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NEW STRATEGIES FOR THE PREPARATION OF HIGH-PERFORMANCE BIO-BASED POLYMERS

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Abstract (English)

The research topics discussed here involve the preparation of new monomers, polymers and copolymers from renewable resources following strategic synthetic pathways.

The adopted procedures are essentially the following:

1) Development of syntheses from biomass to get traditional polymers, currently obtained from petroleum;
2) Exploitation of monomers deriving from biomass to get new polymeric structures aimed at substituting the synthetic ones (derived from petroleum) or at imparting advanced features.

Research was mainly focused on aromatic polymers, in particular on polyethylene terephthalate (PET), one of the most employed polymers in the word, especially for food packaging.

With this purpose in mind, relatively to strategy 1), the preparation of a monomer, p-toluic acid (the terephthalic acid (TPA) and therefore PET precursor) from natural molecules (acrylic and sorbic acids) was set up by exploiting a Diels-Alder (DA) reaction. The developed strategy involved milder reaction conditions with respect to those reported in literature for DA reactions, contributing to a more sustainable production of TPA, the actually most industrially exploited aromatic monomer and, therefore, contributing to obtaining a 100% bio-PET.

By adopting strategy 2), on the other hand, aromatic polymers exhibiting a chemical structure similar to that of PET were prepared. More into detail, starting from vanillic acid, a monomer from natural resources, the synthesis of polyethylene vanillate, an homopolymer whose melting and glass transition temperatures are close to those of PET, was set up. The poor reactivity of its phenolic group was overcome by an etherification reaction with ethylene carbonate, a molecule from biomass, too. To improve its processability and to reduce its brittleness, random copolymers with ε-polycaprolactone or polyricinoleic acid units were subsequently prepared. The new materials showed that their properties could be easily changed by controlling the composition; new possible functionalities (such as antibacterial activity) were furthermore introduced in copolymers containing ricinoleic acid.

According, again, to strategy 2), the preparation of new completely aliphatic or copolymers having aromatic groups was furthermore studied by exploiting DA reactions between furans (obtainable from natural resources) and maleimides. Only monomers with furan or maleimidic moieties on their extremities are currently employed to get linear or cross-linked polymeric structures. The developed innovative idea consisted in using a monomer with a DA adduct resulting from furan and maleimide moieties within its structure. The above mentioned monomer was synthetized with two acidic groups on its extremities making it suitable to take part in polyesterification reactions. A copolymer was prepared by exploiting the tendency by DA adducts to break over 100°C and to recombine at lower temperatures. The success of such process was demonstrated through DSC analysis. In this case, the possibility to obtain materials exhibiting groups able to associate and dissociate in a reversible manner depending on the temperature was demonstrated: these properties can be used to produce innovative self-mending materials.

Finally, in the context of the study of the preparation of new materials from biomass (strategy 2)), a research activity dealt with the valorization of compounds deriving from the vegetal oil biorefinery to produce new aliphatic materials. Project main fundamental points were:

- the development of an hydrogen transfer model reaction between a fatty acid with ketone functionalities in its carbon backbone and glycerol;
- the exploitation of dihydroxyacetone (DHA), the by-product of the above mentioned reaction, for obtaining totally innovative and bio-based polycarbonates and polyesters.

Different parameters, such as temperature, solvent, type and quantity of the catalyst were tested and permitted to set up a new strategy for exploiting DHA (also derived from glycerol through different green routes) for the production of polyesters and polycarbonates.

In conclusion, in the present thesis new synthetic strategies to get monomers, polymers and copolymers from biomass were studied. These strategies were aimed at obtaining completely renewable polymers (bio-PET), new bio-polymers that can substitute PET even with advanced functionalities (e.g. antibacterial properties), innovative bio-copolymers for self-mending materials and new polyesters and polycarbonates making the most of byproducts of other reactions.

Abstract (Italian)

I temi di ricerca trattati nel presente lavoro di tesi riguardano lo sviluppo di procedure sintetiche per la preparazione di nuovi monomeri, polimeri e copolimeri provenienti da fonti rinnovabili.

Le strategie utilizzate sono essenzialmente due:

1) Sviluppo di sintesi per ottenere da biomassa polimeri tradizionali, attualmente ottenuti da petrolio;
2) Sfruttamento di monomeri derivati da biomassa per ottenere nuove strutture polimeriche che possano sostituire quelle sintetiche, derivate da petrolio, o che abbiano funzionalità avanzate.

