^{o}C the contact angles go to their maximum value at even lower fluorine concentrations. Both the diffusion rate and the reaction rate decrease at a lower temperature, but, as expected, by lowering temperature the reaction rate decreases more than the diffusion rate. Although the plateau value is reached at lower fluorine content when cured at 150 ^{o}C, the maximally attainable contact angle is the same for both temperatures, indicating that the type of fluorine additive determines this value. The cure

rate at 150 °C (3 h) is unacceptably low in practice, but fortunately low surface tensions are also attainable in 15 min. at 200 °C, which is an acceptable curing temperature.
Self-stratification, which is probably the origin of these phenomena, should result in a higher fluorine content of the surface top-layer. The composition of the surface layer was measured by XPS to validate this assumption and the results are shown in figure 6.3.
The F/C atomic ratio was calculated from the XPS spectra by comparing the F_{1s} and C_{1s} peak intensities, taking the sensitivity factors into account. In XPS analysis only the composition of the 8 to 10 nm thin top-layer is measured, and it can be seen in figure 6.3 that the F/C atomic ratio in that top layer reaches 0.65, whereas the calculated value in the bulk is lower than 0.04. These results prove that there is a strong enrichment of fluorine in the surface top-layer. The maximum value of the contact angle (figure 6.2) on adding the fluorine additive is reached at a lower fluorine concentration than the maximum in the F/C atomic ratio (figure 6.3), and this is particularly the case at 200 °C.

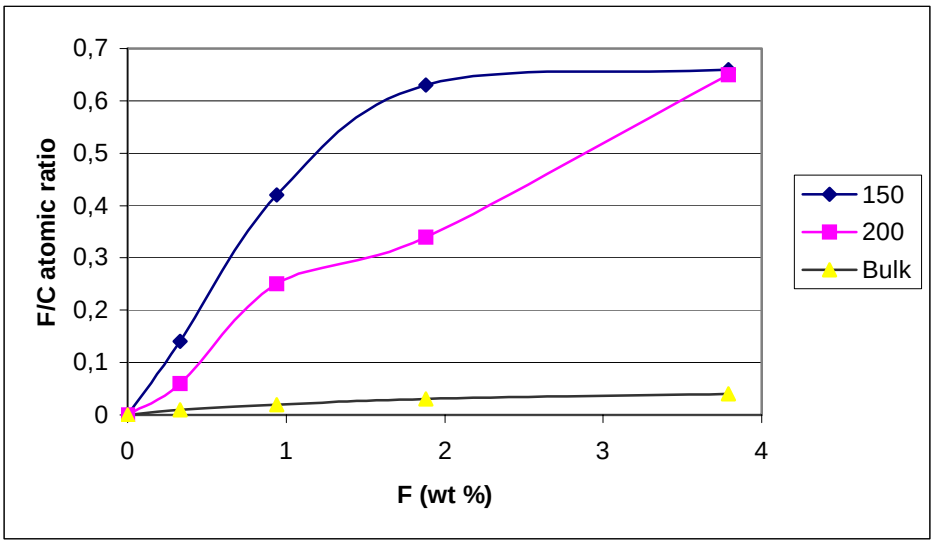


Figure 6.3: F/C atomic ratio in the top layer of the coating in function of the total percentage of fluorine in the coating, measured by XPS.

An explanation for this difference could be that the XPS measurements give the composition of about 8 nm of the top layer, while the contact measurement gives information of the surface only. Hence, the maximum in the surface tension is reached at lower fluorine content. Nevertheless, both measurements reflect the same trend. The profile at 200 °C is probably preferred, since the enriched top layer is then thicker and less vulnerable to be damaged.

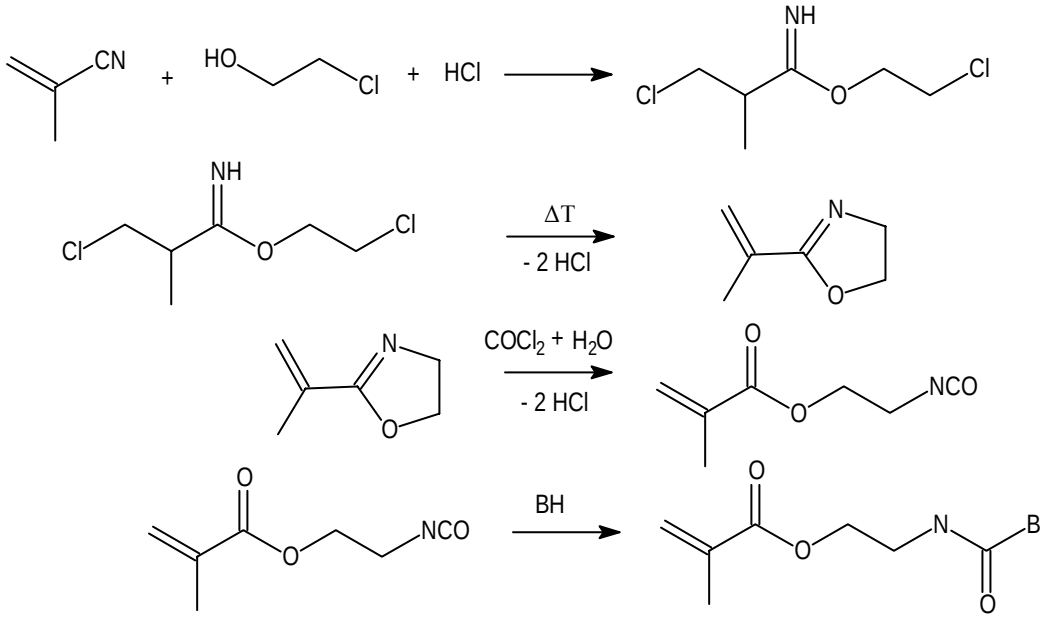
The high contact angles, corresponding to a surface tension of about 10 mN/m, clearly show a large effect of adding small amounts of fluorine additives on the surface tension, if compared with the virgin coating (40 mN/m), but particularly in comparison with well-known low-surface-tension materials such as Teflon (20 mN/m).
This example clearly demonstrates one of the objectives of this thesis, showing that small amounts of reactive additives, containing groups with exceptional properties, can have a large impact on the final properties of polymeric materials.

6.4 Self-crosslinkable polymethacrylate coatings

6.4.1 Introduction

In the previous chapter it has been demonstrated that the reactivity of CBC with primary amines is much higher than with alcohols. This difference in reactivity enables the preparation of hydroxy functional BIs by reacting CBC with amino alcohols. The objective was to make an acrylate monomer comprising a blocked isocyanate group from this, and to make subsequently copolymers of this monomer with hydroxy ethyl methacrylate and other (meth)acrylates to obtain self-crosslinkable coatings.
In quite a number of publications the application of (meth)acrylate monomers containing blocked isocyanate groups have been described[5]. However, there is no convenient method to make these products. Showa Denko produces commercially caprolactam blocked 2-isocyanato-ethyl methacrylate (KarenzMOI). The starting product, 2-isocyanato-ethyl methacrylate, is produced in a multi-step synthesis[6] and is, apart from its very high toxicity, very expensive. The synthetic procedure of Showa Denko is not public, but from the literature a reasonable synthesis can be deduced. The last step in that synthesis, the conversion of isopropenyl-2-(2-oxazoline) into 2-isocyanato-ethyl methacrylate by phosgene as depicted in scheme 6.4, is described by Showa Deko[6] and Dow[7]. Dow[7] produced commercially isopropenyl-2-(2-oxazoline), which is the important intermediate in scheme 6.4. It is reasonable to assume that Showa Denko uses the same process in the first steps to make 2-isocyanato-ethyl methacrylate (scheme 6.4). The synthesis requires a number of steps and the yields are rather low, according to the literature. Furthermore, several of the intermediate products are toxic.

The number of publications[5], for the preparation of polymers with interesting properties, indicate the high value of this monomer, and therefore a safer and cheaper route to make it would be very welcome.



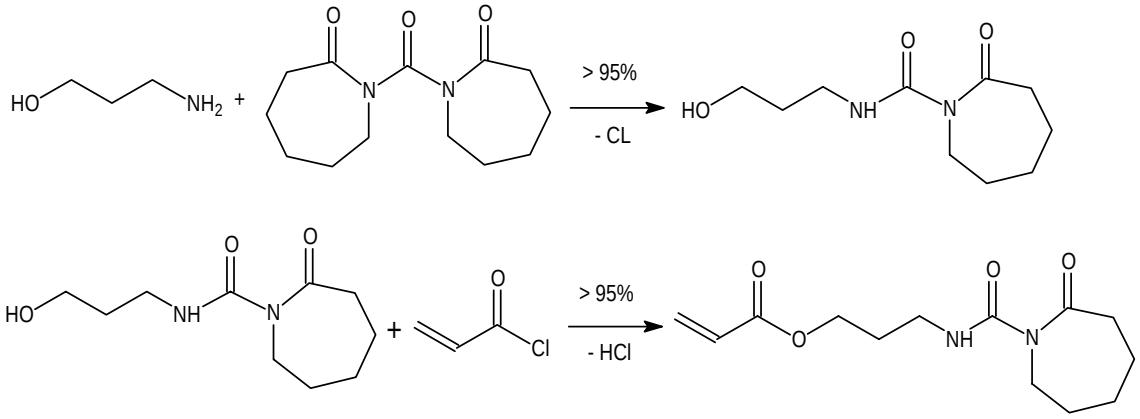
Scheme 6.4: Possible synthetic route towards caprolactam blocked 2-isocyanato ethyl methacrylate (BH = blocking group).

6.4.2 Preparation of acrylate esters of caprolactam ω-hydroxy-alkyl carbamates

As described in *chapter 5*, the reaction of 3-amino-propane-1-ol with CBC gives a hydroxy functional BI with a yield of more than 95 %, with caprolactam as the only detectable side product (scheme 6.5). The general procedure to remove caprolactam by an aqueous extraction is not feasible in that case, since the product itself is quite well water-soluble.

Since this mixture contains caprolactam and caprolactam hydroxy propyl carbamate only the reaction was continued without further purification. The preparation of the corresponding acrylate ester (Scheme 6.5) was done with acryloyl chloride. It was expected that the reactivity of acryloyl chloride towards caprolactam would be less than towards the hydroxy group of the carbamate. These reactions were carried out in the presence of triethyl amine as HCl scavenger. The generated triethylamine-HCl salt is

insoluble in the reaction medium and can easily be removed by filtration. Caprolactam and caprolactam blocked 3-isocyanato propyl acrylate remain dissolved in toluene.
Caprolactam does not interfere in the reaction between hydroxy propyl carbamate and acryloyl chloride. As expected it was found that the acrylate ester of caprolactam hydroxy propyl carbamate is much less water-soluble than the starting product, and caprolactam could be removed in that stage by the aqueous extraction. The ^{1}H-NMR showed that after three aqueous extractions the product still contained some traces of caprolactam. In order to make polymers from highly pure monomers the remaining traces of caprolactam were removed by column chromatography.



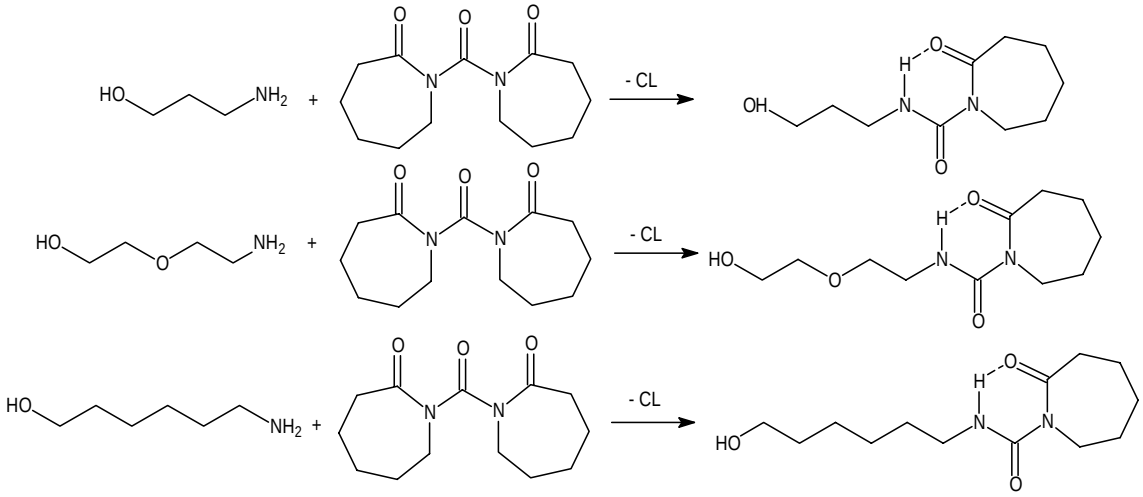
Scheme 6.5: The preparation of an acrylate monomer containing a blocked isocyanate group, starting from CBC and 3-hydroxy propyl amine (CL = ε-caprolactam).

By comparing scheme 6.4 with 6.5 it can be seen that a more convenient synthesis of caprolactam blocked 3-isocyanato propyl acrylate seems possible. Later on a more elegant method was found to remove the hydrochloric acid, by using caprolactam instead of triethyl amine as an acid scavenger[1)]. However, the monomers that are used in this study for the preparation of copolymers were still prepared with the "old" method by using triethyl amine as base.

[1)] Caprolactam, which is present in the reaction mixture, is a weak base, but in apolar non-protic solvents, like toluene, its basicity is high enough to form salts with hydrochloric acid. Caprolactam can be used to remove the HCl instead of using trietylamine. The elegance of this method is that no new chemicals (e.g. like triethyl amine) have to be added and that caprolactam is being removed as a salt by filtration. Furthermore there is less chance that caprolactam reacts with acryloyl chloride, preventing the formation of side products.

In contrast to the Showa Denko route this novel route offers the possibility to prepare caprolactam alkyl carbamates with various spacer lengths between the BI-groups and the olefinic double bond. This advantage was utilized to make several monomers, and to study the influence of the spacer length on the toughness of the coatings.

The first step of the reaction with other amino alcohols, such as 6-amino hexan-1-ol or 2-(2-aminoethoxy)-1-ethanol, with CBC was carried out in exactly the same way as has been described for 3-amino propane-1-ol, and also in these cases the corresponding hydroxy functional BIs were obtained in a nearly quantitative yield (scheme 6.6).



Scheme 6.6: Preparation of hydroxy functional blocked isocyanates from various amino alcohols and CBC (CL = ε-caprolactam).

Because the reaction products with longer aliphatic spacers are less water-soluble than with propanol amine, caprolactam can be removed by the usual aqueous extraction. The overall yields are reasonable (50 – 70 %) but not (yet) exceptionally high due to the losses during the aqueous extraction, since the reaction products still have some water solubility. But, the aqueous extraction procedure has not been fully optimized yet.

Also the acrylate esters of the two hydroxy functional blocked isocyanates with the longest spacer groups are prepared from acryloyl chloride, in the presence of triethyl amine. As expected the esterification proceeds quite similar to those obtained with caprolactam 3-hydroxy propylcarbamate. In general, the esterification of these hydroxy functional BIs proceeds similarly as with ordinary aliphatic alcohols.

In commercial applications the direct esterification with acrylic acid would be much more attractive. Therefore some trials were done to esterify the hydroxy compound directly with acrylic acid, which is much cheaper than the acid chloride and no waste (salt) is produced. Several ordinary esterification catalysts, such as p-toluene sulfonic acid, sulfuric acid and BF_3 etherate, were used without success. In the presence of hafnium chloride ($HfCl_4(THF)_2$)[8] or scandium triflate ($Sc(SO_3CF_3)_3$)[9], the direct esterification of the hydroxy alkyl carbamates with acrylic acid was successful. It was, however, necessary with these catalysts to remove caprolactam beforehand because otherwise this compound was partially acrylated as well. These promising routes have not fully been explored yet.

6.4.3 Terpolymers of caprolactam blocked ω-isocyanato-alkyl acrylates, hydroxy-ethyl methacrylate and methyl methacrylate.

In polymethacrylate (powder) coating systems two crosslink mechanisms are frequently in use. Epoxy functional polymethacrylate coatings -containing glycidyl (meth)acrylate- are crosslinked with dodecane dicarboxylic acid, and hydroxy functional polymers –containing hydroxyethyl (meth)acrylate- are crosslinked with (blocked) isocyanates. The latter system gives excellent properties, especially with respect to durability. These poly(urethane-methacrylate) coatings are two component systems, prepared by mixing hydroxy functional resins with trifunctional (blocked) isocyanates.

Here the preparation of copolymers is studied in which the crosslinkers are built-in in the resin to omit the compounding step and to ensure excellent transparency, thanks to a perfect compatibility of the crosslinker with the resin. Moreover, the emission of (toxic) crosslinkers is impossible in this case.

The synthesized caprolactam blocked ω-isocyanato-alkyl acrylates were copolymerized with HEMA (HydroxyEthyl MethAcrylate) and MMA (Methyl MethAcrylate) in a standard radical solution polymerization. Two series of terpolymers were prepared, one with 5 mol % of the new monomers and 5 mol % of HEMA, and one with 10 mol % of the new monomers and 10 mol % of HEMA, whereas the remaining monomer (90 en 80 mol %, respectively) was methyl methacrylate. In a typical experiment the polymerizations were carried out in toluene at 120 ^oC with 3 wt % of AIBN

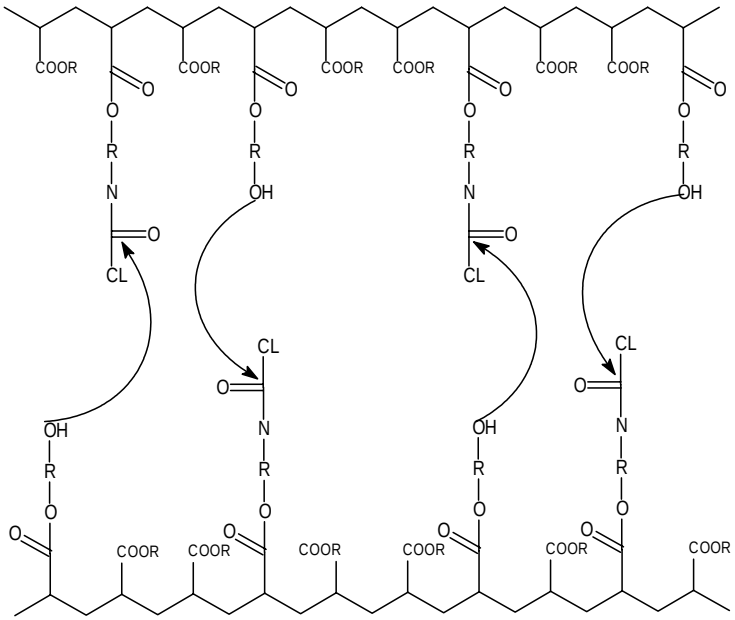
(AzoIsoButyroNitril) as initiator. This rather high temperature for a radical polymerization and high concentration of AIBN were chosen to make low molecular weight resins, which is important in coating applications to get good flow, and as a consequence good film forming properties. No chain transfer agents were added, since these may reduce the durability. The polymerization temperature (120 ^{o}C) is low enough to prevent the premature reaction of the hydroxy groups of HEMA with the blocked isocyanate groups. The molecular weights of these resins, measured by SEC, were about 7000 g/mol. The calibration of the SEC columns was done with polystyrene standards, hence these values are only indicative.

The preparation of these terpolymers is done by adding the monomers and the initiator to the reaction vessel in an inert atmosphere and then heating the mixture for a few hours. No data on the reactivity ratios of these new monomers in radical polymerizations with other methacrylate monomers were available. So, at the moment there is no information on the monomer sequence distribution and degree of randomness. Since caprolactam blocked isocyanato-acrylates (and not the methacrylate derivatives) are prepared, it is reasonable to assume that these monomers react faster than methacrylates and that these monomers will most probably be built-in completely into the terpolymers. According to the ^{1}H-NMR data the composition of the terpolymers is indeed quite similar to the composition of the monomer mixture. Much more work has to be done to determine the reactivity ratios to get a better understanding of the real molecular fine structure of these terpolymers.

In spite of this, some preliminary tests with these self-crosslinkable coating resins were carried out to see whether coatings were obtained with promising properties. The terpolymers that have been actually tested contained 10 mol % of the novel monomer, 10 mol % of HEMA and 80 mol % of MMA. A schematic representation of the crosslinking reaction of the self-crosslinkable coating resin is shown in scheme 6.7.

Before applying these coatings onto substrates their curing behavior was studied by measuring the change of the rheological behaviour at 180 ^{o}C in time. In figure 6.4 the results are given of the copolymers containing 10 mol % caprolactam blocked 5-isocyanato-2-(2-ethoxy)-ethyl acrylate, 10 mol % HEMA and 80 mol % MMA. It can be seen that the phase angle δ goes from 90 to 0^{o} in about 400 seconds (7 min), meaning that

the crosslinking of the network is complete within this time span. The viscosity (and modulus) first drops due to melting of the material, followed by an increase due to the crosslink reaction. Although the composition of the resins is not optimized yet, these results show that crosslinking takes place within an acceptable time, comparable to that of the commercial systems. Also in commercial systems the phase angle δ decreases in about 400 seconds from 90 to 0^{o} (not shown here).



Scheme 6.7: Schematic representation of the self-crosslinkable polymethacrylates (CL = ε-caprolactam).

Terpolymers with the monomers with different spacer lengths were tested in the same way and showed a similar behaviour. From these rheology data it was concluded that coating resins with 10 mol % of built-in crosslinkers have a good curing speed, making them suitable for further evaluation.

Although the T_g of these resins is a high enough to make powder coatings, these resins were applied from solution for the sake of simplicity. First toluene, the solvent in which the copolymers were prepared, and the residual monomers were removed under reduced pressure. The coatings were subsequently dissolved in THF (30 wt %), and then they were applied as 125-µm-thick layers on aluminum plates. After THF had been evaporated by heating the plates for 30 minutes at 60 ^{o}C, the coatings were cured for 30 minutes at 180 ^{o}C. Curing during 30 minutes seems quite long, and is according to the rheology

measurements not necessary, but it is usually done in first trials to be sure that the coatings are fully cured. Coatings are evaluated at first by a visual inspection and the appearance was in all these cases satisfying. Transparent, colourless smooth coatings were obtained, still having a few craters, but that can probably be optimized by adding anti-cratering agents. The rather high molecular weight of the resins may also have a negative influence on this behavior.