La ricerca si è occupata principalmente di polimeri aromatici, in particolare del polietilene tereftalato (PET), che rappresenta uno dei polimeri tradizionali più utilizzati a livello mondiale, principalmente per l'imballaggio alimentare.

A tale scopo, relativamente alla strategia 1), è stata studiata la preparazione di un monomero, l'acido p-toluico, che è precursore dell'acido tereftalico (TPA) e, quindi, del PET, a partire da molecole ottenibili da risorse naturali (acido acrilico e acido sorbico), attraverso la reazione di Diels-Alder (DA). La strategia di sintesi messa a punto prevede condizioni di reazione più blande rispetto a quelle riportate in letteratura per le reazioni di DA: questo risultato ha quindi portato un contribuito ad una produzione maggiormente sostenibile di TPA, il monomero aromatico attualmente più sfruttato a livello industriale e, quindi, alla possibilità di produrre un 100% bio-PET.

Adottando la strategia 2), invece, si sono sviluppati polimeri aromatici dalla struttura simile al PET partendo da molecole presenti in natura. In particolare, partendo da un monomero di origine naturale, l'acido vanillico, è stata messa a punto la sintesi del polietilene vanillato (PEV), un omopolimero caratterizzato da temperature di fusione e di transizione vetrosa simili a quelle del PET. La scarsa reattività dei gruppi fenolici dell'acido vanillico è stata superata sfruttando una reazione di eterificazione con etilene carbonato, che è anche esso una molecola derivabile da biomassa. Successivamente, al fine di migliorare la processabilità del PEV e di diminuirne la fragilità, sono stati preparati copolimeri random con unità di ε-policaprolattone e di

acido poliricinoleico. I nuovi materiali hanno mostrato proprietà facilmente modificabili rispetto a quelle degli omopolimeri in funzione della composizione; sono state introdotte, anche, possibili nuove funzionalità, quali proprietà antibatteriche nei copolimeri contenenti acido poliricinoleico.

Sempre in accordo alla strategia 2), la preparazione di nuovi copolimeri completamente alifatici o contenenti gruppi aromatici è stata, poi, studiata sfruttando reazioni DA tra furani (molecole ottenibili da fonti rinnovabili) e maleimmidi. Attualmente, solamente monomeri aventi funzionalità furaniche e maleimmidiche alle proprie estremità vengono impiegati per ottenere strutture polimeriche lineari o ramificate. L'idea innovativa sviluppata consiste nell'utilizzo di un monomero con un adotto DA derivante da unità furaniche e maleimmidiche all'interno della propria struttura. Tale monomero è stato sintetizzato con due gruppi acidi alle proprie estremità che lo rendono adatto ad essere sottoposto a reazioni di poliesterificazione. E' stato preparato un copolimero sfruttando la tendenza da parte degli addotti DA di essere soggetti a rottura sopra ai 100°C e di ricombinarsi a temperature inferiori. La riuscita di tale processo è stata dimostrata tramite analisi DSC. In questo caso, si è dimostrata la possibilità di ottenere materiali contenenti gruppi che possono associarsi e dissociarsi in maniera reversibile, a seconda della temperatura a cui si trovano: questa proprietà può essere sfruttata per la produzione di materiali auto-riparanti innovativi.

Infine, nell'ambito dello studio rivolto alla preparazione di nuovi materiali derivati da biomassa (strategia 2)), un'attività di ricerca è stata dedicata alla valorizzazione di composti provenienti dalla bioraffineria di oli vegetali per ottenere nuovi polimeri alifatici. Il progetto ha come punti fondamentali:

- lo sviluppo di una reazione modello di trasferimento di idrogeno tra un acido grasso con funzionalità chetoniche nella catena carboniosa e glicerolo;
- lo sfruttamento del diidrossiacetone (DHA), il sottoprodotto della sopracitata reazione, per l'ottenimento di policarbonati e poliesteri rinnovabili e totalmente innovativi.

Differenti parametri, fra cui la temperatura, il solvente, la tipologia ed il quantitativo di catalizzatore, sono stati testati ed hanno consentito la messa a punto di nuove strategie per lo sfruttamento del DHA (derivabile altresì da glicerolo attraverso differenti processi sostenibili) per la preparazione di poliesteri e policarbonati.

In conclusione, in questo lavoro di tesi sono state studiate nuove vie di sintesi di monomeri, polimeri e copolimeri da biomassa al fine di ottenere polimeri completamente rinnovabili (bio-PET), nuovi bio-polimeri che possano sostituire il PET, anche con funzionalità avanzate (per esempio, proprietà antibatteriche), innovativi bio-copolimeri per materiali auto-riparanti e nuovi poliesteri e policarbonati che sfruttino sottoprodotti di altre reazioni.

Table of contents

1. Aim of the work

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Nowadays, the development of sustainable polymers with convenient properties to substitute the traditional petroleum-based materials, is one of the major issues for material science. In particular, the utilization of renewable resources as feedstock for bio-polyesters is a challenging target.

For example, polyethylene terephthalate (PET), the most common thermoplastic polyester, used in a vast variety of applications, is produced from ethylene glycol (EG) and dimethyl terephthalate (DMT) or terephthalic acid (TPA). Only EG can be readily obtained from natural resources, TPA (and, of course, the correspondent dimethyl ester) is actually petrol-based.

The research work described in the present thesis is aimed at contributing to the development of new bio-based homopolyesters and copolymers from biomass characterized by properties that can get them suitable to practical applications.

More into detail, the research activities were divided into four main groups, namely:

- the preparation of a completely bio-based PET. TPA precursor, p-toulic acid, was synthetized through a completely sustainable synthesis and from bio-based reagents;
- identifying bio-based new polymeric structures that can mimic PET. The synthesis of polyethylene vanillate, a semi-aromatic homopolymer characterized by melting and glass transition temperatures close to those of PET, was set up. To improve its processability and to lower its brittleness, it was randomly copolymerized with ε–polycaprolattone and polyricinoleic acid to get polymeric structures characterized by tunable properties and a new possible antibacterial activity;
- synthetizing self-mending and recyclable partially bio-based materials. The thermoreversibility of Diels-Alder reactions between furans (F) (molecules from natural resources) and maleimides (M) was exploited: two polyesters able to break and recombine depending on the temperature applied were prepared, and from those a random copolymer. The two polyesters derive from a diacidic monomer

with a F and M adduct within its structure (until now such reactions in polymer science were used with monomers with those functionalities on their extremities);
- valorizing compounds from vegetable oils that are triglycerides extracted from a plant (in turn composed of fatty acids and glycerol) according to the principles of biorefinery. A model reaction between a fatty acid with ketone functionalities in its structure and glycerol was studied. Its by-product, dihydroxyacetone (that can be obtained from glycerol through different green routes, too), was exploited to get innovative polycarbonates and polyesters.

2. Introduction

2.1. Bio-polymers: definitions and production capacity data

During the last few decades, synthetic polymers, obtained from petrol, and their derived materials have become indispensable materials in people's lives. Due to the availability of raw materials, easy processing, tunable properties, lightness, and low cost, they are used in a very wide range of applications from household to aerospace applications, from agriculture to medicine or pharmacy. They have even replaced traditional metals, ceramic and glass-based materials for a number of applications.

In the last years, the term "**bio-polymer**" has been extensively used in the scientific and technical literature and several meanings are associated to it. One of those is related to biomedical applications: within such a framework, a bio-polymer can be defined as a material intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body.[1] In this context, the concept of bio-polymer is closely related to that of biocompatibility,[2] which is the ability to be in contact with a living system without producing an adverse effect.[3]

In addition to this specific context, a peculiar attention has been recently spent to environmentally friendly polymers, due to the growing awareness on environmental care and thanks to an increasing sensitivity towards problems such as the large-scale accumulation of plastics in our environment and the excessive use of not renewable fossil resources. These polymers are called bio-polymers too, and, in this context, this term has got two specific meanings:

- <u>Biodegradable</u>: The term 'biodegradability' refers to the degradation processes that results from the action of naturally-occurring micro-organisms such as bacteria, fungi and algae.[4]

  Biodegradability is not related to the origin of the material (fossil or renewable), but it depends on both polymer chemical structure (functional group stability, reactivity, crystallinity, molecular weight) and the environmental degrading conditions.
- <u>From natural resources</u>: These materials are defined bio-based. Bio-based products are wholly or partly derived from materials of biological origin, excluding materials embedded in geological formations and/or fossilized.[5]

Therefore, according to Figure 2.1., a bio-polymer can be bio-based and/or biodegradable. It must be underlined that bio-based polymers can be biodegradable, such as polylactic acid (PLA) and polyhydroxyalkanoates (PHA), or non-biodegradable (e.g., bio-polyethylene terephthalate, bio-PET). Moreover, not all biodegradable polymers are bio-based (e.g., polycaprolactone, PCL) (Figure 2.1.).