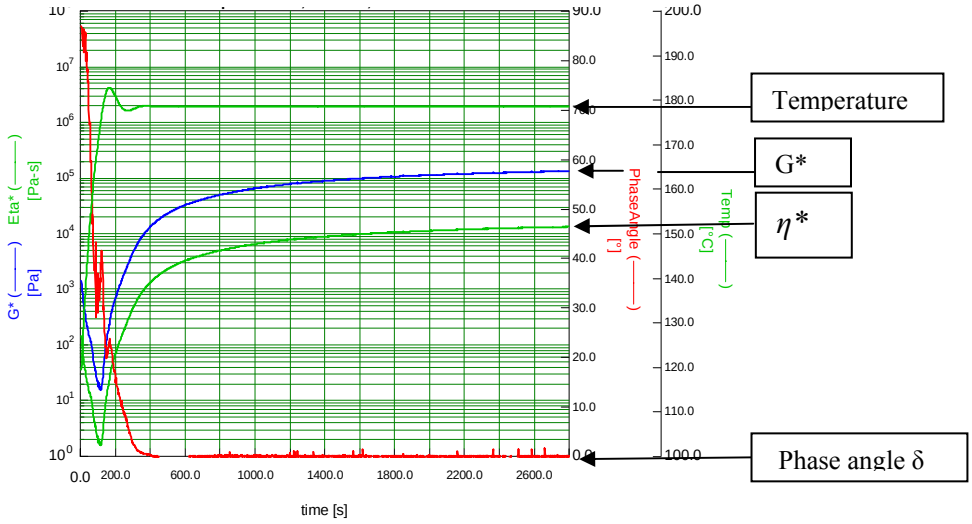


Figure 6.4: The curing behaviour of a self-crosslinkable polymethacrylate coating resin (10 mol% 5-isocyanato-2-(2-ethoxy)-ethyl acrylate, 10 mol% HEMA and 80 mol % MMA).

Some preliminary mechanical tests (T-bend) showed that these coatings were rather tough particularly compared to common polymethacrylates. The longer spacer lengths in the acrylate blocked isocyanate seem to enhance the toughness. This is in line with the expectations for ordinary (meth)acrylate coatings, by which the coatings become tougher if crosslinkers with longer spacers are used. More quantitative work has to be done to validate this for the novel coatings.

The acetone double rub test is a simple test, but it is a very good indication of the crosslink density. In this test a sample is rubbed with a tissue saturated with acetone, and the number of rubs, before any damage is seen, is a measure for the crosslink density. The crosslink density is satisfactory if the number of rubs exceeds 100. With these cured

polymethylacrylates the number of acetone double rubs exceeded even 300, which is very high, indicating a very high crosslink density. This very high crosslink density in combination with a relatively good toughness is an encouraging result.

So, acrylate monomers containing a BI function are not new[5], but a simpler, safer and cheaper way of preparing them is found, which offers additionally the possibility to vary the spacer length between the BI-groups and the double bond.[10].

6.5 Conclusions

Two types of coatings with improved properties have been prepared by making BIs, using the selective reactivity of CBC. In one case BIs containing perfluoroalkyl chains as functional group have been prepared by reacting CBC with perfluorine alcohols. This ring opening reaction proceeds in high yields, particularly when tetra (2-ethyl-hexyloxy) titanium is used as catalyst. Several coating systems were prepared consisting of hydroxy functional polyesters, trifunctional blocked isocyanates and various amounts of these new perfluorine blocked isocyanates. Coatings are obtained with high contact angles (124^{o} with water) when only small amounts (< 4 wt% F) of these perfluorine compounds are added. The surface tension calculated from the contact angles is as low as 10 mN/m, whereas Teflon has a surface tension of 20 mN/m.

Such a low surface tension with a fluorine content as low as 4 wt% is only possible via a self-stratification process. In such a process low surface energy compounds tend to migrate to the air-coating interface to lower the total free energy of the system. XPS measurements indeed show a strong enrichment of the fluorine atoms in the top level of the coating, proving that the self-stratification process indeed took place.

In another investigation a number of novel acrylates containing blocked isocyanate groups, have been prepared by a new synthetic method. In the first step various hydroxy alkyl amines are reacted with CBC, yielding hydroxy functional caprolactam alkyl carbamates (BIs) in high yields. Subsequent esterification of these compounds with acryloyl chloride yields the corresponding esters. These hydroxy functional carbamates behave as ordinary aliphatic alcohols in that esterification step. The spacer length between the blocked isocyanate moiety and the olefin double bond is adjustable, making this method more flexible than the current method. Next, terpolymers of these BI-

functional acrylates with methyl methacrylate and hydroxy ethyl methacrylate are prepared. These terpolymers, containing built-in crosslinking groups, are tested as self-crosslinkable coating systems. When these self-crosslinkable resins are applied onto metal substrates and cured at 180 ^{o}C for 30 minutes they yield colourless, transparent crosslinked coatings. The toughness of these coatings is quite high, and they resist 300 acetone double rubs, indicating that high crosslink densities have been obtained. The combination of a high crosslink density and a rather good toughness is a very promising result.

6.6. Experimental section

Materials

CBC was obtained from DSM New Business Development, ALLINCO (>99.0 % pure, according to HPLC) and used without further purification. Perfluorine alcohols, 3-hydroxy-propyl amine, 6-hydroxy-hexyl amine, 5-hydroxy-2-(2-ethyoxy) amine, acryloylchloride, acrylic acid, methyl methacrylate, 2-hydroxyethylmethacrylate, AIBN, toluene, THF, hexadecane and tetra (2-ethyl-hexyloxy) titanate were obtained from Aldrich or from Acros, and used as received. Desmodur BL 3272 MPA was obtained from Bayer.

Instrumentation

IR spectra were recorded under dry N_2 atmosphere on a BioRad Excalibur spectrophotometer equipped with a mercury-cadmium-telluride (MCT) detector, a MKII Golden gate heated diamond 45^{o} ATR top plate (Specac Ltd., England) and a 3000 series high stability temperature controller (Specac). The reactive mixture of BL-3272 and the resins was deposited on the diamond unit and cured at elevated temperatures. Spectra (eight scans per spectrum at a resolution of 4 cm^{-1}) were collected each minute until crosslinking was completed.

XPS measurements were performed on a VG-Escalab spectrometer using an aluminium anode (Al Kα = 1486.3 eV) operating with a background pressure of 2 x 10^{-9} mbar. A take-off angle of 90^{o} (between the film surface and the axis of the analyzer lens) was used, corresponding roughly to a sampling depth of about 8 nm. Spectra were recorded within 2 min in order to minimize radiation damage of the sample. Curve fitting was done with CasaXPS version 2.19 software.

Contact angle measurements were measured with deionized water and hexadecane (>99 % purity, Merck) on a contact angle microscope (G10, Krüss, Hamburg).

The SEC (size exclusion chromatography) analysis was done on a system containing two HR 0.5 (M_n < 1000 g/mol), one HR1 (up to M_n = 5000 g/mol) and one HR2 (up to M_n = 20,000 g/mol) columns, and provided with a Waters 2410 RI detector and a Waters 487 UV detector. The data were collected with a computer and processed with Waters Millenium32 software.

Synthesis

Perfluorine alcohols ($CF_3(CF_2)_7CH_2CH_2OH$) + CBC

A mixture of the perfluorine alcohol (25 g, 54 mmol), CBC (13.6 g, 54 mmol) and $Ti(OCH_2CH(C_2H_5)(CH_2)_3CH_3$ (0.6 g, 1.06 mmol) was heated in an oil bath to 125 ^oC. After 5 minutes the suspension became clear. The reaction mixture was stirred for 4 hours and then cooled down to room temperature. The yield was 100 % and the colour was slightly yellow. Colourless compounds were obtained by dissolving 38.6 g of the reaction product in toluene (100 ml) and adding carbon black (3 g). After 1 hour at room temperature the carbon black was removed by filtration and the toluene by evaporation at reduced pressure (rotavap). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.39 (2H, q, $CH_2CH_2C\underline{H}_2CH_2$ CH_2, open ring), 1.55 – 1.70 (8H, broad, CH_2 ring + $CH_2C\underline{H}_2CH_2C\underline{H}_2CH_2$, open ring), 2.34 (2H, t, CF_2CH_2), 2.45 (2H, t, $CH_2C(O)O$), 2.71 (2H, t, $COCH_2$ ring), 3.28 (2H, q, $C\underline{H}_2NH$), 3.98 (2H, t, CH_2N), 4.38 (2H, t, $OC(O)CH_2$), 9.27 (1H, broad, NH).

3-Amino propanol + CBC, subsequently reacted with acryloyl chloride

To a solution of CBC (12.61 g, 50 mmol) in toluene (40 ml) 3-amino propanol (3.76 g, 50 mmol) was added and heated under nitrogen atmosphere during 4 hours at 120^{o}C. According to TLC measurements CBC was completely converted. The mixture of caprolactam and caprolactam hydroxypropyl carbamate (10.7 g, 50 mmol) in toluene was cooled to 0^{o}C and then triethyl amine (5.06, 50 mmol) was added. Subsequently a solution of acryloyl chloride (4.56 g, 50 mmol), dissolved in toluene (25 ml), was added drop wise. The stirring was continued for 1 hour after the mixing was completed. The solution was washed successively with an aqueous $CaCl_2$ solution (20 ml, 10 wt %), with an aqueous HCl solution (20 ml, 0.1 mol/l) and with water (20 ml). The toluene layer was dried with anhydrous sodium sulfate, filtered and the toluene was removed under reduced pressure (rotavap). The oil was further dried in an oven at 60 ^{o}C under reduced pressure (50 mBar) in a nitrogen atmosphere. Yield 9.82 g (73 %). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.7 (6H, m, CH_2 ring), 1.9 (2H, qn, $CH_2C\underline{H}_2CH_2$), 2.7 (2H, t, $CONCH_2$), 3.4 (2H, q, $NHC\underline{H}_2$), 4.0 (2H, t, CH_2N), 4.2 (2H, t, CH_2O), 5.8 (1H, dd, C=CH, E to the ester group), 6.1 (1H, m, COCH=), 6.4 (1H, dd, C=CH, Z to the ester group), 9.4 (1H, broad, NH).

6-Amino-hexanol + CBC, subsequently reacted with acryloyl chloride

To a solution of CBC (25.3 g, 100 mmol) in toluene (100 ml) 6-amino hexanol (11.76 g, 100 mmol) was added and heated under nitrogen atmosphere at 120^{o}C for 4 hours. According to TLC measurements CBC was completely converted. The mixture of caprolactam and caprolactam hydroxyhexyl carbamate (21.4 g, 100 mmol) in toluene was cooled to 0^{o}C and then acryloylchloride (9.15 g, 100 mmol) dissolved in toluene (50 ml) was added. Stirring continued for 1 hour after the mixing had been completed. The precipitate (caprolactam.HCl salt) was filtered off and the solvent was removed under reduced pressure (rotavap). The product was dissolved in a mixture of hexane and ethyl acetate (75:25) and purified on a silica gel column. The solvent was removed under reduced pressure (rotavap). The oil was further dried in an oven at 60 ^{o}C under reduced pressure (50 mBar) in a nitrogen atmosphere. Yield 18.47 g (60 %). ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.7 (14H, broad, various aliphatic CH_2), 2.6 (2H, t, CH_2CO), 3.2 (2H, q,

$NHC\underline{H}_2$), 3.9 (2H, t, NCH_2), 4.1 (2H, t, OCH_2), 5.7 (1H, dd, C=CH, E to the ester group), 6.0 (1H, m, COCH=), 6.3 (1H, dd, C=CH, Z to the ester group), 9.2 (1H broad NH).

2-(2-aminoethoxy)-1-ethanol + CBC, subsequently reacted with acryloyl chloride
To a solution of CBC (12.61 g, 50 mmol) in toluene (40 ml) 2-(2-aminoethyoxy)-1-ethanol (5.27 g, 50 mmol) was added and heated under nitrogen atmosphere at 120°C for 4.5 hours. According to TLC measurements CBC was completely converted. The mixture of caprolactam and caprolactam hydroxyethyoxyethyl carbamate (12.2 g, 50 mmol) in toluene was cooled to 0°C and then triethyl amine (5.06, 50 mmol) was added. Subsequently a solution of acryloylchloride (4.56 g, 50 mmol), dissolved in toluene (25 ml), was added drop wise. Stirring continued for 1 hour after the mixing had been completed. The solution was washed successively with an aqueous $CaCl_2$ solution (20 ml, 10 wt %), with an aqueous HCl solution (20 ml, 0.1 mol/l) and with water (20 ml). The toluene layer was dried on anhydrous sodium sulfate, filtered and the toluene was removed under reduced pressure (rotavap). The oil was further dried in an oven at 60 °C under reduced pressure (50 mBar) in a nitrogen atmosphere. Yield 7.80 g (52 %). ^{1}H-NMR (300 MHz, DMSO-D_6) δ = 1.4-1.8 (6H, broad, CH_2 ring), 2.7 (2H, t, CH_2CO), 3.4 (2H, q, $NHC\underline{H}_2$), 3.5 (2H, q, $NHCH_2C\underline{H}_2O$), 3.7 (2H, t, $OC\underline{H}_2CH_2OCO$), 3.9 (2H, t, NCH_2), 4.1 (2H, t, O $CH_2C\underline{H}_2OCO$), 6.0 (1H, dd, C=CH, E to the ester group), 6.2 (1H, m, COCH=), 6.4 (1H, dd, C=CH, Z to the ester group), 9.3 (1H, broad, NH).

6-Amino-hexanol + CBC, subsequently reacted with acrylic acid
To a solution of CBC (12.62 g, 50 mmol) in toluene (50 ml) 6-amino hexanol (5.87 g, 50 mmol) was added and heated under a nitrogen atmosphere at 120°C for 4 hours. According to TLC measurements CBC was completely converted. After the mixture was cooled down to 50 °C, toluene (25 ml), 2,6-di-tert-butyl-4-methylphenol (0.0788 g), scandiumtriflate (0.0728 g) and acrylic acid (8.84 g, 100 mmol) were added. After this, the glass flaks was equipped with a Dean Stark condensor, the mixture was refluxed over night and cooled down to room temperature. The organic layer was washed with 25 ml of an aqueous $NaHCO_3$ solution and two times with 25 ml water. The toluene solution was dried with anhydrous Na_2SO_4, and after the salt was removed by filtration the solvent was removed by distillation (rotavap). The ^{1}H-NMR revealed that two types of acrylates were formed.

Copolymer of MMA, HEMA and caprolactam blocked 2-isocyanato-propyl acrylate
Methyl methacrylate (MMA, 8.01 g, 80 mmol), 2-hydroxy ethyl methacrylate (HEMA, 1.3 g, 10 mmol), caprolactam blocked 2-isocyanato-propyl acrylate (2.7 g, 10 mmol) and 2,2'-azo-bis-(isobutyronitrile) (AIBN, 0.36 g, 3 wt% with respect to the monomers) were dissolved in toluene (50 ml). The mixture was heated to the reflux temperature and kept at that temperature (120 °C) for 5 hours. Toluene was removed under reduced pressure (rotavap) and dried overnight in an oven in a nitrogen atmosphere at 60 °C. Yield was 9.23 g (77 wt%). ^{1}H-NMR ($CDCl_3$) confirmed the presence of the blocked isocyanate group (3.93ppm) and of the hydroxy groups (3.80 and 4.05 ppm). The number average molecular weight (calibrated with polystyrene standards) was 7826D.

Copolymer of MMA, HEMA and caprolactam blocked 6-isocyanato-hexyl acrylate
Methyl methacrylate (MMA, 8.01 g, 80 mmol), 2-hydroxy ethyl methacrylate (HEMA, 1.3 g, 10 mmol), caprolactam blocked 6-isocyanato-hexyl acrylate (3.12 g, 10 mmol) and 2,2'-azo-bis-(isobutyronitrile) (AIBN, 0.382 g, 3 wt% with respect to the monomers) were dissolved in toluene (50 ml). The mixture was heated to the reflux temperature and kept at that temperature (120 ^{o}C) for 5 hours. Toluene was removed under reduced pressure (rotavap) and dried overnight in an oven in a nitrogen atmosphere at 60 ^{o}C. Yield was 10.05 g (81 wt%). ^{1}H-NMR ($CDCl_3$) confirmed the presence of the blocked isocyanate group (3.93ppm) and of the hydroxy groups (3.80 and 4.05 ppm). The number average molecular weight (calibrated with polystyrene standards) was 8540D.

Copolymer of MMA, HEMA and caprolactam blocked 5-isocyanato-2-(2-ethoxy)-ethyl acrylate
Methyl methacrylate (MMA, 8.01 g, 80 mmol), 2-hydroxy ethyl methacrylate (HEMA, 1.3 g, 10 mmol), caprolactam blocked 5-isocyanato-2-(2-ethoxy)-ethyl acrylate (2.96 g, 10 mmol) and 2,2'-azo-bis-(isobutyronitrile) (AIBN, 0.368 g, 3 wt% with respect to the monomers) were dissolved in toluene (50 ml). The mixture was heated to the reflux temperature and kept at that temperature (120 ^{o}C) for 5 hours. Toluene was removed under reduced pressure (rotavap) and dried overnight in an oven in a nitrogen atmosphere at 60 ^{o}C. Yield was 9.62 g (78 wt%). ^{1}H-NMR ($CDCl_3$) confirmed the presence of the blocked isocyanate group (3.93ppm) and of the hydroxy groups (3.80 and 4.05 ppm). The number average molecular weight (calibrated with polystyrene standards) was 6746D.

Coating tests
All the polymers were prepared, applied and tested under the same conditions. The resins were dissolved in THF (30 wt% solid) and a 125 μm coating layer was applied with a Bird BA 25 applicator on aluminum plates (Q-panel A-46). The solvent was removed by heating the plates for 30 minutes at 60 ^{o}C. The coatings were cured at 180 ^{o}C for 30 minutes. The inspection of the coatings was done visually. The resistance against acetone double rubs is a measure for the crosslinked density. In that test the coatings are rubbed by a tissue impregnated with acetone and the number of rubs is counted. If the number of rubs exceeds 100 then the coatings are considered as being well crosslinked. In this case all the coatings resist > 300 acetone double rubs. The aluminium plates were bent to an angle of 90^{o} to get some preliminary indications of the toughness and adhesion.

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Chapter 7

Polyrotaxanes

Abstract

A synthetic method has been developed to prepare three conceptually different types of rotaxanes monomers and polymers: rotaxane polymer networks, linear main-chain polyrotaxanes and linear side-chain polyrotaxanes.

In preparing BI-based rotaxane monomers the advantage was taken of the high selectivity of CBC in its reaction with amines containing primary and secondary amino groups. The transformation of primary amino groups into BIs, is followed by the conversion of the secondary amino groups into the amide of fumaric acid. The fumaramide group is purposely introduced, because it is an excellent template to clip around a macrocycle that is composed of two molecules of xylylene diamine and two molecules of isophthaloyl chloride.

Polyrotaxanes are prepared from polymerizable rotaxane monomers, in which the caprolactam blocked isocyanates are bulky stopper groups, as well as the polymerizable groups. The properties of the corresponding poly(urea-rotaxanes) can be broadly tailored, thanks to the availability of a large number of amine functional monomers or oligomers.

Another target is to induce locally motion due to the spinning or shuttling of the macrocycles, triggered by external stimuli, such as UV-light. The isomerisation of the fumaramide unit into the maleic structure lowers the bonding strength, allowing the macrocycle to spin at room temperature.

7.1 Introduction

In *chapter 5* it is shown that amines containing primary and secondary amino groups react exclusively with carbonyl biscaprolactam (CBC) via the primary amine at temperatures of 100 ^{o}C or lower, leaving the secondary amine free for further elaboration. To demonstrate the applicability of this methodology in polymers a new route is designed to make polyrotaxanes[1] based on mainly standard starting materials. Rotaxanes (figure 7.1) are compounds in which a macrocyclic compound circumscribes a linear thread molecule to which the macrocycle is not covalently attached, and is therefore allowed to spin or to shuttle freely up and down along the thread. Bulky stopper groups at either end of the thread provide enough steric hindrance to prevent the macrocycle from 'falling off' and dethreading. The macrocycles can fall off the thread if no blocking groups are present and in that case the system is called a pseudo-rotaxane. The aim of this study is to find synthetic methods to prepare well-defined rotaxane monomers and the corresponding polymers, in a convenient way.

An important challenge in developing new functional polymers is to try to assemble existing cheap monomeric building blocks in a new array, using novel types of molecular architectures to improve properties and to provide added value. For instance, it is thought that by incorporating rotaxanes into macromolecules, some of the properties seen for rotaxanes in solution (i.e. the ability to switch, shuttle or alter shape[2]) could be transferred to a polymeric state where easier handling and processibility might provide the basis for new types of smart materials and/or molecule-based devices[3].

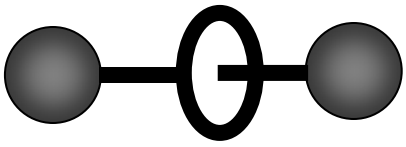


Figure 7.1: Schematic representation of a rotaxane.

The synthesis of polyrotaxanes is obviously more complicated than that of rotaxanes due to the need to incorporate polymerizable groups onto the monomer rotaxane, while still maintaining its unique structure.

Until now, three major strategies have been developed towards synthesizing these materials:

1. A preformed polymer is dissolved in a solution of a macrocycle that, over time, threads onto the polymer chain forming pseudo-polyrotaxanes. The macrocycle is free to thread or de-thread from the polymer chain at any time resulting in an unstable polyrotaxane species, hence the use of the term pseudo.

2. Polymerization of the 'thread' monomers occurs in the presence of the macrocycle. This strategy again results in unstable pseudo-polyrotaxanes, as the macrocycles are free to dethread from the polymer chain. Moreover, this method is only applicable if the macrocycle does not interfere with the polymerisation process.

3. Polymerization is done in the presence of a macrocycle using 'thread' monomers that contain bulky blocking groups that prevent the macrocycle from falling off the newly formed polymer chain. This is again only possible if the macrocycle does not disturb the polymerisation process.

In all these cases threading the macrocycle onto the (growing) polymer chain is done in an entirely reversible and statistical manner, which inevitably yields difficulties in controlling the amount of threaded macrocycle in the polymer. There was a clear need for a methodology to make polyrotaxanes starting from well-defined rotaxane monomers.

Caprolactam blocked isocyanates are bulky groups, applicable as stopper groups preventing the macrocycle to fall off the monomer thread. Moreover, blocked isocyanate groups are polymerizable groups and thus they are monomers able to make polyurethanes or polyureas by reacting them with diols or diamines respectively[4]. Blocked isocyanate rotaxane derivatives can thus act as readily accessible building blocks for polyrotaxanes, topological analogues of a wide range of commercial polymeric systems[5]. By introducing additionally a variety of mechanically interlocked architectures, the macrocycle is not able to dissociate from the growing polymer chain during the synthesis, and therefore the degree of macrocycle threading in the final product is controlled with great precision[6].

To achieve these targets, the advantage is taken of the newly developed technology for making blocked isocyanates from compounds containing primary amino and secondary amino groups[7] (*chapter 5*). After the primary amines are converted into BIs, the free secondary amine can be transformed into a fumaramide unit.

Leigh et al.[8] have shown that rotaxanes are prepared in high yields by clipping the macrocycle around a fumaramide thread unit as a template, thanks to its capability to

form hydrogen bonds with the macrocycle. A four-amide macrocycle, composed of two molecules of xylylene diamine and two molecules of isophthalic acid, has been shown to be very suitable to clip around a fumaramide template.

Here the preparation of rotaxane monomers is described, starting from multifunctional blocked isocyanates, provided with a fumaramide unit rendering the template to make the rotaxanes, as well as the preparation of the corresponding polyrotaxanes by heating these rotaxane monomers together with diamines.

7.2. Preparation of threads for rotaxane monomers containing blocked isocyanates

Three conceptually different kinds of polyrotaxanes can be conceived: polymer networks with a macrocycle at each knot, linear polymers with the macrocycle in the side chain, and linear polymers with the macrocycle in the main chain. By varying the structure of the amines, the number and location of the BI stopper groups, the location of the macrocycle can be chosen at will (figure 7.2).

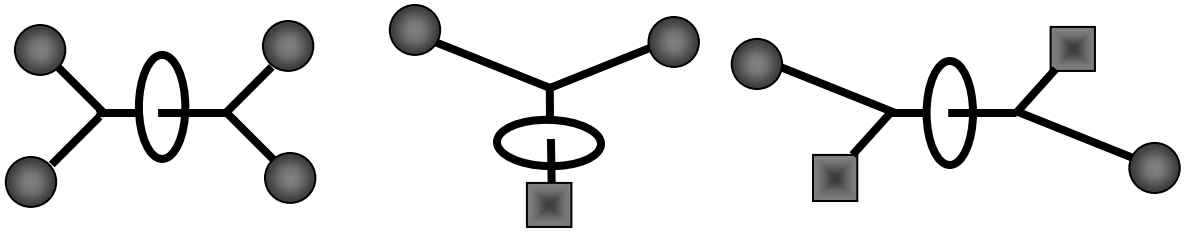
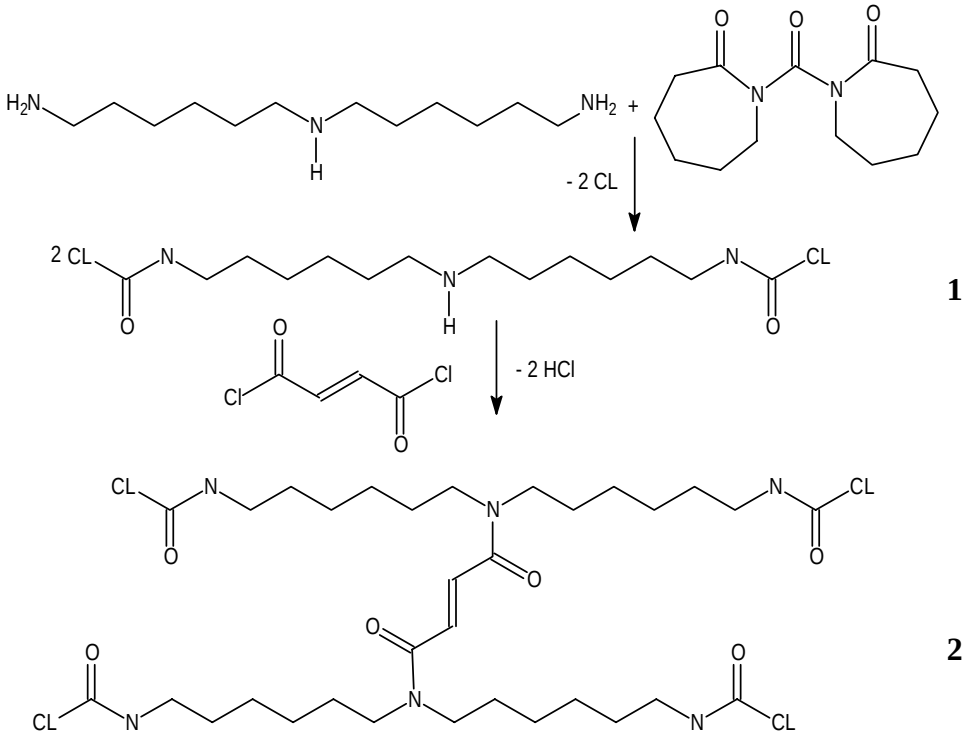


Figure 7.2: Representation of three conceptually different structures for network (left), linear side chain (middle) and linear main chain (right) rotaxane monomers. ● *=BI,* ■ *= stopper group.*

To make the polymer network, a thread for a four-functional BI is designed, starting from bis-(hexamethylene) triamine (BHTA) (scheme 7.1). In a typical experiment, one mole of BHTA and two moles of CBC are mixed in toluene and heated for several hours at 80 ^{o}C. The reaction of CBC with BHTA (in stoichiometric amounts) gives the corresponding α,ω-functional BI (**1,** BHTA-BI) in a nearly quantitative yield, without affecting the secondary amine in the middle of molecule **1**. The purification of the product only requires a few aqueous extractions to remove caprolactam, since no other side products are formed. The water solubility of the product is low, and so it remains in the organic phase. Next, two moles of **1** are mixed with one mole of fumaroyl chloride (in toluene, in

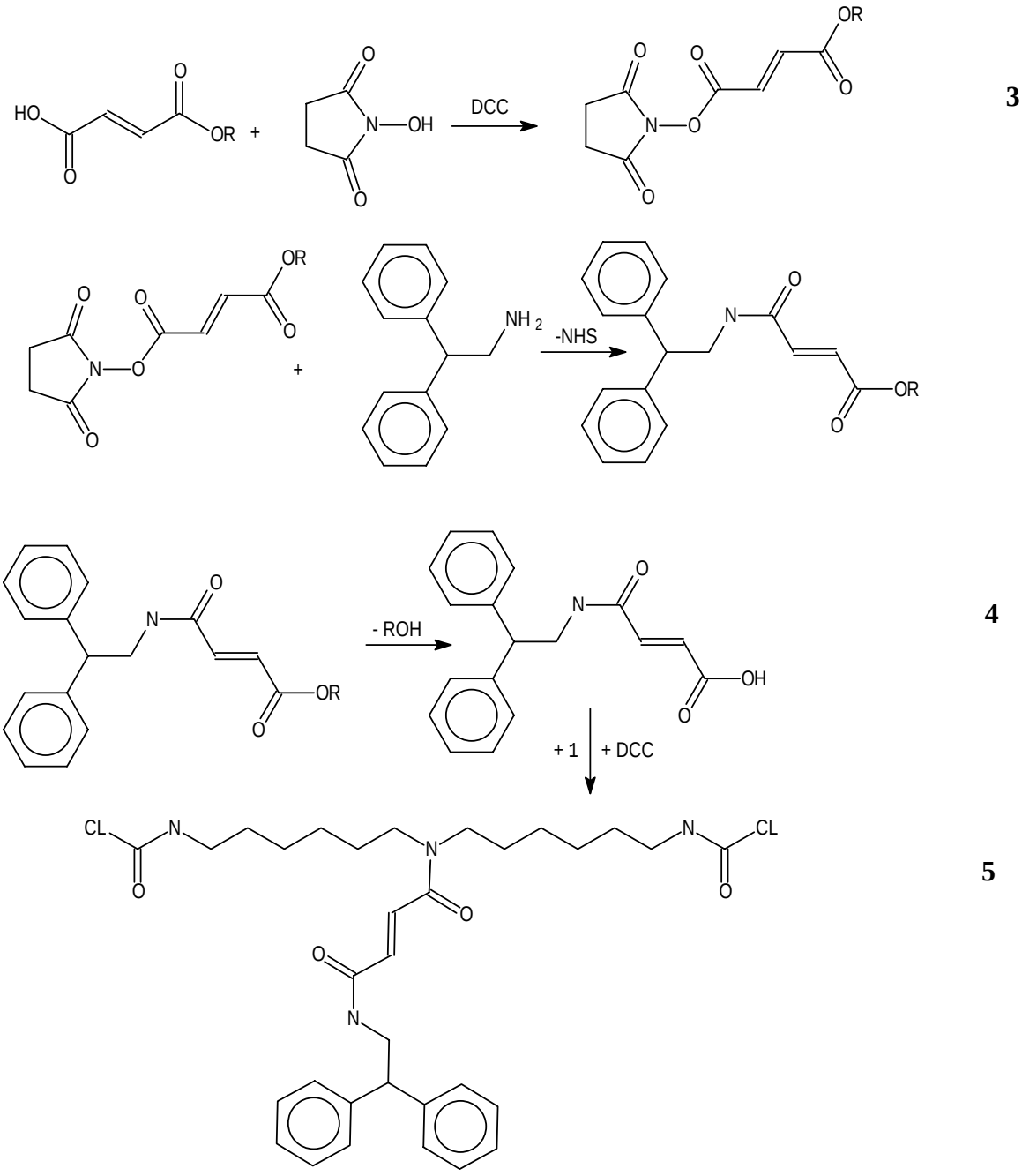
the presence of triethyl amine) to introduce the fumaramide template. This coupling product is the thread for the four functional BI monomer **2**. It was necessary to get the thread in its pure form, and as a consequence the yield was only modest (56%), partially due to losses in the purification step by column chromatography. The next step, the preparation of the corresponding rotaxane monomer based on template **2,** is described in paragraph 7.3.



*Scheme 7.1: Reaction scheme for the preparation of the thread of the network rotaxane monomer (**2**, CL = caprolactam).*

The first step in making the monomer for the linear side chain polyrotaxanes is the same as above, thus reacting BHTA with CBC in stoichiometric amounts in toluene and heating this mixture for several hours at 80 ^{o}C, resulting in compound **1 (**scheme 7.1). After the primary amines have been transformed into BIs the secondary amine is utilized for linking a fumaramide side chain, which is again used as the template for the macrocycle. For this purpose the acid group of the monomethylester of fumaric acid is reacted with N-hydroxysuccinimide (in the presence of DCC, DiCyclohexyl Carbodiimide) to obtain the activated acid ester **3** in high yields (scheme 7.2). Next 2,2-diphenylethylamine substituted the N-hydroxysuccinimide nearly quantitatively and

subsequently the ester function is hydrolysed to obtain the fumaric acid amide **4** (scheme 7.2). 2,2-Diphenylethylamine is incorporated as bulky blocking group to prevent the macrocycle from falling off the thread on one side.



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4

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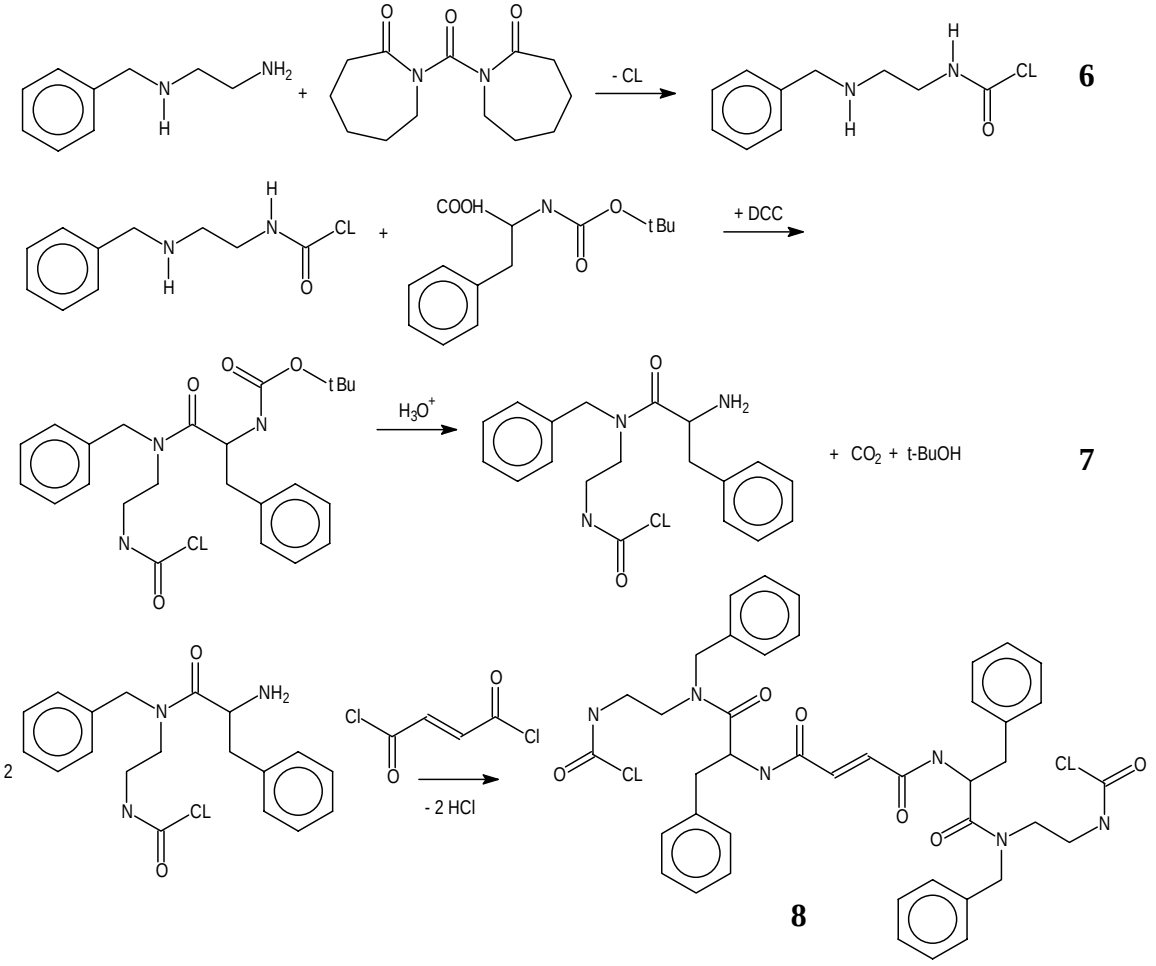
Scheme *7.2: Reaction scheme for the thread preparation for the side chain rotaxane monomer (***5***, CL = caprolactam, NHS = N-hydroxysuccinimide, DCC = DiCyclohexyl Carbodiimide).*

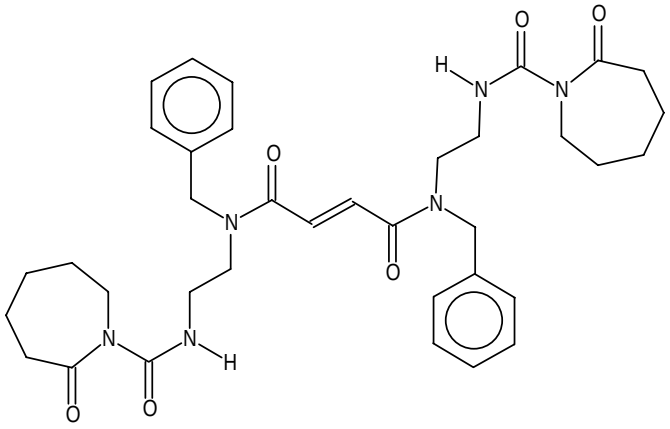
The BI groups are needed to prevent the macrocycle from falling off on the other side of the thread, as well as to function as reactive groups to make the polymer backbone. Finally, the acid amide **4** is coupled via the free acid group onto the secondary amine of the reaction product of BHTA and CBC (**1**) (in the presence of DCC) to obtain the monomer thread **5**. In paragraph 7.3 the preparation of the corresponding side chain rotaxane monomer is described.



*Scheme 7.3: Reaction scheme for the preparation of a main chain thread monomer with two benzylic stopper groups at each side of the fumaramide unit (***8***, CL = caprolactam).*

Two types of main chain rotaxane monomer are prepared (scheme 7.3). In a first approach an equimolar amount of N-benzylethylenediamine is added to a solution of CBC in toluene and heated to 60 ^{o}C overnight, rendering the corresponding blocked isocyanate **6** in nearly quantitative yield, still containing the free secondary amino group.

Caprolactam is removed by a number of aqueous extractions, in the presence of $CaCl_2$ to improve the solubility of caprolactam in water. In this first approach the fumaramide **9** (figure 7.3) is prepared by reacting compound **6** with fumaroyl chloride, introducing again the fumaramide unite as a template for the macrocycle. This linear main-chain rotaxane monomer thread **9** (figure 7.3) contains one benzylic group and one caprolactam ring stopper group at each side of the fumaramide unit to prevent the macrocycle to fall off the thread.



9

Figure 7.3: Structure of the first thread ***9*** *for the main chain rotaxane monomer.*

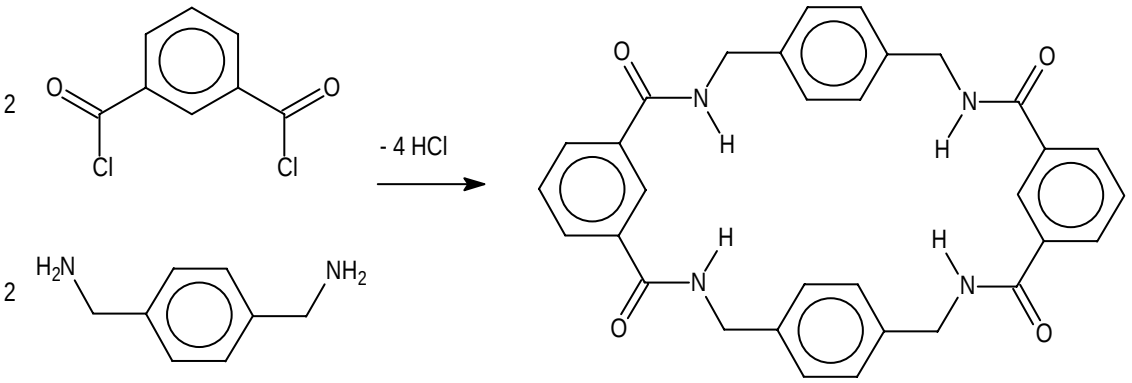
It was expected that these two blocking groups should be appropriate to prevent the macrocycle falling off the thread and thus a stable rotaxane monomer should be obtained. However, during polymerization, when the caprolactam rings were removed, it was found that benzylic groups alone were not sufficient to prevent the macrocycles from falling off. NMR analysis revealed that the polymer still contained a substantial amount of macrocycles, but no longer on every monomer thread unit. Thus, in this approach there was lack of control, resulting in polyrotaxanes in which the macrocycles were distributed in a statistical manner along the polymer chain, and this is clearly not the aim of this study. Hence in a second approach two aromatic groups are introduced to keep the macrocycle on the thread. For this purpose the reaction product of N-benzylethylenediamine and CBC **6** is added to t-BOC-D,L-phenylalanine to react via the acid group with the free secondary amine. Subsequently, the t-BOC protecting group is removed and then two equivalents of the intermediate **7** are transformed into the amide **8** (thread) by adding one equivalent of fumaroyl chloride (scheme 7.3).

Although the thread preparation for the main chain rotaxane monomer requires more steps than the synthesis of the two other thread monomers, the synthetic route consist of straight forward organic reactions, rendering rather good yields.

So, in this second approach two aromatic rings are introduced at each side of the fumaramide unit and based on our experience with 2,2-diphenyl ethylamine as a stopper group it was expected that this should be sufficient to prevent the macrocycle from falling off, even after the caprolactam ring is removed during polymerisation. The preparation of the corresponding rotaxane monomers is described in the next paragraph.

7.3 Preparation of rotaxane monomers

The preparation of the macrocycle of all the rotaxanes is carried out according to Leigh et al.[8], who found that the hydrogen bonding between fumaramide carbonyl groups and the hydrogen atoms of the amide group of a macrocycle considerably favours the formation of macrocycles. Accordingly, if isophthaloyl chloride is brought into contact with xylylene diamine in the presence of a fumaramide as a template the rotaxane is formed in high yields. Yields of 50 or even up to 80 % are remarkably high for this kind of reactions since four reactant molecules and one template molecule are involved during the clipping process to form the macrocycle around the thread. All five molecules have to be arranged in the perfect way to finalize the ring closure reaction. These monomers are selected because they are "predestined" to form cycles due to their bent structure. Models show that the 2 + 2 macrocycle fits well particularly because of the 1,3 structure of isophthalic acid (scheme 7.4).



Scheme 7.4: Formation of macrocycle from xylylene diamine and isophthaloyl chloride.

Along this route three rotaxane monomers are prepared based on the three threads as described in paragraph 7.2. In a typical experiment separated solutions of xylylene diamine and isophthaloyl chloride in chloroform are slowly added to a chloroform solution of the thread. Chloroform is selected as solvent because it has the right solubility balance keeping the products in solution, but being not too polar to prevent the formation of hydrogen bonds. The hydrogen bonds between the macrocycle and the fumaramide unite are essential to render high yields. Triethyl amine is added to scavenge HCl that is liberated in the course of this reaction. The slow addition of xylylene diamine and isophthaloyl chloride was done by means of syringes that were automatically moved by an electrically controlled device to ensure that both compounds are being added to the thread solution at the same speed (figure 7.4). The slow addition of the two components results in a low concentration of the reactants and that turns out to be the most favourable condition to avoid the formation of polyamides.