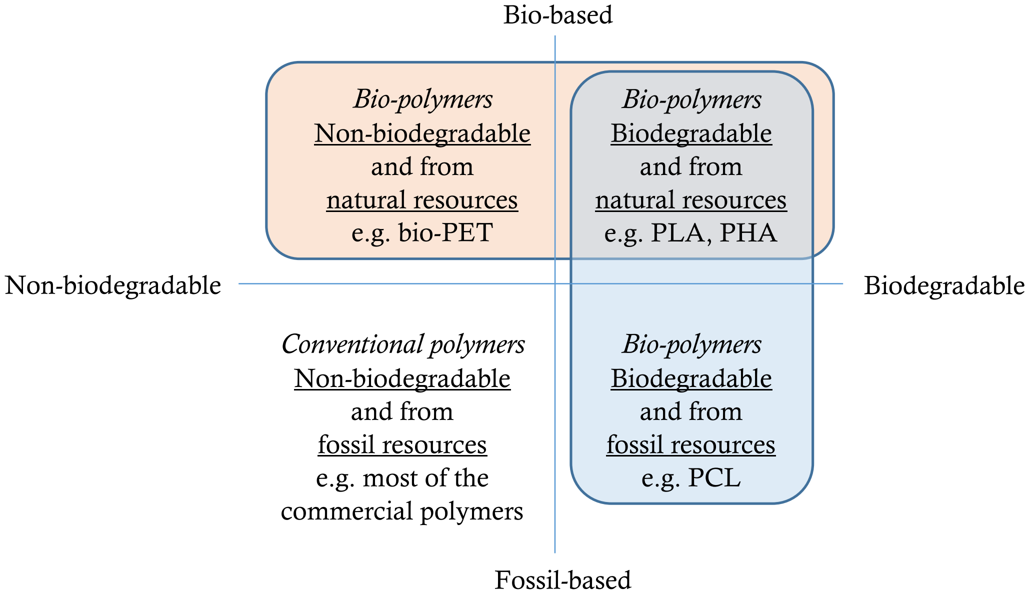

Figure 2.1.: Classification of bio-polymers and fossil-based polymers.

Nowadays the production of bio-plastics is not really high. Indeed, it was 2.05 million tonnes in 2017,[6] representing only a small percentage of the 320 million tonnes of plastics produced annually. The bio-polymers with a larger success and request are bio-polyethylene terephthalate (bio-PET) and bio-polyammides (bio-PA), according to Figure 2.2. These data suggest that, for the moment, the market of bio-polymers tends to try to substitute traditional plastics with the corresponding materials obtained partially or totally from biomass. For bio-PET, indeed, only one (ethylene glycol) of the two monomers is obtained from biomass, resulting in a polymer only 33% bio-based.

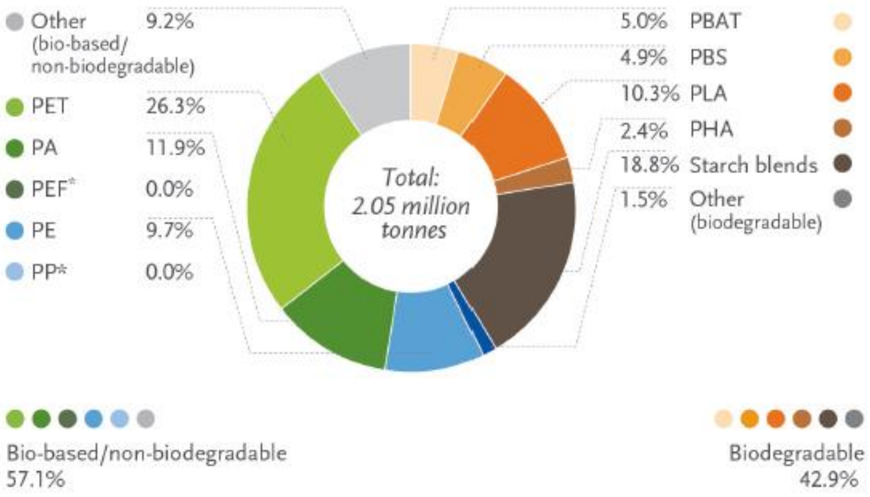

Figure 2.2.: Global production capacities of bio-plastics in 2017 (by material type).