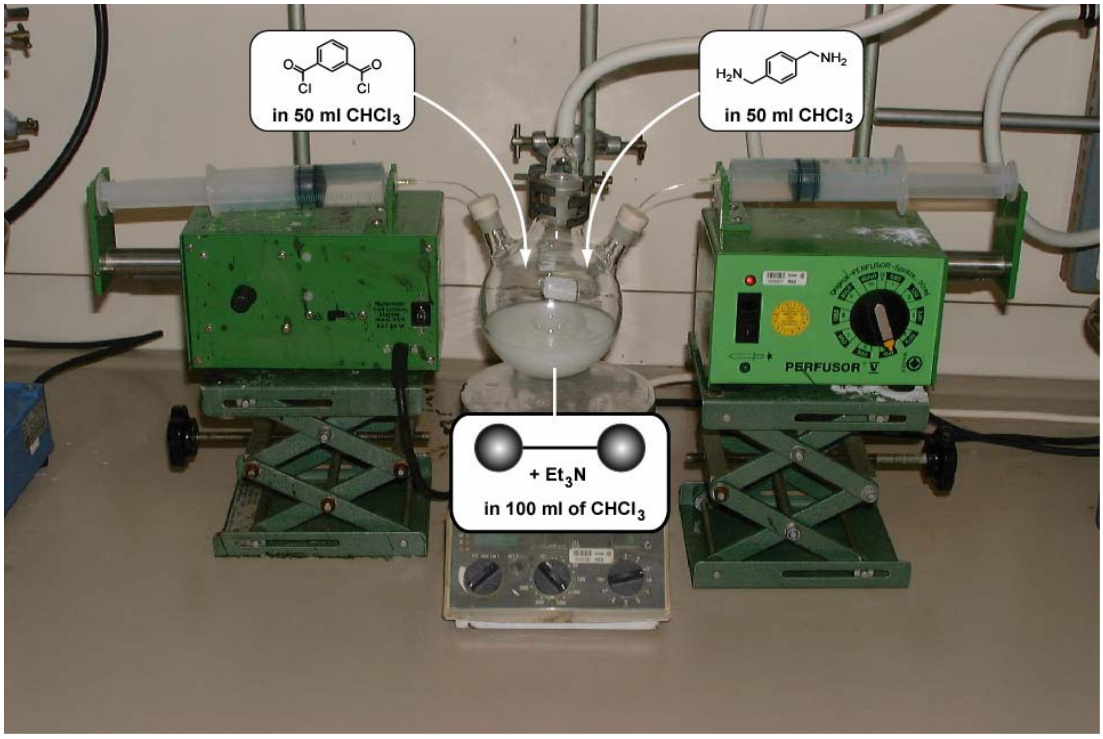


Figure 7.4: Experimental set-up for the preparation of rotaxane monomers.

Xylylene diamine and isophthaloyl chloride are added in a 10-fold molar excess with respect to the thread to get high yields (70 %) of the rotaxane. The synthesis was optimised to get the best yields with respect to the thread, as the synthesis of this is the most laborious. The rotaxanes are soluble in chloroform and the excess of xylylene diamine and isophthaloyl chloride is almost completely consumed by the formation of catenanes as side products. The catenanes are two interlocking rings of the same macrocycle as present in the rotaxane. These catenanes are characterized by a very low solubility in chloroform giving a precipitate. Thus, although xylylene diamine and isophthaloyl chloride are added in large excess, the resulting side products are easily separated from the reaction mixture due to the low solubility of the catenanes. After filtering off the catenanes and the triethyl amine.HCl salt, an aqueous extraction is carried out to remove the remaining traces of salts. After drying and removing of the drying agent by filtration, the organic layer was distilled off at reduced pressure yielding the rotaxane monomers, which were still contaminated with some bare thread. The advantage is taken of the better solubility of threads in diethyl ether than rotaxanes, to separate both compounds. The mixture of the thread and the rotaxane monomer was dissolved in chloroform and poured out into a large excess of diethyl ether. The rotaxane precipitated, whereas the thread stayed in solution. All three rotaxane monomers are prepared according to the same procedure. If the separation of the thread and the rotaxane by the precipitation procedure was insufficient, the product was purified by column chromatography (Chloroform/methanol 95/5). Rotaxane monomers are characterized by ^{1}H-NMR, particularly by comparing them with the bare thread (figure 7.5). In general the aromatic protons are easily assigned and can be used to determine the purity of the product. The shift of the hydrogens of the double bond in fumaric acid (m in figure 7.5) with respect to the thread is characteristic for the presence of the macrocycle around the fumaramide unit. Due to the shielding of the macrocycle this hydrogen peak shifts more than 1 ppm upfield. This large shift is a general phenomenon, always found with this type of rotaxanes, and is used to determine the presence and/or the location of the macrocycle.
From grown crystals, the crystal structure of the four functional “network” rotaxane monomer **A** (figure 7.6, see for the thread of rotaxane **A** structure **2** in scheme 7.1) was determined by X-ray diffraction.

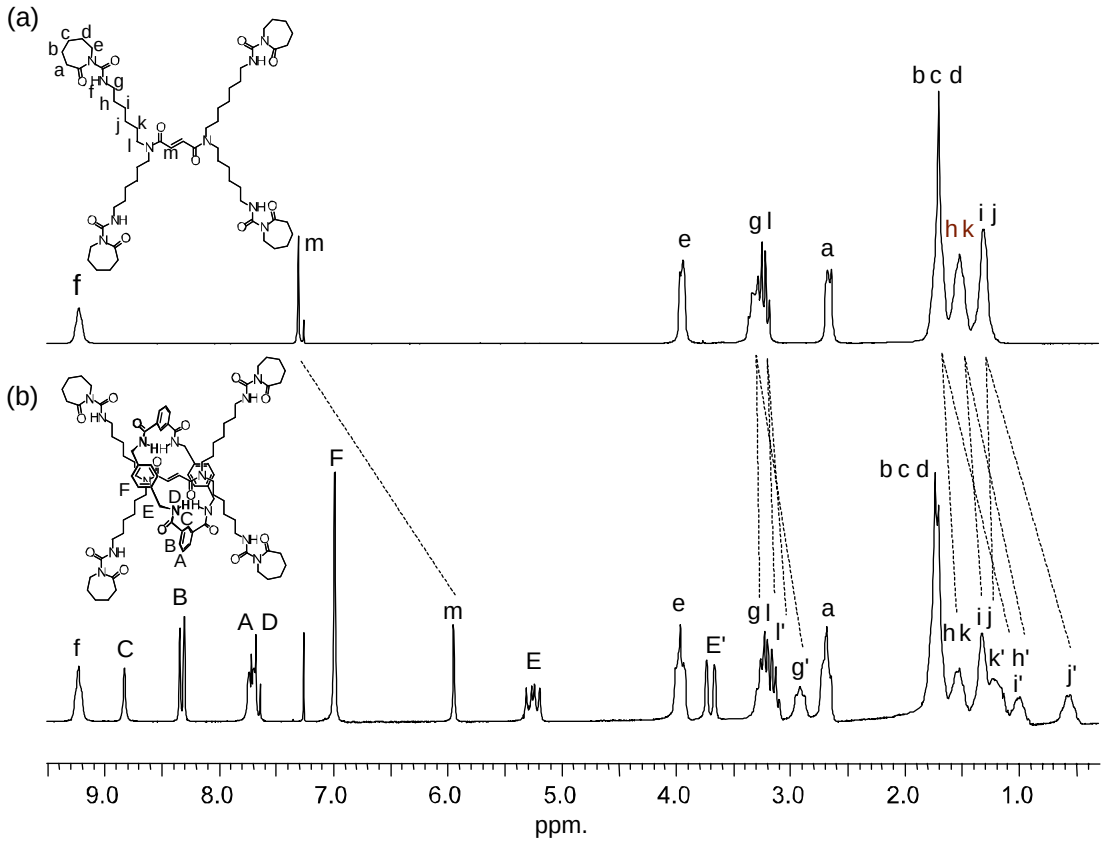


*Figure 7.5: The [1]H-NMR spectrum of the four functional BI thread **2** and corresponding "network" rotaxane **A**.*

It can be observed that the space for the macrocycle between the four BI groups is very limited. It is amazing to see how crowded this molecule is, whereas at the same time it can be prepared in such a high yield, taking into account that the macrocycle is formed out of four reactant molecules and one template molecule. The macrocycle, which has adapted a chair configuration, just fits between the four arms of the thread and is fixed (by hydrogen bonds) in a tilted way, which makes the environment of the macrocycle at both sides of the molecule different. The arrows in figure 7.6 indicate the identical environment of the xylylene (CH_2) moiety of the macrocycle, whereas environment at the other side of the macrocycle is different. This can clearly be seen from the splitting of the CH_2 protons of xylylene diamine (E and E' in figure 7.5). This dissymmetry is not only present in the crystal structure but remains intact even in solution at room temperature. But if the ^{1}H-NMR measurements are carried out at higher temperatures, up till 117 ^{o}C,

these two E peaks fade away, indicating that the bond between the macrocycle and the thread weakens and the macrocycle starts to move within the NMR time frame (Figure 7.7). A new peak is evolving between the disappearing peaks E and E', suggesting that the spinning of the macrocycle has started.

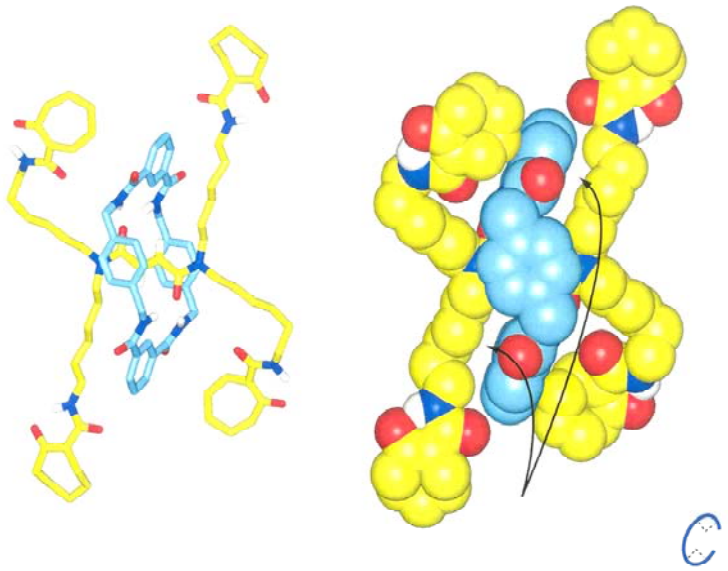


Figure 7.6: Molecular models based on the crystal structure of the tetra functional "network" rotaxane monomer ***A****.*

One objective was to prepare rotaxane monomers and polymers, of which the macrocycle is able to spin or shuttle, initiated by external stimuli. The fading away of the two CH_2 protons of xylylene diamine through heating of the monomer, indicate that the macrocycle starts to spin, and is already a first example of this concept. However, heating is not a technology that can be used for making products in which permanent changes are required. This process will reverse on cooling, fixing the macrocycle again in its starting position.

In a second approach, a more durable method was used to change the properties, by making use of the trans-cis isomerisation of the fumaric double bond into the corresponding maleic double bond. The bond strength of the macrocycle to the maleic amide is substantially weaker (7 kJ/mol) than to the fumaramide (14 kJ/mol)[8]. So it should be possible to decrease considerably the bond strength of the macrocycle to the

thread by isomerisation of the fumaric unit into a maleic unit. This could even lead to spinning of the macrocycle at room temperature. By this way areas with fixed and areas with spinning macrocycles could be made, addressed by an external stimulus, resulting in a 0/1 situation.

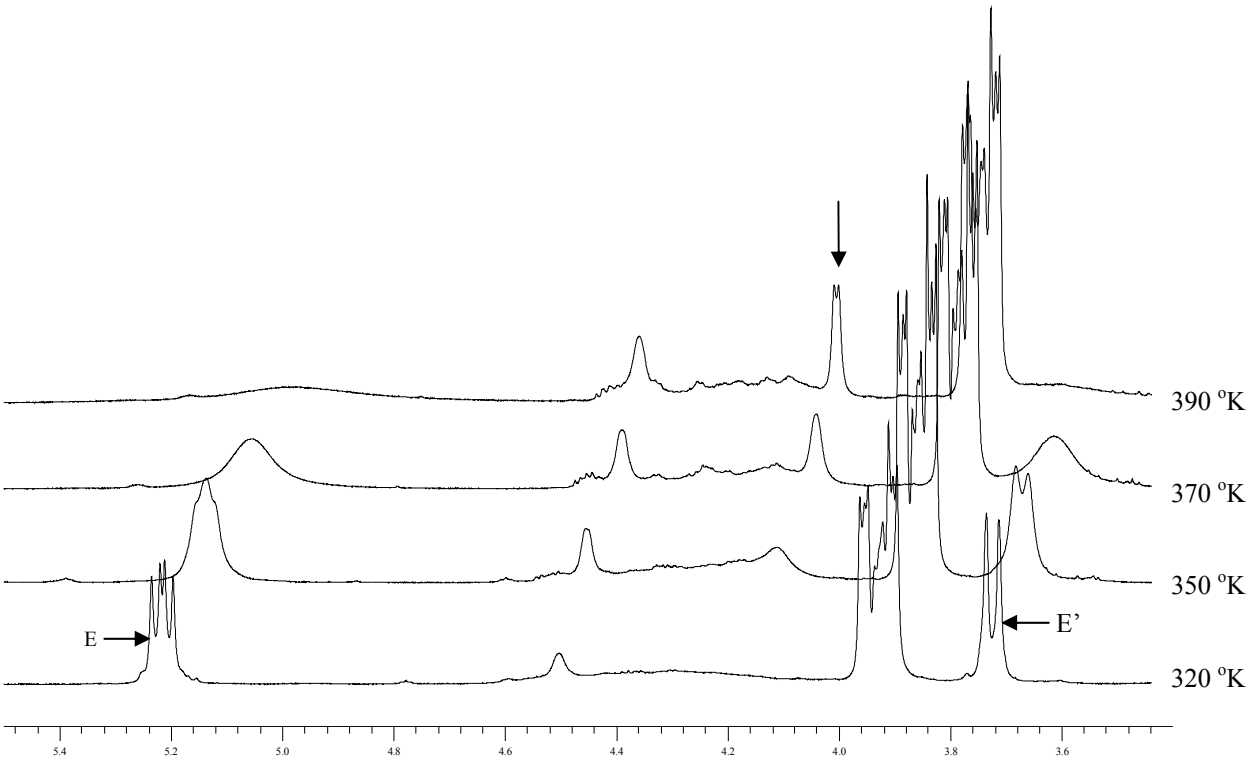


*Figure 7.7: ^{1}H-NMR spectra of rotaxane monomer **A** at various temperatures. E and E' are from the CH_2 groups of xylylene diamine (the arrows indicate the CH_2 position of xylylene diamine).*

It is known that the trans-cis isomerisation of the fumaric double bond into the maleic double bond can be induced by UV light (λ = 255 nm). The reversed reaction, the isomerisation of the maleic bond into the fumaric double bond can be done by a thermal treatment, since the fumaric configuration is thermodynamically more stable than the maleic structure. Thus, the configuration of the double bonds can be changed in both directions.

Whether this isomerisation of the double bond can be done, while shielded by the macrocycle, was uncertain. In addition the fumaramide structure is stabilised by hydrogen bonds with the macrocycle and the carbonyl groups of the fumaramide unit.

The isomerisation by UV-light was carried out in solution ($CHCl_3$) during 30 minutes at room temperature by way of a mercury lamp. In spite of the presence of the macrocycle, the isomerisation of the fumar unit proceeded, but the conversion was not complete and cis-trans mixtures were obtained. The cis and trans compounds could be separated by column chromatography and identified by ^{1}H-NMR.

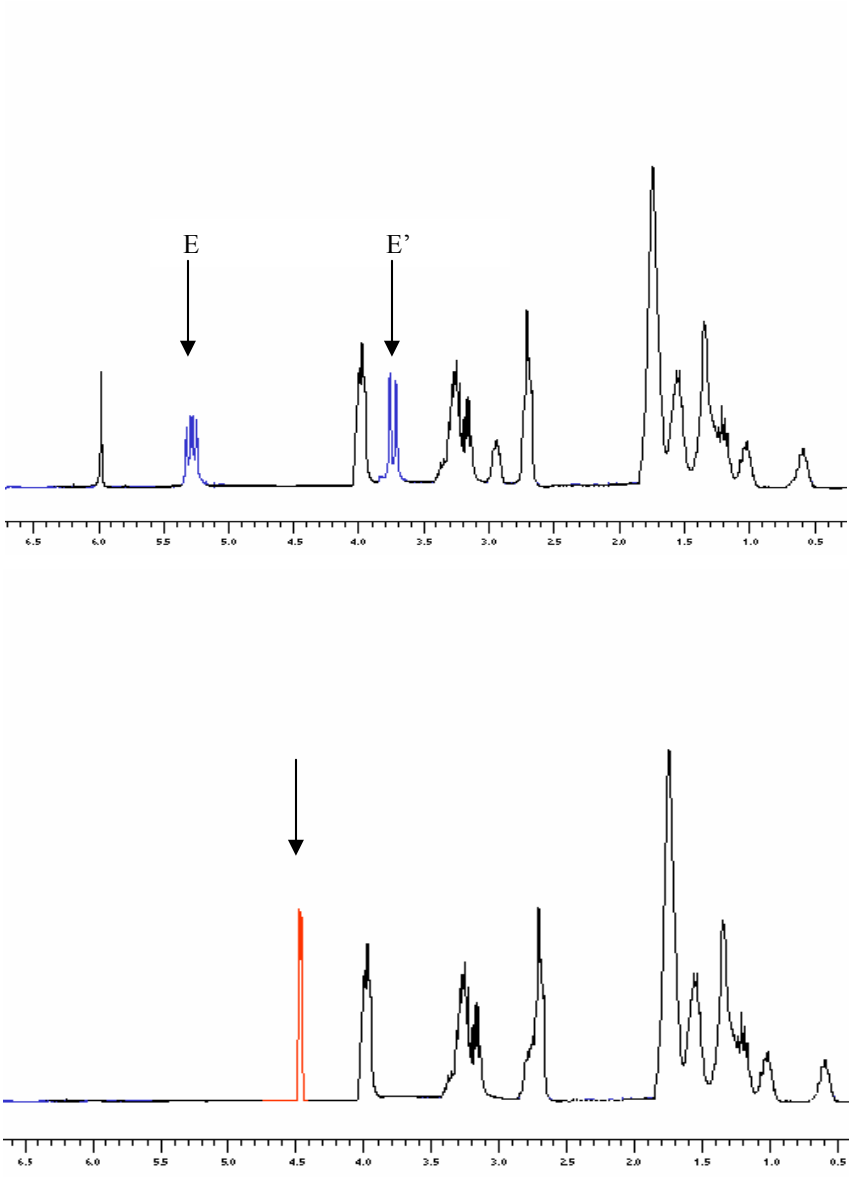


Figure 7.8: The ^{1}H-NMR spectra of the four-functional rotaxane monomer before (fumaric unit; top) and after (maleic unit; bottom) irradiation. The arrows indicate the position of the CH_2 protons of xylylene diamine.

The weaker bond strength of the macrocycle onto the thread in the cis-(maleic) configuration is visible indeed by the enhanced motion (spinning) of the macrocycle, resulting in the coalescence of the two CH_2 protons of xylylene diamine in the ^{1}H-NMR spectrum (figure 7.8). This proves that the isomerisation occurs in spite of the presence of the (shielding) macrocycle. The wavelength applied was far from optimal, due to the selected light source. It is conceivable that monochromatic light will improve the extent of the isomerisation. So, it is possible to create areas with spinning and areas with fixed macrocycles, which might lead to some useful applications. Although much more work has to be done to get a well working system, this is a prototype of a material in which molecular motion is induced by an external stimulus (UV-light). Extension of this work is still in progress, but this is outside the scope of this thesis.

Since crystal structures are the ultimate proof for the characterisation of the structure of compounds, several attempts were carried out to crystallise the other rotaxane monomers. Fortunately, it was possible to make suitable crystals of the rotaxane monomers **B** (side chain, see for the thread of rotaxane **B** structure **5** in scheme 7.2) and **D** (main chain, see for the thread **9** of rotaxane **D** figure 7.3) too, allowing the determination of their crystal structures (figure 7.9). Rotaxane **D** is the main chain rotaxane monomer without phenylalanine (figure 7.3, thread **9**), because it was not (yet) possible to make crystals of rotaxane **C**, which is based on thread **8**, containing phenylalanine. The crystal structures of the molecules **A**, **B** and **D** are particularly important, since this is the unambiguous evidence for the successful synthesis of these complex molecules.

Interestingly, the macrocycle in the rotaxane monomer **B** exists in a boat configuration, whereas in monomer **A** and **D** a chair structure is found. This may be due to the fact that the groups at both sides of the macrocycle in monomer **B** are different, while the monomers **A** and **D** are symmetrical.

The rotaxane monomers, for the linear polymers**,** **B**, **C** and **D** were characterised by ^{1}H-NMR. The protons of the fumaramide unit showed the expected shift of about 1 ppm in the NMR spectra with respect to the thread, due to the shielding of the macrocycle, proving the presence and location of the macrocycle.

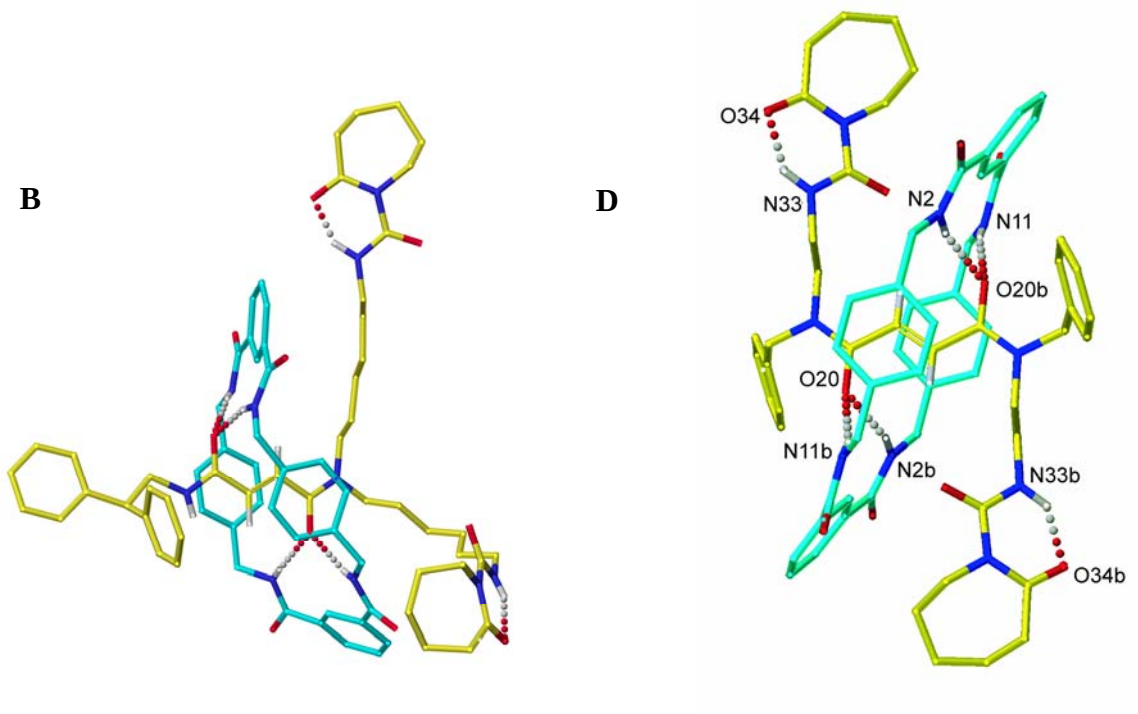


*Figure 7.9: Crystal structures of the side chain (monomer **B**; left) and (first) main chain rotaxane (monomer **D**; right) monomers.*

After all three conceptually different rotaxane monomers were prepared and well characterised, they were processed with diamines to make the corresponding polyrotaxanes.

7.4 Preparation of polyrotaxanes

The rotaxane monomers, with polymerizable blocked isocyanate groups, enable the preparation of well-defined poly(urethane-rotaxanes) and poly(urea-rotaxanes). Polyurethanes or polyureas are very versatile polymers because they can be prepared with a great variety of excellent properties. Their versatility is due to the large variability of the system constituents. Polyurethanes and polyureas are prepared from (blocked) isocyanates and oligmeric or low molecular weight di- or triols, respectively, di- and triamines. The broad spectrum of possibilities to make regular polyurethanes and polyureas is in fact already an example of a modular approach concept, although the number of (blocked) isocyanates is limited, and the availability of functional BIs is lacking. A method to make additionally a wide variety of functional BIs, next to the availability of a large number of polyols and polyamines, makes the number of options to tailor the properties almost unlimited.

In this work only the polyureas were studied, whereas the polyurethanes were not yet explored. The preparation of polyurea from diamines and blocked diisocyanates is carried out at high temperatures, which are needed to start the deblocking of BIs. The deblocking temperature depends on the blocking agent[4], but varies generally between 110 and 150 ^{o}C. The rotaxane monomers that have been prepared contain caprolactam as blocking group, which need temperatures of 150 ^{o}C or higher in order to react with diamines. There were some concerns beforehand whether the amide groups in these monomers could withstand these conditions, without giving trans-amidation reactions. Therefore, the polymerisations were carried out at temperatures not higher than 180 ^{o}C in order to avoid these side reactions.

The polymerisations of both tetra-BI "network" compounds, thread **2** of the rotaxane monomer **A** and rotaxane monomer **A,** were done by mixing these monomers with Jeffamine D400 (α,ω-amino-functional poly(propylene glycol) with a $\overline{M}_n$ of 400D) in dichloromethane and, after removing of the solvent, heating the samples at 180 °C. Rubbery materials were obtained with a typical plateau modulus of about 5 MPa and an elongation at break of >100%. The DMTA graphs of the network of the thread of rotaxane **A (**without macrocycle) are shown in figure 7.10 and the network of the rotaxane **A** in figure 7.11.

The glass transition temperature of – 80 ^{o}C, visible in both materials, is due to the polypropylene glycol, whereas the transitions at –15 ^{o}C for the polyrotaxane **A** (fig 7.11) and – 30 ^{o}C for the polythread **A** (fig 7.10) is due to bishexamethylene units. The low T_g material was purposely chosen in order to introduce mobility at room temperature. Indeed, the light-induced motion of the macrocycle probably needs a low T_g material to have enough "room" to move.

The rubbery material was insoluble in various solvents, proving the existence of the polymer network. Repeatedly washing of the swollen network with dichoromethane was done to remove traces of non-crosslinked product. A ^{1}H-NMR spectrum of a swollen sample of this polyrotaxane in deuterated chloroform confirmed the presence of the rotaxane subunits as an integral part of the polymer material. Within the accuracy of NMR for swollen networks it appears that every knot of the network contains a macrocycle, meaning that the polymerisation proceeds well controllable.

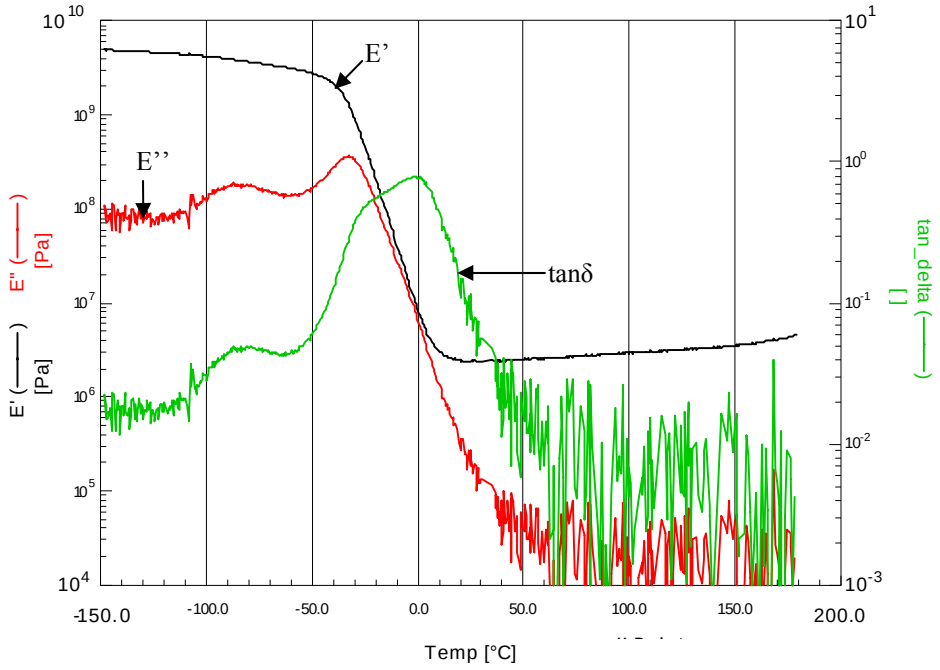


Figure 7.10: DMTA spectrum of polymer network of the thread of rotaxane ***A*** *(without macrocycle).*

Following the same procedure the "side chain" rotaxane monomer **B** was polymerised with Jeffamine D400. Contrary to the sample with the four-functional blocked isocyanate, this polymer is soluble in dichloromethane. A preliminary SEC analysis reveals that a high molecular weight material with a number average molecular weight ($\overline{M}_n$) of 86,800D ($\overline{M}_w/\overline{M}_n$ = 1.9) was obtained, meaning that the polymer chains contain on the average 66 macrocycles. Within the accuracy of the measurements of polymeric materials, ^{1}H-NMR proved that all the macrocycles were completely built-in into the polymer.

Under equal conditions the main chain polyrotaxanes were prepared from "main chain" rotaxane monomer **D**, and here again a polymer was obtained that was soluble in dichloromethane. As mentioned before, the ^{1}H-NMR spectra of this polyrotaxane based on rotaxane monomer **D** containing only one benzylic stopper group at each side of the

template unit revealed that this polymer contained less rotaxane units than calculated, meaning that some of these units had fallen off the thread.

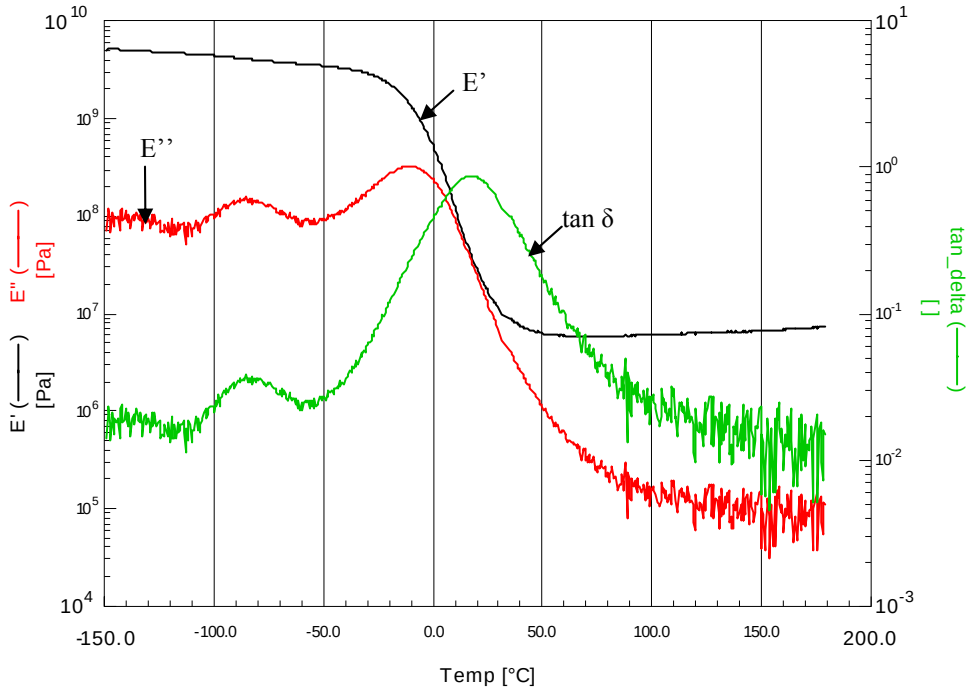


*Figure 7.11: DMTA spectrum of polymer network of rotaxane **A** (with macrocycle).*

The second "main chain" rotaxane monomer **C**, which contains two benzylic stopper groups at each side of the template unit, performed as expected. ^{1}H-NMR proved that the macrocycles of the monomer were still present in the polymer. The number average molecular weight ($\overline{M}_n$) of this polymer was 53,750D ($\overline{M}_n/\overline{M}_n$ = 1.6), meaning that on average every polymer chain contains about 36 macrocycles.

None of the polymers showed any indication in the ^{1}H-NMR spectra that trans-amidation with the macrocycle took place. A polymerisation temperature of 180 ^{o}C seems to be low enough to prevent side reactions, but still high enough to make the polymers within a reasonable time (1h). Thus it can be concluded that this novel route of making polyrotaxanes in a controlled way was successful, and this yields a platform on which a wide variety of novel polymer structures can be built.

7.5 Conclusions

By using a novel technology of forming blocked isocyanates selectively from amines containing primary and secondary amines and CBC, a simple and versatile route to polyrotaxanes, with a variety of topologies, is available through the synthesis and subsequent polymerization of readily accessible, stable, rotaxane monomers containing bulky, blocked isocyanate stopper groups. These monomeric[7] rotaxanes represent a new kind of functional chain extender, which is wholly compatible with the methodology currently used to make a range of commercial polymers, and could thus lead to the facile incorporation of a number of rotaxane systems into materials, where the effects of the properties could be tested and realistically exploited. In principle, this system can also be applied to the modular generation of rotaxane-based polymeric 'devices' in which specific components can be introduced by using different combinations of individual components. One of the challenging issues in functional polymers is to induce, on a molecular scale, local mobility by external stimuli. A primitive example of motion through spinning of the macrocycle, caused by heat, is shown to illustrate feasibility of the concept. Slightly more advanced is the motion that is introduced into these materials by UV light. For that purpose the trans configuration of a fumaric unit (template), which is responsible for the strong hydrogen bonding with the macrocycle, is converted into a cis double bond (maleic unit). As a result the macrocycle starts spinning around the thread thanks to the lower bond strength between the macrocycle and the maleic unit. In this way a local durable motion is introduce, which can lead to on-off systems. It is conceivable that such on-off systems can find their way in electronic materials.

To summarize, a novel method is found to make rotaxane monomers based on the selective reactions of CBC with compounds containing primary and secondary amines, whereas the free secondary amines are used to introduce fumaramide templates that are circumscribed by macrocycle molecules. Furthermore these monomers are polymerized with diamines in a standard procedure to make polyurea. These polymers still contain all the macrocycles that are present in the monomers, meaning that none of them de-thread during the polymerization. Furthermore, these macrocycles that are kept in a fixed

position by hydrogen bonds can start spinning through an external stimulus (UV light), resulting in zero-one/on-off situations.

7.6 Experimental

Instrumental

NMR spectra were recorded on a Brucker ACF 300 MHz in chloroform.
The SEC spectra were recorded by means of a (Hewlett Packard) HP 1090 liquid chromatograph, equipped with a UV-DAD detector system. The refractive index is measured on the HP 1047A differential refractometer at 35 ^{o}C and the viscosity on the Viscotek H502B at 38 ^{o}C. The used Viscotek data manager was DM400. The signal of the light scattering was collected under an angle of 90^{o}. The column set (3 PPS PFG linear XL, 7μ8*300 mm) could handle the molecular weight mass ranges for 100 to 1,000,000D. The eluent was hexafluoro isopropanol (T = 35 ^{o}C) containing 0.1 wt % potassium trifluoro acetate and the flow rate was 0.4 ml/min. The computer operating system had three software systems: a) HP chemstation for the processing the UV data of the chromatograph, b) Astra version 4.73.04 for operating of the MALLS, c) Viscotek software TriSEC 3.0 or OmniSEC 2.0 to collect the signals and to process the data.
The IR measurements were carried out on a Perkin Elmer Spectrum one. The UV measurements on a Perkin Elmer UV/VIS Lambda 20 with cell part no B0631072 size 10*10 mm.
The materials for the DMTA measurements are pressed in films of ca. 70x40 mm and with a thickness of ca. 0.08 mm according to the following procedure: 5 min T = 180°C, P = 0 kN; 3 min T = 180°C, P = 10kN; 3 min T = 180°C, P = 50 kN and cooling down under a pressure of P = 180kN until T = 25°C. Test bars were punched and the thickness was measured by the calibrated Heidenhain thickness meter. The dynamic mechanical thermal analysis (DMTA) are performed according to the ASTM norm D5026 (1995) on the Rheometrics RSA-II (Rheometrics Solids Analyser II) at a frequency of 1Hz and within a temperature range of -130°C tot 180°C with a heating rate of 5°C/min. By this method the storage modulus (E'), the loss modulus (E") and the tangens delta (tanδ) is measured as function of temperature.

Crystallographic data

Rotaxane **A:** $C_{86}H_{122}N_{14}O_{14}$, M=1574, crystal size 0.56*0.30*0.24mm, triclinic P-1, a=10.59560(10), b=11.5272(2), c=15.3861(2) Å, α=110.5020(10), β=101.6830(10), γ=92.5240(10)°, V=1710.13(4) Å^3, Z=1, ρ_{calcd}=1.320 Mg m^{-3}; MoK_a radiation (graphite monochromator, λ=0.71073 Å), μ=0.239 mm^{-1}**,** T=180(2) K. 15779 data (8127 unique, R_{int}=0.0284*,* 1.90<θ<29.13°); Rotaxane **B:** $C_{76}H_{90}N_{10}O_{10}$, M=1302, crystal size 0.96*0.22*0.10mm, triclinic P-1, a=10.9198(2), b=14.0083(2), c=14.80100(10) Å, α=88.35, β=88.44, γ=70.6730(10)°, V=2121.95(5) Å^3**,** Z=1, ρ_{calcd}=1.246 Mg m^{-3} **;** MoK_a radiation (graphite monochromator, λ=0.71073 Å), μ=0.084 mm^{-1}**,** T=180(2) K. 13810 data (9853 unique, R_{int}=0.0181*,* 1.39< θ <29.11°). Rotaxane **D**: $C_{68}H_{74}N_{10}O_{10}$, M = 1190, crystal size 0.40*0.27*0.19mm, monoclinic, $P2_1/c$, a = 20.5953(16), b = 20.3996(16), c = 18.8652(15) Å, β = 115.0790(10)°, V = 7178.7(10) Å^3, Z = 4, ρ_{calcd} = 1.279 Mg m^{-3}; $Mo_{K\alpha}$ radiation **(**graphite monochromator, λ= 0.71073 Å**)**, μ= 0.123 mm^{-1},

T = 150(2)K. 44134 data (17301 unique, R_{int} = 0.0661, 1.48 < θ < 28.93°), All three structures were collected on a Siemens SMART CCD diffractometer using narrow frames (0.3° in ω), and were corrected semi-empirically for absorption and incident beam decay (transmission 0.88-1.00 **A**; 0.63-1.00 **B**; 0.74-1.00 **D**). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 values of all data (G.M.Sheldrick, SHELXTL manual, Siemens Analytical *X*-ray Instruments, Madison WI, USA, 1994, version 5) to give for **A**: $wR=\{\Sigma[w(F_o^2F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ =0.2347**,** conventional R=0.0754 for F values of 8127 reflections with $F_o^2>2\sigma F_o^2$), S=1.081 for 436 parameters. Residual electron density extremes were 0.885 and -1.068 Å^{-3}. For **B**: $wR=\{\Sigma[w(F_o^2F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ =0.1982**,** conventional R=0.0608 for F values of 9853 reflections with $F_o^2>2\sigma F_o^2$), S=1.067 for 539 parameters. Residual electron density extremes were 0.664 and -0.367 Å^{-3}. For **D**: $wR = \{\Sigma[w(F_o^2F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.2031**,** conventional R = 0.0704 for F values of 17301 reflections with $F_o^2 > 2\sigma F_o^2$), S = 1.019 for 938 parameters. Residual electron density extremes were 0.059 and 0.952 Å^{-3}. Amide hydrogen atoms in all three structures were refined isotropically with the all other hydrogen atoms constrained to a Riding model; anisotropic displacement parameters were used for all non-hydrogen atoms. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 188836, 188837 and 197400. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: teched@chemcrys.cam.ac.uk; fax: (+44) 1223-336-033).

Synthesis

Materials

CBC was obtained from DSM New Business Development, ALLINCO (purity > 99 %, HPLC) and used as received. All chemicals, solvents and catalysts were purchased from Aldrich or Acros and used without any purification. Jeff amines ® D400 were purchased from Hunstman and used as obtained.

Reaction product of bis-(hexamethylene) triamine and CBC , compound 1

CBC (246.84 g, 0.980 mol) was added to a solution of bis-(hexamethylene) triamine (100.00 g, 0.466 mol) in dry toluene (400 ml) at 80 °C and the resultant mixture was stirred for eighteen hours. The reaction was then cooled to room temperature, concentrated under reduced pressure to half its original volume and washed with distilled water (8 x 250 ml) followed by saturated aqueous calcium chloride solution (5 x 250 ml). Drying of the organic layer with anhydrous magnesium sulphate and filtering, followed by completely removing the solvent under reduced pressure afforded the desired product as a brown waxy solid. Yield: 198.32 g, 0.439 mol, 94%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.35 (8H, m, C$\underline{H}_2$), 1.56 (8H, m, C$\underline{H}_2$), 1.73 (12H, m C$\underline{H}_2$, ring), 2.57 (4H, t, C$\underline{H}_2$NHCO), 2.68 (4H, m, C$\underline{H}_2$NCOC$\underline{H}_2$), 3.26 (4H, m, CONHC$\underline{H}_2$), 3.98 (4H, m, C$\underline{H}_2$NH), 9.26 (2H, bt, CON$\underline{H}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 23.45, 26.52, 26.74, 28.31, 29.09, 29.38, 39.75, 40.45, 43.68, 46.86, 48.24, 154.78, 179.32; MS (EI): *m/z* 494 $[M+H]^+$; anal. calcd. for $C_{26}H_{47}N_5O_4$: C, 63.3%; H, 9.6%; N, 14.2%, found: C, 63.0%; H, 9.5 %; N, 13.9%.

Reaction product of fumaric acid mono-ethyl ester *N*-hydroxysuccinimide, compound 3

Dicyclohexylcarbodiimide (31.49 g, 0.153 mol) was added to a solution of fumaric acid mono-ethyl ester (20.00 g, 0.139 mol) and *N*-hydroxysuccinimide (17.57 g, 0.153 mol) in anhydrous tetrahydrofuran (200 ml). The mixture was stirred for one hour and then filtered. The organic solvent was removed under reduced pressure to render an oil, which was recrystallized from ethyl acetate to further remove residual dicyclohexylurea. Removal of the solvent under reduced pressure afforded the desired product as a light brown waxy solid. Yield: 33.12 g, 0.137 mol, 98%, mp 30.1-32.0 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.43 (3H, t, *J* = 6.9 Hz, $CH_2C\underline{H}_3$), 2.88 (4H, s, $C\underline{H}_2$), 4.23 (2H, q, *J* = 6.9 Hz, $C\underline{H}_2CH_3$), 7.05 (2H, dd, *J* = 14.5 Hz, C<u>H</u>=C<u>H</u>); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 13.87, 25.52, 62.83, 137.36, 138.54, 163.76, 164.95, 167.73; MS (EI): *m/z* 242 $[M+H]^+$; anal. calcd. for $C_{10}H_{11}NO_6$: C, 49.8%; H, 4.6%; N, 5.8%, found: C, 49.7%; H, 4.7%; N, 5.5%.

Reaction product of 3 with 2,2-diphenyl ethylene amine, followed by hydrolysis of the methyl ester, compound 4

3 (6.11 g, 25.3 mmol) in tetrahydrofuran (60 ml) was added dropwise to a stirred solution of 2,2-diphenylethylamine (5.00 g, 25.3 mmol) in tetrahydrofuran (75 ml) and the resultant solution was refluxed at 68 °C for one and a half hours. After this time the reaction mixture was cooled and the solvent was removed under reduced pressure yielding a brown solid. This solid was dissolved in ethanol (100 ml) followed by adding 4 M sodium hydroxide solution (100 ml). The mixture was then refluxed for 3 hours, cooled to 0 °C and acidified to pH 6 producing a light brown precipitate. The precipitate was filtered and washed with distilled water (3 x 200 ml) then dried under reduced pressure. Recrystallization of the precipitate from toluene yielded the pure product as a colourless solid. Yield: 4.56 g, 15.4 mmol, 61%; ^{1}H-NMR (300 MHz, $[D_6]$DMSO) δ = 3.74 (2H, bt, $C\underline{H}_2NH$), 4.23 (1H, t, *J* = 6.0 Hz, $Ar_2C\underline{H}$), 6.49 (1H, d, *J* = 14.5 Hz, $C\underline{H}CO_2H$), 6.78 (1H, d, *J* = 14.5 Hz, C<u>H</u>CONH), 7.29 (10H, m, ArC<u>H</u>), 8.67 (1H, bt, CON<u>H</u>), 12.85 (bs, $CO_2\underline{H}$); ^{13}C-NMR (75 MHz, $[D_6]$DMSO) δ = 43.35, 46.21, 126.55, 127.64, 128.39, 133.41, 141.23, 163.98, 166.45; MS (EI): *m/z* 318 $[M+Na]^+$; anal. calcd. for $C_{18}H_{17}NO_3$: C, 73.2%; H, 5.8%; N, 4.7%, found: C, 72.9%; H, 5.9%; N, 4.8%.

Reaction product of N-benzylethylenediamine and CBC, compound 6

CBC (8.39 g, 33.3 mmol) was added to a stirred solution of N-benzylethyenediamine (5.00 g, 33.3 mmol) in dry toluene (100 ml) at 60 °C. The reaction was stirred for a further eighteen hours at 60 °C before being allowed to cool to room temperature. The organic mixture was subsequently washed with distilled water (4 x 200 ml) followed by saturated aqueous calcium chloride solution (2 x 200 ml). Drying of the organic layer with anhydrous magnesium sulphate and filtering, followed by removing the solvent under reduced pressure yielded the desired product as pale yellow oil. Yield: 9.23 g, 30.6 mmol, 92%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.74 (6H, bs, CH_2), 2.71 (2H, bm, $C\underline{H}_2NCONH$), 2.81 (2H, t, *J* = 6.5 Hz, $C\underline{H}_2NH$), 3.35 (2H, q, *J* = 6 Hz, $C\underline{H}_2NHCO$), 3.81 (2H, s, $C\underline{H}_2Ar$), 3.97 (2H, bm, $C\underline{H}_2CON$), 7.27 (5H, m, ArC<u>H</u>), 9.45 (1H, bt, CON<u>H</u>); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.37, 29.30, 29.34, 38.61, 39.05, 39.89, 50.20, 51.31,

129.96, 130.20, 130.40, 139.53, 157.35, 176.78; MS (EI): *m/z* 290 $[M+H]^+$; anal. calcd. for $C_{16}H_{23}N_3O_2$: C, 66.4%; H, 8.0%; N, 14.5%, found: C, 65.6%; H, 7.8%; N, 14.3%.

Reaction product of 6 + *t*-BOC-DL-phenylalanine, compound 7

1,3-Dicyclohexylcarbodiimide (0.78 g, 3.8 mmol) was added to a stirred solution of *t*-BOC-DL-phenylalanine (1.00 g, 3.8 mmol), stopper **6** (1.09 g, 3.8 mmol) and 4-dimethylaminopyridine (0.23 g, 1.8 mmol) in dichloromethane (10 ml) in an atmosphere of nitrogen at 0 °C. The reaction was stirred at 0 °C for half an hour and at room temperature followed for another hour before being filtered to remove precipitated dicyclohexylurea. The solvent was removed under reduced pressure and yielded a colourless oil, which was taken up in ethyl acetate (100 ml). 4 M hydrochloric acid (100 ml) was added to this solution and the reaction was stirred at room temperature for 15 hours under an atmosphere of nitrogen. After this time the reaction was cooled to 0 °C and neutralized using 3 M sodium hydroxide. Extraction of the product with ethyl acetate (3 x 100 ml) followed by drying of the organic portion ($MgSO_4$), filtering and removing the solvent under reduced pressure yielded the product as colourless oil. Yield: 1.46 g, 3.4 mmol, 89%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.74 (6H, bs, C$\underline{H}_2$), 2.69 (2H, bm, C$\underline{H}_2$NCONH), 3.02 (2H, m, C$\underline{H}_2$Ar), 3.19 (2H, m, C$\underline{H}_2$N), 3.38 (2H, m, C$\underline{H}_2$NH), 3.74 & 4.04 (1H, m, C$\underline{H}$CH$_2$Ar), 3.94 (bm, 2H, C$\underline{H}_2$CON), 4.34 (2H, m, N$\underline{H}_2$), 5.30 (m, 2H, C$\underline{H}_2$Ar), 7.25 (10H, m, ArC$\underline{H}$), 9.31 (1H, bm, CON$\underline{H}$); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.73, 29.37, 29.40, 38.61, 39.11, 39.95, 43.07, 44.17, 49.20, 53.17, 127.68, 128.40, 128.85, 129.28, 129.67, 137.53, 138.20, 155.47, 176.21, 179.92; MS (EI): *m/z* 437 $[M+H]^+$, 324 $[(M\text{-caprolactam})+H]^+$; anal. calcd. for $C_{25}H_{32}N_4O_3$: C, 68.8 %; H, 7.4%; N, 12.8%, found: C, 68.6%; H, 7.3%; N, 12.3%.

Thread of rotaxane A, compound 2

Fumaroyl chloride (1.54 g, 10.0 mmol) in dichloromethane (50 ml) was added dropwise to a stirred solution of **1** (10.00 g, 22.1 mmol) in dichloromethane (50 ml) at 0 °C under an atmosphere of nitrogen. After one hour triethylamine (2.24 g, 22.1 mmol) was added to the stirred solution and a dark brown precipitate formed. The reaction was stirred for another hour at room temperature before being filtered, and the solvent was washed with 0.1M hydrochloric acid (2 x 100 ml), followed by saturated sodium hydrogen carbonate solution (2 x 100 ml). The organic fraction was dried over magnesium sulphate, and after filtration the solvent was removed under reduced pressure to yield dark brown oil. Column chromatography (methanol/dichloromethane, 3:97) produced the pure product as orange oil. Yield: 6.35 g, 5.5 mmol, 55%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.35 (16H, m, C$\underline{H}_2$), 1.56 (16H, m, C$\underline{H}_2$), 1.83 (28H, m C$\underline{H}_2$), 2.68 (8H, m, C$\underline{H}_2$NCONH), 3.26 (16H, m, C$\underline{H}_2$), 3.98 (8H, m, C$\underline{H}_2$CON), 7.34 (2H, s, C$\underline{H}$), 9.26 (4H, bt, CON$\underline{H}$); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.46, 26.51, 26.72, 28.36, 29.09, 29.38, 39.75, 40.45, 43.68, 46.86, 48.24, 131.28, 154.78, 164.67, 179.32; MS (EI): *m/z* 1090 $[M+Na]^+$; anal. calcd. for $C_{56}H_{94}N_{10}O_{10}$: C, 63.0%; H, 8.9%; N, 13.1%, found: C, 63.1%; H, 9.2%; N, 13.5%.

Thread of Rotaxane B, compound 5

Dicyclohexylcarbodiimide (0.49 g, 2.4 mmol) was added to a stirred solution of **1** (1.07 g, 2.4 mmol), **4** (0.70 g, 2.4 mmol) and 4-dimethyaminopyridine (0.15 g, 1.2 mmol) in anhydrous tetrahydrofuran (20 ml). The resultant mixture was stirred for twelve hours at

room temperature and then filtered to remove precipitated dicyclohexylurea. Removal of the organic solvent produced light brown oil, which after recrystallisation from ethyl acetate to remove residual dicyclohexylurea and removal of the solvent under reduced pressure yielded the pure product as colourless oil. Yield: 1.68 g, 2.3 mmol, 97%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.33 (8H, bm, C$\underline{H}_2$), 1.54 (8H, bm, C$\underline{H}_2$), 1.73 (14H, bm, C$\underline{H}_2$), 2.68 (4H, bm, C$\underline{H}_2$NCONH), 3.27 (8H, m, C$\underline{H}_2$), 3.97 (6H, m, C$\underline{H}_2$), 4.24 (1H, t, *J* = 8.0 Hz, C$\underline{H}$CH$_2$Ar$_2$), 6.07 (1H, bt, *J* = 5.7 Hz, CON$\underline{H}$), 6.70 (1H, d, *J* = 14.5 Hz, CH=C$\underline{H}$CONR), 7.27 (11H, m, CH=C$\underline{H}$CONH & ArC$\underline{H}$), 9.25 (2H, m, CH$_2\underline{H}$NCON); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.11, 26.08, 26.32, 26.40, 27.21, 27.97, 28.75, 29.04, 39.42, 40.03,43.37, 46.25, 47.81, 126.55, 127.65, 128.41, 130.17, 133.41, 141.26, 154.46, 163.96, 164.25, 179.01; MS (EI): *m/z* 794 $[M+Na]^+$; anal. calcd. for $C_{44}H_{62}N_6O_6$: C, 68.5%; H, 8.1%; N, 10.9%, found: C, 68.1%; H, 8.2%; N, 10.8%.

Thread of Rotaxane C (mixture of diastereoisomers), compound 8

Fumaroyl chloride (0.25 g, 1.6 mmol) in dichloromethane (10 ml) was added drop wise to a stirred solution of **7** (1.43 g, 3.3 mmol) in dichloromethane (10 ml) at 0 °C under an atmosphere of nitrogen. After one hour, triethylamine (0.33 g, 3.3 mmol) was added to the stirred solution and a dark brown precipitate formed. The reaction was stirred for another hour at room temperature before being filtered and the solvent was washed with 0.2 M hydrochloric acid (2 x 150 ml), followed by saturated sodium hydrogen carbonate solution (2 x 100 ml). The organic fraction was dried over anhydrous magnesium sulphate and after filtration the solvent was removed under reduced pressure to yield dark brown oil. Column chromatography (methanol/dichloromethane, 3:97) produced the pure product as a light brown glassy solid. Yield: 1.29 g, 1.4 mmol, 85%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.73 (12H, bs, C$\underline{H}_2$), 2.68 (4H, bm, C$\underline{H}_2$NCONH), 3.30 (14H, bm, mixture of H), 3.95 (4H, bm, C$\underline{H}_2$CON), 5.28 (4H, m, C$\underline{H}_2$Ar), 6.85 (4H, m, C$\underline{H}$=C$\underline{H}$ & CON$\underline{H}$), 7.23 (20H, m, ArC$\underline{H}$), 9.28 (2H, bt, CH$_2\underline{H}$NCON); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.75, 29.34, 29.38, 38.61, 39.10, 39.89, 43.06, 44.20, 49.22, 53.18, 127.70, 128.40, 128.85, 129.28, 129.67, 131.30, 137.53, 138.20, 155.47, 164.21, 176.21, 179.92; MS (EI): *m/z* 954 $[M+H]^+$, 976 $[M+Na]^+$; anal. calcd. for $C_{54}H_{64}N_8O_8$: C, 68.1%; H, 6.8%; N, 11.8%, found: C, 68.3%; H, 6.7%; N, 11.5%.

Net work rotaxane monomer, A

Separate solutions of isophthaloyl chloride (1.90 g, 9.4 mmol) and *p*-xylylene diamine (1.28 g, 9.4 mmol) in anhydrous chloroform (50 ml each) were added drop wise *via* syringes to a stirred solution of thread **2** (1.00 g, 0.9 mmol) and triethylamine (1.90 g, 18.7 mmol), also in anhydrous chloroform (150 ml), over a period of two hours. After this time, ethanol (10 ml) was added and the reaction filtered. The resultant solution was washed with distilled water (2 x 200 ml) followed by 0.1M hydrochloric acid (2 x 200 ml) and then saturated aqueous sodium hydrogen carbonate solution (2 x 200 ml). The organic portion was then dried over anhydrous magnesium sulphate and after filtration the solvent was removed under reduced pressure to produce a pale brown solid. This solid was taken up in chloroform (2.5 ml) and precipitated into diethyl ether (100 ml). The precipitate was washed with diethyl ether (2 x 10 ml) and dried to produce the pure rotaxane as a colourless solid. Yield: 1.05 g, 0.66 mmol, 70%, mp 164.4-166.7 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ δ = 0.57 (4H, m, C$\underline{H}_2$), 1.01 (4H, m, C$\underline{H}_2$), 1.24 (XH, m,

C$\underline{H}_2$), 1.34 (XH, m, C$\underline{H}_2$), 1.73 (XH, m, C$\underline{H}_2$), 2.70 (8H, m, C$\underline{H}_2$NCONH), 2.93 (4H, m, C$\underline{H}_2$), 3.22 (12H, m, C$\underline{H}_2$), 3.72 (4H, bd, J = 13.8 Hz, Ar-C$\underline{H}_2$), 3.98 (8H, m, C$\underline{H}_2$CON), 5.25 (4H, bdd, J = 14.3 Hz, Ar-C$\underline{H}_2$), 5.97 (2H, s, C$\underline{H}$=C$\underline{H}$), 7.0 (8H, s, ArC$\underline{H}$), 7.70 (6H, m, ArC$\underline{H}$ & CON$\underline{H}$), 8.34 (4H, d, J = 7.8 Hz, ArC$\underline{H}$), 8.85 (2H, bs, ArC$\underline{H}$), 9.24 (4H, bt, CON$\underline{H}$); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.72, 26.89, 28.13, 28.58, 29.39, 29.54, 40.06, 40.48, 43.63, 43.97, 48.35, 49.40, 122.79, 128.44, 129.17, 129.98, 132.43, 133.59, 138.32. 155.05, 165.23, 165.45, 179.64; MS (EI): *m/z* 1623 $[M+Na]^+$; anal. calcd. for $C_{88}H_{122}N_{14}O_{14}$: C, 66.1%; H, 7.7%; N, 12.3%, found: C, 66.2%; H, 7.6%; N, 12.0%.

The linear side chain rotaxane monomer, B

Separate solutions of isophthaloyl chloride (1.98 g, 9.7 mmol) and *p*-xylylene diamine (1.32 g, 9.7 mmol) in anhydrous chloroform (50 ml each) were added drop wise *via* syringes to a stirred solution of thread **5** (0.50 g, 0.7 mmol) and triethylamine (1.97 g, 19.5 mmol), also in anhydrous chloroform (100 ml), over a period of two hours. After this time ethanol (10 ml) was added and the reaction filtered. The resultant solution was washed with distilled water (2 x 300 ml) followed by 0.1M hydrochloric acid (2 x 300 ml) and then saturated aqueous sodium hydrogen carbonate solution (1 x 200 ml). The organic portion was then dried over anhydrous magnesium sulphate and after filtration the solvent was removed under reduced pressure to produce a colourless solid. This solid was dissolved in chloroform (2.5 ml) and precipitated into diethyl ether (100 ml). The precipitate was washed with diethyl ether (2 x 10 ml) and dried to yield the pure rotaxane as a colourless solid. Yield: 0.59 g, 0.50 mmol, 70%, mp 156.5-157.3 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 0.51 (2H, m, C$\underline{H}_2$), 1.08 (10H, m, C$\underline{H}_2$), 1.38 (4H, q, J = 7.4 Hz, C$\underline{H}_2$), 1.73 (12H, m, C$\underline{H}_2$), 2.69 (4H, m, C$\underline{H}_2$), 2.79 (2H, m, C$\underline{H}_2$), 3.05 (2H, m, C$\underline{H}_2$), 3.13 (4H, m, C$\underline{H}_2$), 3.97 (6H, m, C$\underline{H}_2$), 4.33 (5H, m, Ar-C$\underline{H}_2$ & C$\underline{H}$Ar$_2$), 4.54 (4H, bd, Ar-C$\underline{H}_2$), 5.67 (1H, d, J = 14.5 Hz, CH=C$\underline{H}$CONR), 5.93 (1H, d, J = 14.5 Hz, CH=C$\underline{H}$CONH), 6.87 (8H, s, ArC$\underline{H}$), 7.29 (10H, m, ArC$\underline{H}$), 7.64 (2H, t, J = 7.6 Hz, ArC$\underline{H}$), 7.70 (4H, bt, J = 4.9, CON$\underline{H}$), 8.22 (4H, d, J = 7.6 Hz, ArC$\underline{H}$), 8.57 (2H, bs, ArC$\underline{H}$), 9.21 (2H, t, J = 5.4 Hz, CH$_2\underline{H}$NCON); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.56, 26.32, 26.55, 26.62, 27.69, 28.42, 28.45, 29.26, 39.88, 40.31, 43.85, 45.07, 47.52, 48.87, 123.82, 126.27, 127.46, 128.01, 129.07, 129.12, 129.55, 131.83, 132.31, 133.69, 137.49, 141.60, 154.96, 164.46, 166.03, 166.13, 179.58; MS (EI): *m/z* 1304 $[M+H]^+$; anal. calcd. for $C_{76}H_{90}N_{10}O_{10}$: C, 70.0%; H, 7.0%; N, 10.8%, found: C, 69.3%; H, 6.9%; N, 11.6%.

The linear main chain rotaxane monomer, C

Separate solutions of isophthaloyl chloride (2.40 g, 11.8 mmol) and *p*-xylylene diamine (1.61 g, 11.8 mmol) in anhydrous chloroform (50 ml each) were added drop wise *via* syringe to a stirred solution of thread **8** (0.75 g, 0.8 mmol) and triethylamine (2.39 g, 23.6 mmol) also in anhydrous chloroform (100 ml) over a period of two hours. After this time ethanol (10 ml) was added and the reaction filtered. The resultant solution was washed with distilled water (2 x 250 ml) followed by 0.2 M hydrochloric acid (2 x 250 ml) and then saturated aqueous sodium hydrogen carbonate solution (2 x 250 ml). The organic portion was then dried over anhydrous magnesium sulphate and the solvent removed under reduced pressure to produce a pale yellow solid. This solid was taken up in chloroform (10 ml) and precipitated into diethyl ether (250 ml). The precipitate was washed with diethyl ether (2 x 50 ml) and dried to yield the pure rotaxane as a colourless

solid. Yield: 0.53 g, 0.36 mmol, 45%, mp 167.1-169.3 °C; ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.71 (12H, bs, C$\underline{H}_2$), 2.25-4.50 (20H, bm, mixture of H), 4.68 & 5.38 (8H, m, C$\underline{H}_2$Ar), 4.98 & 5.68 (8H, m, C$\underline{H}_2$), 5.64 (2H, s, C$\underline{H}$=C$\underline{H}$), 6.78 (8H, bm, ArC$\underline{H}$), 7.20 (20H, m, ArC$\underline{H}$), 7.49 (6H, m, ArC$\underline{H}$ & CON$\underline{H}$), 8.10 (6H, m, ArC$\underline{H}$), 8.78 & 9.28 (2H, bt, $CH_2\underline{H}$NCON); ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 23.61, 28.39, 29.26, 38.68, 39.03, 39.70, 43.84, 46.01, 50.46, 53.05, 125.21, 126.28, 127.68, 127.98, 128.48, 128.90, 129.11, 129.47, 129.80, 130.43, 131.26, 133.67, 133.81, 136.30, 136.61, 137.06, 137.34, 155.11, 166.68, 171.79, 172.19, 179.31; MS (EI): *m/z* 1487 $[M+H]^+$, 1509 $[M+Na]^+$; anal. calcd. for $C_{86}H_{92}N_{12}O_{12}$: C, 69.5%; H, 6.2%; N, 11.3%, found: C, 68.9%; H, 6.3%; N, 10.9%.

Linear main chain thread without phenylalanine residues

Fumaroyl chloride (1.2 g, 7.8 mmol) in dichloromethane (25 ml) was added drop wise to a stirred solution of **6** (5.00 g, 17.3 mmol) in dichloromethane (50 ml) at 0 °C under an atmosphere of nitrogen. After three hours, triethylamine (1.75 g, 17.3 mmol) was added to the stirred solution and a dark brown precipitate formed. The reaction was stirred for another hour at room temperature before being filtered and the solvent was washed with 0.1 M hydrochloric acid (2 x 100 ml), followed by saturated sodium hydrogen carbonate solution (2 x 100 ml) and water (1 x 150 ml). The organic fraction was dried over magnesium sulphate and the solvent removed under reduced pressure to produce dark brown oil. Column chromatography (methanol/dichloromethane, 2:98) yielded the pure product as a colourless solid. Yield: 2.90 g, 4.4 mmol, 56%; ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 1.72 (12H, m, C$\underline{H}_2$), 2.67 (4H, m, C$\underline{H}_2$CON), 3.55 (8H, m, C$\underline{H}_2$), 3.95 (4H, m, C$\underline{H}_2$NO), 4.70 (4H, bdd, Ar-C$\underline{H}_2$), 7.30 (12H, m, ArC$\underline{H}$ & C$\underline{H}$=C$\underline{H}$), 9.36 (2H, m, $CH_2\underline{H}$NCON); ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 23.43, 28.27, 29.04, 38.22, 39.29, 39.56, 43.75, 46.22, 49.49, 51.89, 126.60, 127.75, 128.14, 131.73, 136.30, 155.10, 155.20, 179.37; MS (EI): *m/z* 659 $[M+H]^+$; anal. calcd. for $C_{36}H_{46}N_6O_6$: C, 65.6%; H, 7.0%; N, 12.8%, found: C, 65.9%; H, 7.0%; N, 12.9%.

Linear main chain rotaxane without phenylalanine residues, D

Separate solutions of isophthaloyl chloride (3.47 g, 17.1 mmol) and *p*-xylylene diamine (2.33 g, 17.1 mmol) in anhydrous chloroform (50 ml each) were added dropwise *via* syringe to a stirred solution of corresponding thread (0.75 g, 1.1 mmol) and triethylamine (3.46 g, 34.2 mmol) also in anhydrous chloroform (100 ml) over a period of two hours. After this time, ethanol (10 ml) was added and the reaction filtered. The resultant solution was washed with distilled water (3 x 150 ml) followed by 0.1 M hydrochloric acid (3 x 150 ml) and then saturated aqueous sodium hydrogen carbonate solution (2 x 150 ml). The organic portion was then dried over magnesium sulphate and the solvent removed under reduced pressure to produce a creamy solid. This solid was taken up in chloroform (5 ml) and precipitated into diethyl ether (250 ml). The precipitate was washed with diethyl ether (2 x 50 ml) and dried to yield the pure rotaxane as a colourless solid. Yield: 0.77 g, 0.60 mmol, 56%, mp 198.0-199.3 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 1.34 (4H, m, C$\underline{H}_2$), 1.71 (12H, m, C$\underline{H}_2$), 2.63 (4H, m, C$\underline{H}_2$CON), 3.24 (8H, bm, C$\underline{H}_2$), 3.68 (4H, m, C$\underline{H}_2$NO), 4.00 & 4.75 (8H, m, Ar-C$\underline{H}_2$), 4.55 (8H, m, Ar-C$\underline{H}_2$), 6.41 (2H, m, C$\underline{H}$=C$\underline{H}$), 6.93 (8H, s, ArC$\underline{H}$), 7.18 (20H, m, ArC$\underline{H}$), 7.68 (2H, t, *J* = 7.9 Hz, ArC$\underline{H}$), 7.75 (4H, bt, CON$\underline{H}$), 8.28 (4H, m, ArC$\underline{H}$), 8.93 (2H, s, ArC$\underline{H}$), 9.34 (2H, m, $CH_2\underline{H}$NCON); ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 23.27, 27.88, 28.94, 38.18, 39.40, 40.06, 43.64, 46.90, 47.92,

48.03, 51.84, 125.33, 127.90, 128.68, 128.86, 129.03, 129.13, 129.25, 131.82, 133.33, 134.49, 137.30, 154.97, 155.26, 166.20, 179.47; MS (EI): *m/z* 618 $[M+2Na]^{2+}$, 1213 $[M+Na]^{+}$; anal. calcd. for $C_{68}H_{74}N_{10}O_{10}$: C, 68.6%; H, 6.3%; N, 11.8%, found: C, 68.7%; H, 6.3%; N, 11.9%.

General method for the polymerization of rotaxane monomer A

A mixture of rotaxane **A** (100 mg, 0.06 mmol) and Jeffamine® D400 (50 mg, 2.0 eq.) was dissolved in dichloromethane (1 ml) and mixed thoroughly. The solvent was removed under reduced pressure and the dry mixture was heated to 175 °C under an atmosphere of nitrogen for one hour. After this time the polymer was cooled rapidly to room temperature and the resultant gelatinous solid was washed repeatedly with dichloromethane (3 x 10 ml). Repeated attempts to dissolve the polymer in common organic solvents were unsuccessful resulting in a swollen suspension of the polymer in the solvents.

General method for the polymerization of rotaxane monomers B, C *&* D

A mixture of rotaxane **B, C** or **D** (100 mg) and Jeffamine® D400 (1.0 eq.) were dissolved in dichloromethane (1 mL) and mixed thoroughly. The solvent was removed under reduced pressure and the dry mixture heated to 175 °C under an atmosphere of nitrogen for one hour. After this time the polymer was cooled rapidly to room temperature and the resultant colourless solid was dissolved in dichloromethane (1 ml) followed by precipitation into diethylether (100 ml). The resultant solid was filtered and dried under reduced pressure to yield the corresponding polyrotaxane as a colourless solid (typical yields were > 90%).

General method for isomerisation of fumaramide towards maleicamide

Samples (1 mmol/l in chloroform) were irradiated in Perkin Elmer UV/VIS spectrometry cells part no. B0631071 (size 10*10 mm). The irradiation was done for 60 minutes in UV-light (Oriel 200W mercury lamp with an side intensity at 240-260 nm; absorption maximum fumaric unit at 254 nm) at a distance of 30 cm in a nitrogen atmosphere. The reaction was followed by IR and the equilibrium mixture contains about 60-70% maleic units and the rest is still fumaric. The separation of both isomers is done by column chromatography.

7.7 Literature

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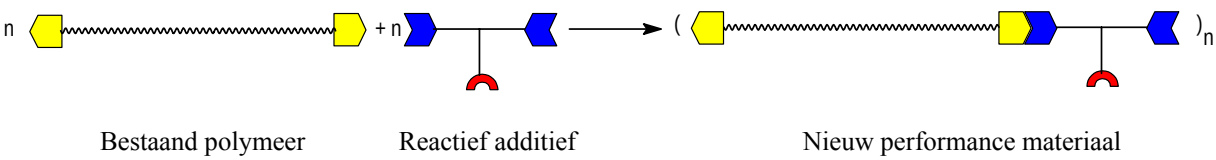
Samenvatting

Naast het voortdurende wereldwijde onderzoek om de kwaliteit van bestaande kunststoffen te verbeteren, is ook er een sterk groei in het ontwikkelen van nieuwe functionele polymeren. Om aan de toenemende eisen voor deze nieuwe materialen te kunnen voldoen is er behoefte aan eenvoudige synthetische concepten om polymeren met die gewenste eigenschappen te maken.

In dit proefschrift wordt zowel de bereiding van reactieve functionele additieven beschreven alsook de bereiding van nieuwe polymeren, door deze additieven aan polymeren te koppelen. Het principe van deze modulaire aanpak is schematisch weergeven in figuur S.1.



Figuur S.1: Een modulaire aanpak om nieuwe performance materialen te maken.

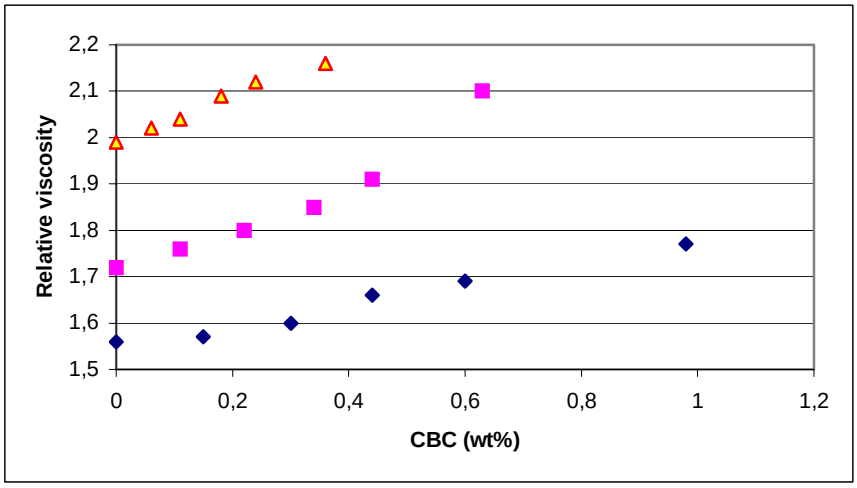
Polyesters, polyamiden en polyethers bevatten hydroxy-, amino- of carbonzuureindgroepen, die uitermate geschikt om gefunctionaliseerd te worden. Echter, tot dusverre is hier relatief weinig onderzoek aan gedaan.

Op basis van de unieke selectiviteit van carbonyl biscaprolactam (CBC; schema 1) zijn een groot aantal reactieve additieven bereid, en van sommige hiervan is de toepasbaarheid onderzocht.

In een model onderzoek is de reactiviteit van CBC met alcoholen onderzocht (bij T > 175 ^{o}C), in aanwezigheid van een groot aantal katalysatoren. Het blijkt dat een redelijk aantal katalysatoren de reactie van alcoholen met CBC veel sneller doen verlopen. Verder is aangetoond dat zich daarbij hoofdzakelijk urethaan bindingen vormen, hetgeen erop wijst dat één caprolactam ring van CBC zich afsplitst, terwijl de andere geopend wordt.

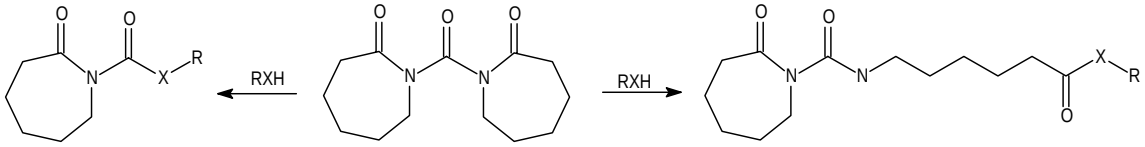
De ketenverlengingseigenschappen zijn bestudeerd, door verschillende polymeren, zoals poly(ethyleen terefthalaat) (PET), poly(butyleen terefthalaat) (PBT), nylon-6 en nylon-6,6 te verwerken met CBC, al dan niet in aanwezigheid van katalysatoren. Het grootste deel van dit onderzoek is uitgevoerd in de DSM micro-compounder, terwijl sommige experimenten in een ZSK30 extruder zijn herhaald. In alle gevallen is er een sterke toename van de viscositeit

waargenomen (figuur S.2). Met rheology en SEC metingen is aangetoond dat de polymeren, na ketenverlenging, nog steeds strikt lineair zijn.



Figuur S.2: De relatie tussen de relatieve viscositeit (in dl/g, in m-cresol) van PET en het gewichtspercentage CBC (na compounderen, in een micro-compounder; start viscositeiten zijn: ◊ = 1.56, □ = 1.72, Δ = 1.99 dl/g).

Onderzocht is of de reactieve intermediaire verbindingen, die zich na de eerste stap tijdens het chain extension proces gevormd hebben, geïsoleerd zouden kunnen worden. Het blijkt dat, bij lagere temperatuur, de reacties van amines met CBC na de eerste stap stoppen, waarbij zich, in bijna kwantitatieve opbrengst, geblokte isocyanates (BIen; carbamaten) gevormd hebben. Er zijn een groot aantal amino functionele verbindingen op deze wijze getest en omgezet in de overeenkomstige BIen (links in schema S.1). Deze methode blijkt een algemene werkwijze te zijn om, uitgaande van primaire amines, caprolactam geblokte isocyanaten te maken.

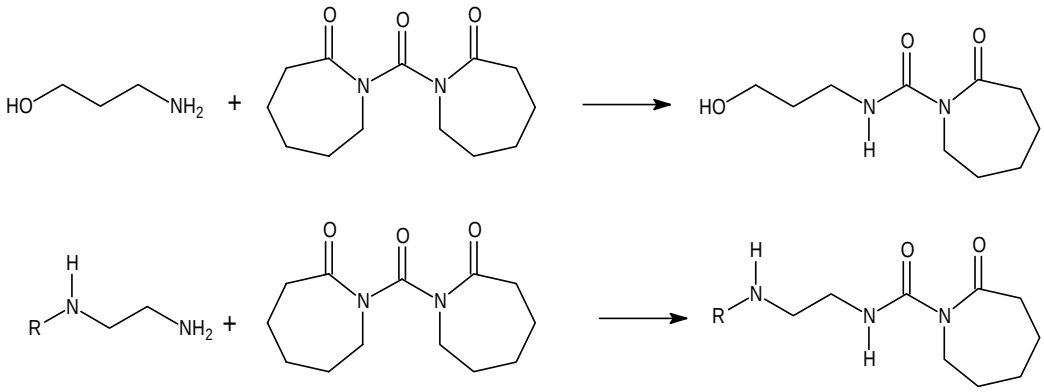


Schema S.1: Eerste stap in de reactie van CBC met een amine (X = NH) of alcohol (X = O).

Met alcoholen opent zich, in de aanwezigheid van geschikte katalysatoren (bij T < 150 ^{o}C), één van de caprolactam ringen van CBC (rechts in schema S.1). Dit is opmerkelijk, omdat met amines uitsluitend substitutie plaatsvindt. Ook met alcoholen zijn, in hoge opbrengst (~90%), geblokte isocyanaten gemaakt.

Om de grenzen van de selectiviteit vast te stellen zijn de reacties van CBC met verbindingen, die primaire amino- en hydroxygroepen of primaire en secondaire aminogroepen bevatten, bestudeerd. CBC reageert selectief met de primaire aminogroepen en niet detecteerbaar met

de hydroxy- of de secondaire aminogroepen (schema S.2). In beide gevallen hebben de BIen nog een reactieve (hydroxy- of amino-) groep beschikbaar om verdere te functionaliseren.



Schema S.2: De reactie van CBC met primaire amines die additioneel een hydroxy- of een secundaire aminogroep bevatten.

Om de toepasbaarheid van deze nieuwe technologie te onderzoeken, zijn fluor bevattend BIen gemaakt om de oppervlaktespanning van verven te verlagen. Ten gevolge van partiële zelf-ontmenging kunnen, met slechts 4 wt% fluor, verven verkregen worden die een oppervlaktespanning hebben, die lager is dan die van Teflon. In een ander voorbeeld zijn acrylaat monomeren gemaakt van de hydroxyfunctionele BIen. Copolymeren van o.a. deze monomeren en 2-hydroxyethyl-methacrylaat zijn zelf-vernetbare verven, die goede mechanische eigenschappen hebben, nadat ze uitgehard zijn bij 180 ^{o}C.

Om de veelzijdigheid van het concept aan te tonen zijn polyrotaxanen gemaakt. Polyrotaxanen zijn polymeren waarbij om polymeerketens niet covalent gebonden macrocyclische verbindingen zitten, die nog vrij beweegbaar zijn. Hierbij wordt gebruik gemaakt van de unieke selectiviteit van CBC om geblokte isocyanaten te maken die nog vrije secundaire amines bevatten. De secundaire amines zijn omgezet in fumaramiden, die dienen als template om er rotaxaan monomeren van te maken. De polycondensatie van die monomeren met Jeffamines leveren goed gedefinieerde polyrotaxanen op.

Samenvattend: In dit proefschrift wordt een eenvoudige verbinding, carbonyl biscaprolactam, beschreven die verrassende veelzijdige blijkt te zijn. Ten eerste werkt CBC uitstekend als ketenverlenger in polycondensaten. Daarenboven blijkt dit eenvoudige molecuul een groot aantal mogelijkheden te bieden, om een breed scala van functioneel geblokte isocyanaten te maken. Met behulp van deze functioneel geblokte isocyanaten zijn nieuwe polymeren gemaakt en zijn eigenschappen van bestaande materialen verbeterd. Het concept van de modulaire aanpak is daarmee in een aantal voorbeelden aangetoond.

Summary

Besides a continuous search for improving properties of existing polymers, there is also a strong growth in the developments of new functional polymeric materials. To cope with the increasing demands for these new materials, there is a need for convenient synthetic methodologies to make polymeric materials with the required properties.

In this thesis preparation of functional linkable additives is described, and a number of new polymers by coupling these additives in a simple way onto existing polymers. The principle of this modular approach is depicted in figure S.1.

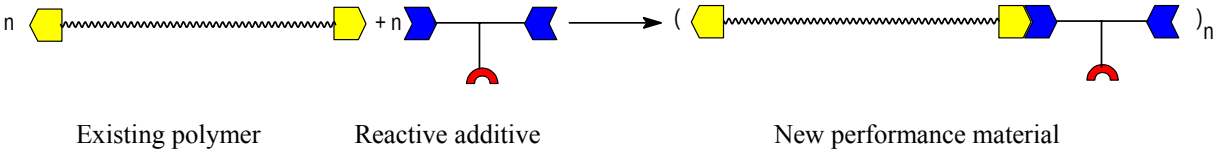


Figure S.1: A modular approach towards novel performance materials.

Polyesters, polyamides and polyethers contain hydroxy, amino or carboxylic end groups, which are extremely suitable to be modified by linkable additives. In spite of that, relatively little research has been done so far in this field.

A large number of linkable additives is prepared, thanks to the unique properties of carbonyl biscaprolactam (CBC; scheme 1), and their applicability is demonstrated in a few cases.

Model experiments were carried out (at T > 175 ^{o}C) to study the reactivity of CBC with alcohols, in the presence of a large number of catalysts. It is shown that catalysts increase the reaction rate between alcohols and CBC considerably. Furthermore, it is found that the urethane bond is the main coupling unit, meaning that one of the caprolactam rings opens, whereas the other one is substituted.

The chain extender properties of CBC are studied by processing various polymers such as, poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), nylon-6 and nylon-6,6 with CBC, with and without catalysts. Most of the experiments are done in the DSM micro-compounder and some of them are repeated in a ZSK30 extruder. In all cases a strong increase in viscosity is observed (figure S.2). Size exclusion chromatography and rheology measurements of the chain extended polymers show that the polymers remain strictly linear.

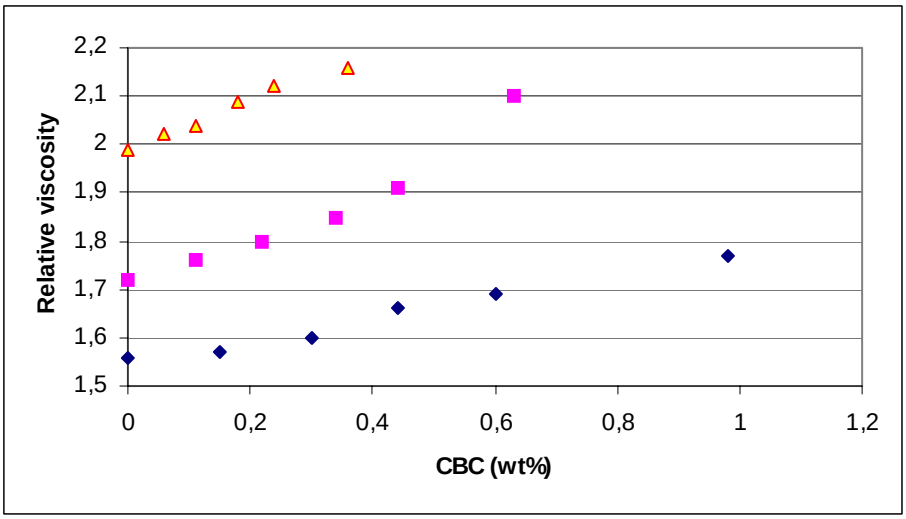
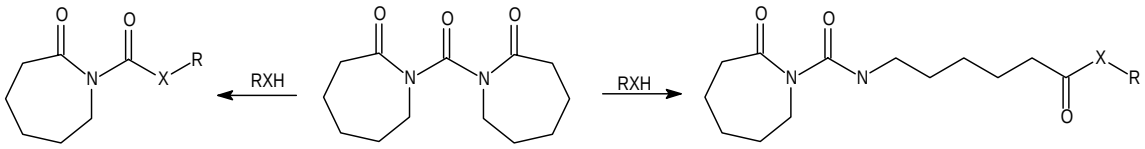


Figure S.2: Relation between the relative viscosity of PET (in dl/g, in m-cresol) and the weight percentage of CBC (after the compounding step in a micro-compounder; starting viscosities: ◊ = 1.56, □ = 1.72, Δ = 1.99 dl/g).

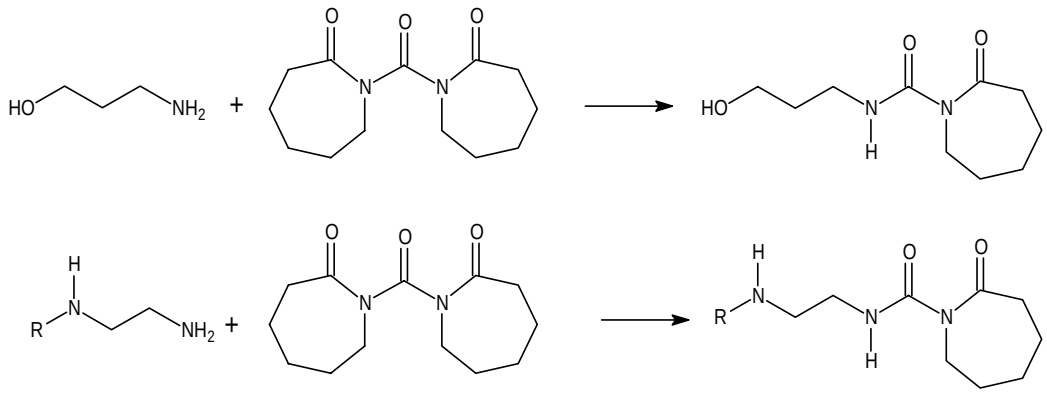
It was investigated whether the reactive intermediates, formed after the first reaction step in the chain extension process, could be isolated. It appears that, at lower temperatures (100 ^{o}C), the reaction of amines with CBC stops after the first reaction step, giving (functional) blocked isocyanates (BIs) in high yields (left in scheme S.1). A large number of other amines is tested and they all show the same excellent behaviour. It appears that this procedure is a general method for making caprolactam BIs.



Scheme S.1: First step of the reaction of CBC with amines (X = NH) or alcohols (X = O).

Alcohols give selectively a ring opening reaction with CBC, yielding BIs too, provided that suitable catalysts are used (at T < 150 ^{o}C; right path of scheme S.1). This is remarkable, because with amines ring only substitution takes place. A numbers of other primary alcohols have been tested and they all give the same good yields (~ 90 %).

To determine the limits of the selectivity, the reaction of CBC with compounds containing both primary amino and primary alcohol groups or primary and secondary amines groups is studied. CBC reacts exclusively with the primary amino group, leaving the hydroxy or the secondary amino groups unaffected (scheme S.2). The free hydroxy or free secondary amino groups are used to make functional BIs.



Scheme S.2: The reaction of CBC with primary amines containing in addition a hydroxy or a secondary amino group.

This technology, to make functional BIs, is applied for making fluorine-containing BIs and used to decrease the surface tension of polyester coating formulations. Thanks to a self-stratification process, coatings with less than 4 wt % of fluorine give surface tensions lower than that of Teflon. In another example the acrylate esters of hydroxy functional BIs (top of scheme S.2) are prepared. Poly(meth)acrylates, containing these monomers as well as hydroxy functional monomers, yield self-crosslinkable coatings, exhibiting good mechanical properties, after curing.

Polyrotaxanes are prepared to demonstrate the versatility of this concept. Polyrotaxanes are polymer threads around which macrocycles are clipped in a non-covalent, free to spin or shuttle along the polymer threads. Here the unique selectivity of CBC is used to make BIs, still containing free secondary amino groups. Fumaramides are made from the free secondary amino groups and used as template to make a rotaxane monomer. These monomers are converted into well-defined polyrotaxanes by heating them with Jeffamines.

In conclusion, in this work a simple chemical compound, carbonyl biscaprolactam, is described, which shows a surprisingly versatile chemistry. First of all it is an excellent chain extender for polycondensates. Furthermore, this molecule enables the development of wide variety of functional blocked isocyanates, thanks to its exceptionally high selectivity. This methodology has been applied in the preparation of specialty polymeric materials. The concept of modular approach is demonstrated in these examples.

Curriculum vitae

Ton (Jacobus Antonius) Loontjens is born in Maastricht on May 18, 1945. In 1969 he started his study chemistry at the university of Nijmegen, and in 1972 he passed his bachelor examination (cum laude). In the same year (1972) he received the Unilever award for the best student in chemistry in Nijmegen. In 1975 the master examination (organic chemistry) was passed (as well cum laude).

He started working at DSM in April 1975, where he became leader of the group on polypropylene chemistry. In 1980 the research field was widened, and polyethylene chemistry and the chemistry of construction resins and printing ink resins was included as well. In 1985 he became head of a polymer chemistry department on coating resins, melamine resins and stabilisation of polymers. In 1992 he was appointed as head of a department on coating resins, polyester resins and polyamide resins. In 1995 he became principal scientist, a position he has held up to now. As a principal scientist his main research activities are to make functional polymers by adding (reactive) additives to existing polymers. This topic forms partly the content of this PhD thesis.

Dankzegging

Het leven wordt, naast talenten en opvoeding, in belangrijke mate bepaald door toevalligheden. Eenieder van ons komt per toeval personen op z'n weg tegen die mede de curve van z'n bestaan in belangrijke mate bepalen. Omdat ik tot nu kan terug zien op een gelukkig leven, ben ik aan al diegenen die mijn pad gekruist hebben veel dank verschuldigd.
In het bijzonder wil ik beginnen met mijn ouders te bedanken voor mijn fijne jeugd en hun niet aflatende belangstelling voor mijn niet gebruikelijk opleidingspatroon. Helaas zijn ze er niet meer bij, ofschoon ze beiden een hoge leeftijd bereikt hebben. Mijn moeder wil ik vooral bedanken voor de warme sfeer thuis en mijn vader vooral vanwege zijn niet aflatende stimulans om verder te studeren, met name in de chemische richting.
In 1969 overwoog ik om, na enige jaren gewerkt te hebben, scheikunde te gaan studeren. Mijn familie stimuleerde mij daarin en mijn zussen boden me zelfs aan om eventueel financieel bij te springen, waarvoor ik hun erkentelijk ben.
In het eerste jaar van mijn studie kreeg ik een meer dan gewoon contact met een jaargenote, Elly Pieterse. Omdat ik uiterst gemotiveerd was om mijn studie tot een goed einde te brengen, was ik aanvankelijk bevreesd dat door haar aanwezigheid mijn studie in gevaar zou komen. Maar ik wilde haar ook niet verliezen en dus hebben we goede afspraken gemaakt over studie en vrije tijd. We zijn tot heden ten dage zeer gelukkig samen, en hebben dus toentertijd een goede beslissing genomen. Ik heb aan Elly zeer veel te danken, niet alleen privé, maar ook vakmatig. Als het voor mijn studie en later voor mijn werk nodig was, dan was alles mogelijk. Er is niet alleen altijd begrip en bovenal ook stimulans van haar om door te gaan. Dit geldt voor mijn baan, maar zeker ook voor het ruime tijdsbeslag dat het schrijven van dit proefschrift gekost heeft, waarvoor zij sterk gemotiveerd was omdat ik dat zo graag wilde. Zonder haar steun had ik dit niet kunnen volbrengen.
Ik wil ook een dankwoord richten aan Prof. B. Zwanenburg. Hij zag indertijd in mij een geschikte kandidaat om een promotie onderzoek te doen (zeer gemotiveerd en cum laude doctoraal), maar realiseerde zich ook dat ik bijna dertig was. Hij adviseerde mij om eerst met DSM (en Philips) te praten alvorens zijn aanbod aan te nemen. Ik ben hem hiervoor dankbaar, omdat ik toen na een promotie, vanwege mijn leeftijd, geen kans meer gehad zou hebben op de arbeidsmarkt. Bij iedere latere ontmoeting spoorde hij mij aan om alsnog mijn promotie te doen. Het zal hem dus vreugdevol stemmen dat ik hier alsnog gehoor aan geef.

Uiteraard ben ik ook DSM veel dank verschuldigd. Ik heb de gelegenheid gekregen om mij zelf te ontplooien in die dingen waarvan ik denk dat ik de meeste capaciteiten heb. In de eerste tien jaren heb ik veel variatie gehad in verschillende polymeerchemische onderzoeksterreinen, als werkgroepsleider. In de volgende tien jaren heb ik ervaring kunnen opdoen, als sectiechef van twee verschillende polymeerchemische afdelingen, op het gebied van management taken. En tot slot in mijn huidige functie, als principal scientist, kan ik weer volop genieten van hetgeen dat mij toch het meeste boeit: de chemie. Ik wil hier met name Jos Put bedanken, niet alleen omdat hij mij benoemd heeft, maar vooral omdat hij mij altijd zeer sterk gestimuleerd en ondersteund heeft.

Daarnaast wil ik ook Ad de Koning bedanken die, als mijn huidige chef, zijn vertrouwen voortdurend in mij uitspreekt en ook vierkant achter mijn promotie staat.

Een speciaal woord van dank wil ik richten tot Cor Koning en Piet Lemstra. Ik ben destijds met Piet en Jos de discussie begonnen over mijn ambities en zij hebben mij sterk gestimuleerd om te gaan promoveren. Ik ben dankbaar dat ik aan hun oproep gehoor gegeven heb. Omdat dit proefschrift overwegend over polycondensatie polymeren gaat was het duidelijk dat de specialist op dat gebied, Cor Koning, hier een voortrekkers rol moest hebben. Dit heeft voor mij een speciale betekenis omdat ik Cor's mentor geweest ben toen hij bij DSM in dienst trad. De leuke ervaring uit die tijd, mijn bijzondere prettige, jarenlange relatie met hem daarna als collega research fellow en nu de intensieve wijze waarop hij deze promotie heeft aangepakt noopt tot dankbaarheid en is de basis voor intensieve contacten in de toekomst.

De leden van de kern commissie, Prof.dr.ir J.C.M van Hest, Prof.dr. M.Möller en Prof.dr.ir H.E.H Meijer, wil ik bedanken voor hun welwillendheid om aan de beoordeling deel te nemen en voor hun nuttige opmerkingen en aanvullingen die bijgedragen hebben aan de kwaliteit van dit proefschrift.

Binnen DSM heb ik met velen, in allerlei teams, op een zeer plezierige manier mogen samenwerken. Het zijn, over die lange periode, teveel mensen om ze allen op te noemen. Ik wil een uitzondering maken voor Boudewijn Scholtens en Bart Plum waar ik, in het kader van het onderwerp van dit proefschrift, de laatste jaren zo intensief mee heb samengewerkt. Boudewijn wil ik bedanken voor de ruimte die hij me binnen het project gegeven heeft om dit onderwerp intensief te exploreren en voor onze talrijke boeiende discussies. We werken, samen met Bart, met veel plezier, maar ook zeer intens aan het ALLINCO project.

Ik wil Bart in het bijzonder noemen, voor zijn grote bijdrage aan het vele experimentele werk uit dit proefschrift, voor de vele nuttige discussies die we samen gehad hebben en voor onze bijzondere prettige relatie.

Verder wil ik ook Tim Kidd nadrukkelijk noemen (thanks Tim) voor zijn bijdrage aan het onderzoek aan polyrotaxanen.
Ik wil bovenal mijn kinderen, Bas en Chantal, niet onvermeld laten. Zij hebben binnen het gezin er mede voor gezorgd dat er een goede sfeer en rust was, waardoor de aandacht voor (het werk en) de chemie goed heeft kunnen gedijen. Hun partners, Dorinda en Eric, hebben zich naadloos in dit plaatje ingepast.

Tot slot wil ik nog bedanken: A. Nijenhuis, G. van Vliet, F. Derks, E. Sham, T. van der Kolk, M. van de Meulen, J. Heinen, T. Verhoeven, M. van der Leemput, H. Mohammad, M. Rooijmans, M. van Dijck, J. Rietberg, P. van der Spek, T. Sleijpen, C. Kjeldal, P. Steeman, R. Bovee, D. Muscat, H. Janssen, L. van Ravenstein, W. Ming, R. Mülhaupt, S.Maier, D. Leigh, J. Wong, S. Globisch en W. Ballet, die op een of andere manier een bijdrage aan die proefschrift geleverd hebben.

Appendix A: **Patents concerning carbonyl biscaprolactam**

1. Loontjens, J.A., Derks, F., Sham, E.,WO9634909, (4-5-95). High molecular weight polyamides.
2. Loontjens, J.A., Plum, B.,WO9847940, (22-4-97). High molecular weight polyesters and polyamides.
3. Loontjens, J.A., Plum, B., WO017169, (25-9-98). Process for the preparation of an N-alkylcarbamoyl derivatives.
4. Loontjens, J.A., WO01/40178A1, 2-12-99. Process for the preparation of carbonic acid derivatives.
5. Loontjens, J.A., Plum, B. Rietberg J., EP 1149848, (28-04-00). Powder paint composition.
6. Loontjens, J.A., Molhoek, L., Spoolder, B., Plum, B., WO0164769, (29-02-00). Powder paint binder composition.
7. Loontjens, J.A., van Benthem, R., Plum, B., Rietberg, J., WO 01/66609, (10-03-00). Thermosetting composition.
8. Loontjens, J.A.,WO 01/66617, (10-03-00). Process for the preparation of branched polymers.
9. Loontjens, J.A., Plum, B., WO 01/66633 A1, (10-03-00). Chain extension process.
10. Loontjens, J.A., Plum, B., Muscat, D., NL 1017555, (11-09-01). Lactam geblokt N-(alcoxycarbonylalkyl)isocyanaat.
11. Loontjens, J.A., Plum, B., NL 1017667, 22-03-00 Process for the preparation of lactam activated acids.
12. Loontjens, J.A., NL 1018905 (07-09-01). Process for the preparation of a functional silane couplings agent.
13. Loontjens, J.A., Scholtens, B.J.R. WO03/035767, (26-10-01) New polymer composition, and the preparation and the application thereof.
14. Loontjens, J.A., Plum B., Nijenhuis, A., NL 1019369, (14-11-01). Preparation of low coloured carbonylbislactam.
15. Loontjens, J.A., Plum, B., van Geenen, A., Ming, W., WO03/070785A1, (21-02-2002). Preparation of functional chain extenders/crosslinker.
16. Loontjens, J.A., WO03/070704A1, (21-02-02). Preparation of ethylenically unsaturated compounds containing blocked isocyanate groups, the synthesis and the use thereof.
17. Loontjens, J.A., WO2004/020501A1, (22-02-02). Process for preparing a high molecular weight polyamide, polyester, copolyesters or polyester-amide block copolymer.
18. Loontjens, J.A., Mülhaupt, R., Zimmermann, J., Maier S., EP02078540.8 (28-08-02). Process for preparing biocompatible hydroxy functional polymer networks.
19. Loontjens, J.A., Plum, B., EP02075724.1, (22-03-02). Process for preparing a high molecular weight polyamide, polyesters, copolyester or copolyamide.
20. Loontjens, J.A., NL 1021825, (04-11-02). Process for preparing of carbonylbislactam.
21. Loontjens, J.A., Plum, B., Mülhaupt, R., Maier, S., EP02079918.5, (20-11-02). Silane coupling agent, process for the preparation of a silane coupling agent, use of said silane coupling agent in a composite or on a substrate, nanoparticles and use thereof in a coating.
22. Loontjens, J.A., EP0377680.0, (27-08-03). Process for the preparation of a polymer composition.

23. Loontjens, J.A., EP03077680, (28-08-03). Process for the preparation of a functionalized polymer, intermediate products, process for the preparation thereof, a functionalized polymer and polymer composition containing a functionalized polymer and shaped parts.
24. PBOX (22-09-2003)

Appendix 2: **Publications related to carbonyl biscaprolactam**

1. Loontjens, J.A., Pauwels, K., Derks, F., Nielen, M., Sham, C., Serné, M., J. Appl. Polym. Sci., **65**, 9, 1813, (1997). The Action of Chain extenders in nylon-6, PET and Model Compounds.
2. Loontjens, J.A., Scholtens, B., Maier, S., Mülhaupt, R., Kunststoffe **92**, 38, (2002). Isocyanate-free Route to Polyurethane.
3. Loontjens, J.A., Maier, S., Scholtens, B., Mülhaupt, R., Macromolecules, **36,** (13), 4727 (2003). Isocyanate-free route to oligomers with caprolactam-blocked isocyanate end groups by means of carbonyl biscaprolactam (CBC) mediated end group conversions.
4. Loontjens, J.A., Maier, S., Scholtens, B., Mülhaupt, R., Polym. Prep., **44**, (1), 115, (2003). Carbonylbiscaprolactam: A versatile reagent for the synthesis of reactive oligomers.
5., Loontjens, J.A., Ming, W., van Ravenstein, L., van de Grampel, R.D., van der Linde, R., de With, G., Thüne, P.C., Niemantsverdriet, J.W., Polym. Mater. Sci. Eng., **88**, 266, (2003). Low Surface Energy Polymeric Films from Novel Fluorinated Blocked Isocyanates.
6. Loontjens, J.A., Kidd, T., Leigh, D., Wong, J., Angew. Chem, **42,** (29), 3379, (2003). Rotaxane Building Blocks bearing Blocked Isocyanate Stoppers – Polyrotaxane through Post-Assembly Chain Extension.
7. Loontjens, J.A., Maier, S., Scholtens, B., Mülhaupt, R., Angew. Chem., **42**, 5094, (2003). Carbonylbiscaprolactam (CBC) a versatile reagent for organic synthesis and isocyanate-free urethane chemistry.
8. Loontjens, J.A., Polym. Sci. Part: Polym Chem **41,** (21), 3198, 2003. Modular Approach for Novel Nanostructered Polycondensates Enabled by the Unique Selectivity of Carbonyl BisCaprolactam.
9. Loontjens, J.A., van Ravenstein, L., Ming, W., van de Grample, R.D., van der Linde, R., de With, G., Thüne, P.C., Niemantsverdriet J.W., Macromol., **37**, 408, (2004). Low surface energy polymeric film from novel fluorinated blocked isocyanates.
10. Loontjens, J.A., Scholtens B., J. Zimmermann, Mülhaupt, R., Biomaterials, **25**, 2713, (2004). The formation of poly(ester-urea) networks in the absence of isocyanate monomers.
11. Loontjens, J.A., Scholtens, B., Plum, B., J. of Org. Coat. In press. New, Isocyanate-free routes to Blocked Isocyanates from the non-toxic chemical Carbonyl BisCaprolactam (ALLINCO®).
12. Loontjens, J.A., Scholtens, B., Kidd, T., Plum, B., EEC conference papers. In press. Novel route to isocyanate-free blocked isocyanates with functional groups.
13. Loontjens, J.A., Scholtens, B., Kidd, T., Plum, B., European Coating Journal, in press Novel Route to Isocyanate-free Blocked Isocyanates with Functional Groups.

Appendix B

Additional remarks on the linearity of polymers chain extended by CBC

Rheology measurements provide information on the viscosity, the storage modulus (G') and the loss modulus (G'') of polymers as a function of the shear rate (angular frequency). The average molecular weight and the temperature determine the position of the curves along the frequency axis. A well-known method to eliminate the effect of the molecular weight and temperature is to evaluate the curve of G' as a function of G". The value of G' at a chosen value of G" (often 500 Pa) is a measure of the broadness of the relaxation time distribution. In literature[1] it has been reported that this value can be used as an indicator for the broadness of the molecular mass distribution ($\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$) of linear polymers. Moreover, very large effects of long-chain branching on the G' value have been demonstrated, making this also a good method to determine branching.

Branched PBT polymers have been made by adding trimethylol propane (TMP) as branching agent, in the presence of CBC[1)]. In figure A.1 it can be seen that the ratio between G' and G'' changes strongly if small amounts of a chain branching agent is added to PBT.

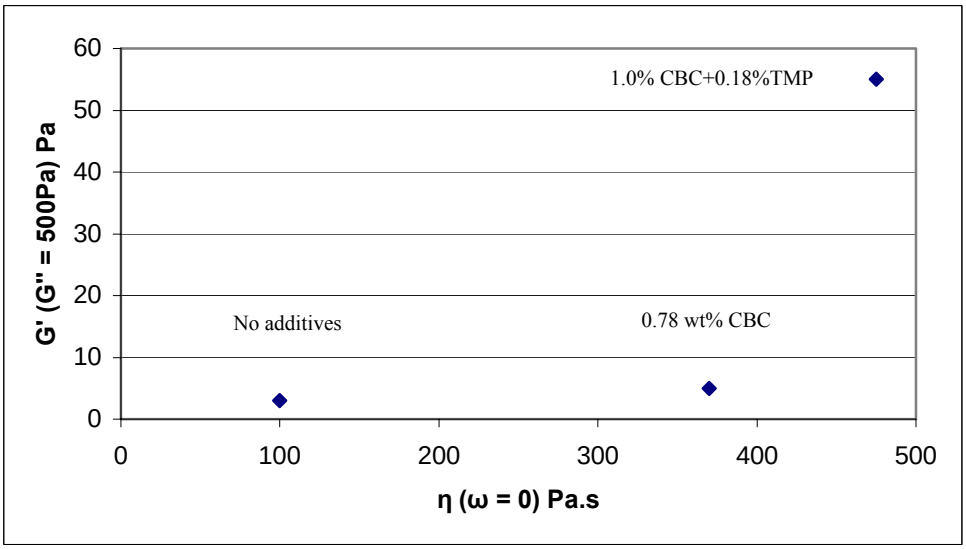


Figure A.1: The relation between the storage modulus G' (at G'' = 500 Pa) and the melt viscosity for PBT, PBT + CBC and PBT + CBC + TMP.

Without any additive the ratio G'/G'' is 3/500, and this value slightly rises to 5/500, after the addition of CBC (0.78 wt%). However, in the presence of only 0.18 wt % of TMP this ratio goes up to 55/500. The PBT case is our benchmark, because these are the only experiments in

[1)] PBT was compounded in the micro-compounder in the presence of CBC or with CBC plus TMP, for 4 minutes at 260 ^{o}C.

which a branching agent is purposely added. These results demonstrate the sensitivity of this ratio G'/G'' for branching.

Table A.1: The values of G' (at G''= 500Pa) and the viscosities of chain extended and regular polymers

Polymer	CBC (wt %)	TMP (wt%)	G' (G''=500Pa) (Pa)	η_o ($\omega = 0$) (Pa.s)	T [1)] (^oC)
PBT [2a)]	0	0	3.0	100	260
PBT [2b)]	0.78	0	5.0	370	260
PBT [2c)]	1.0	0.18	55	475	260
PET [3a)]	0	0	7.0	1132	270
PET [3b)]	0.65	0	8.8	1199	270
Nylon-6 [4a)]	0	0	5.5	412	230
Nylon-6 [4b)]	0.70	0	6.0	870	230
Nylon-6,6 [5a)]	0	0	25	2880	270
Nylon-6,6 [5b)]	0.53	0	32	5000	270

1) Temperature of the melt in the rheometer. 2) PBT samples: a) virgin, b) chain extended and c) chain extended-branched. 3) PET samples: a) chain extended and b) SPP. 4) Nylon-6 samples: a) virgin and b) chain extended. 5) Nylon-6,6 samples: a) virgin and b) chain extended.

In table A.1 the values of G'/G" are given for PET, nylon-6 and nylon-6,6 in the presence of CBC, and for PBT in the presence of CBC, and CBC plus TMP.

In the cases of nylon-6 and nylon-6,6 the chain extended polymers have slightly higher G'/G'' ratios than the starting materials, but this increase is negligible compared to the TMP-branched PBT. The same holds also for PET, where G'/G" values of the chain extended polymer is even slightly less than the SSP product. In general these results show that differences in G'/G" for the chain extended polymers and the virgin counterparts are small. These results are additional evidence that no chain branching takes place when CBC is used as chain extender.

It can be concluded that these results support the statement that chain extension with CBC gives strictly linear polycondensates.

Literature

[1] (a) Shirov, R., Mavrides, J. of Appl. Polym. Sci., **57**, 1605, (1995). (b) Steeman, P., Rheol. Acta, **37**, 583, (1998).

Appendix C, List of abbreviations

ABS	Acrylinotril-butadiene-styrene
Acac	Acetyl acetonate
AIBN	Azobisisobutyronitril
BI(s)	Blocked isocyanate(s)
BHTA	Bishexamtehylene triamine
BHTA-BI	Bishexamethylene triamine BI
BO	2,2'-(2-oxazoline)
CBC	Carbonyl biscaprolactam
DCC	Dicyclohexyl carbodiimide
CDI	Carbonyl diimidazole
COP	Cyclo olefin polymers
DABCO	4-diazabicyclo[2,2,2] octane
DBU	1,8-diazabicyclo[5,4,0]undec-7-ene
DM(T)A	Dynamic mechanical (thermal) analysis
DMAP	N,N'-Dimethyl amino pyridine
DMSO	Dimethyl sulfoxide
DV	Differential viscosity
EGMB	Ethylene glycol monobenzoate
EGDB	Ethylene glycol dibenzoate
HDPE	High density polyethelene
HEMA	2-hydroxyethyl methacrylate
HMDC	1,6-Hexamethylene diisocyanate caprolactamate
HMDI	1,6-Hexamethylene diisocyanate
HPLC	High pressure liquid chromatography
IBC	Isophtaloyl biscaprolactam
IV	Intrinsic viscosity
LC	Liquid chromatography
LC-MS	Liquid chromatography-mass spectroscopy
LCP	Liquid crystalline polymers
LDPE	Low density polyethylene
LS	Light scattering
MMA	Methyl methacrylate
MMD	Molecular mass distribution
η	Viscosity
η_{rel}	Relative viscosity
N-4,6	Nylon-4,6
N-6	Nylon-6
N-6,6	Nylon-6,6
PAR	Polyarylamide
PBO	Phenylene bis(2-oxazoline)
PBOX	Phenylene bis(2-oxazine)
PBT	Poly(butylene terephthalate)
PC	Polycarbonate
PEI	Poly(ether imide)
PEEK	Poly(ether ether keton)

PES	Poly(ether sulfone)
PET	Poly(ethylene terephthalate)
PI	Polyimide
PP	Polypropylene
PTFE	Poly(tetra fluoro ethylene)
PSU	Poly(ether sulfone)
PUR	Polyurethane
PVC	Poly(vinyl chloride)
R	Alkyl group
RI	Refractive index
RO	Ring opening
RS	Ring substitution
RPM	Revolutions per minute
SEC	Size exclusion chromatography
SSP	Solid state post-condensation
TEMPO	2,2,6,6-tetramethyl-1-piperidyloxy
t	Time
τ	Residence time
T	Temperature
T_g	Glass transition temperature
TBC	Terephthaloyl biscaprolactam
TBT	Tetrabutoxy titanium
TLC	Thin layer chromatography
TMP	Trimethylol propane
UV	Ultra violet
XPS	X-ray photo electron spectroscopy

Stellingen

behorende bij het proefschrift

Performance Materials by a Modular Approach

Door

Ton Loontjens

1. Een mens is nooit te oud om te promoveren.

2. De conclusie van Inata et al. over de reactiviteit van bisoxazines met carbonzuur eindgroepen van polyesters, gemeten in een glazen kolf met eenvoudig roerwerk, is misleidend voor de praktijk.
   Inata, H., Matusumura, S., J. of Polym. Sci., **30**, no. 8, 3325, (1985).

3. Er zullen geen polymerisatie fabrieken meer gebouwd worden voor nieuwe polymeren op kton schaal.

4. Het gebruik van s*mart additives* is de slimste mannier om nieuwe polymeren of polymeren met sterk verbeterde eigenschappen op grote schaal te maken.

5. Uitvindingen worden gedaan uit nieuwsgierigheid, innovaties voor het bevredigen van behoeftes.

6. Hypes zijn altijd waar, de verwachtingen daaromtrent niet.

7. Oudere werknemer wordt men niet slechts vanwege leeftijd, maar vooral door de wijze waarop men wordt behandeld.

8. Het gezegde “wiens brood men eet, diens woord men spreekt” geldt niet voor aandeelhouders.

9. Je hoeft niet ziek te zijn om beter te willen worden.

10. Mede omdat biologie de chemie van het leven heeft opgeëist zit “de chemie” met een imago probleem.

11. De ivoren toren van industriële wetenschappers is in de loop der tijden vervangen door een vergulde kooi.

12. Innoveren, het toepassen van vernieuwingen, kan alleen dan wanneer er ook mogelijkheden geboden worden om naar die vernieuwingen te zoeken.

13. Politici gedragen zich als producenten van *foie grass*. Ze duwen je maatregelen door de strot en zeggen dan: “Domme gans jij snapt natuurlijk niet dat dit nuttige maatregelen zijn om straks een fijne paté te maken”.