In any case, the demand of bio-polymers is rising, in particular sophisticated materials for specific applications and products are requested. According to the latest market data compiled by the European Bioplastics Association,[7] global production capacity of bio-plastics is predicted to grow from around 2.05 million tonnes in 2017 to approximately 2.44 million tonnes in 2022 (Figure 2.3.). Indeed, polymers from green sources are attracting large interest, mainly by industries: more than 57% of the bio-plastics production capacity worldwide in 2017 was bio-based, durable plastics, and a similar trend will be maintained in the following 5 years.[7]

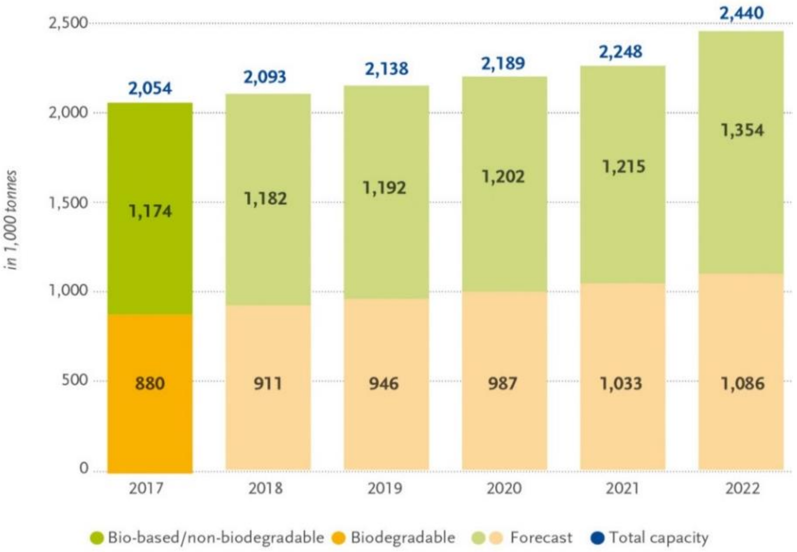

Figure 2.3.: Global production capacities of bio-plastics.

It si noteworthy that in this work the term bio-polymers refers to *polymers from natural resources* (biomass), independently of the fact that they are biodegradable or not. We do not use bio-polymers to indicate biodegradable polymers from fossil resources.

2.2. Environmental impact of bio-based polymers

The field of polymers derived from non-petrochemical feedstocks is gaining a great deal of momentum from both a commercial and academic sense, as several issues are associated to petrol. A big environmental damage occurs when extraction, transportation and processing of oil take place: water bodies located next to the extraction sites or to the processing plants are very frequently polluted. Moreover, it is provided that the cost of oil is likely to increase in the future, since in current years the maximum exploitation of the world's crude oil reserves has been reached. Global stocks will consequentially run out, given its very long period of renewal.

Furthermore, in the end of the lifecycle of petrochemical products a significant release of carbon dioxide stored during the fossilization process occurs. It leads to an evident greenhouse effect that causes, in turn, global warming (this aspect will be deeper discussed below).

In view of all these considerations, current industrial and academic studies are increasingly oriented towards the preparation of chemicals and materials starting from biomasses.

Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources defines biomass as "*the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste*".

Biomasses can be divided into three groups:

- Wastes (usually ligno-cellulosic substances) coming from different sources (e.g. agriculture, food and paper industry etc.);
- Crops of substances for the human and animal feeding;
- Crops solely dedicated to the utilization with energetic and chemical purposes.

As evidenced, biomasses can be exploited for energetic or chemical purposes. In the first case, they can be used in many ways, for example by burning them. In the second one, they are subjected to physical, chemical, biological, and thermal processes, giving rise to substances that can find exploitation in chemistry.

In the view of the topic of this research, only biomasses used for chemical purposes will be taken into account.

The most interesting advantage related to biomasses is given by the fact that they represent *sustainable* and *renewable* carbon sources.

Their *sustainability* is connected to the balance of the carbon emissions and removals associated to materials derived from biomasses. Plants fix carbon dioxide to organic carbon by photosynthesis and it returns in part to the atmosphere by breathing of living organisms. Over geological time ($>10^6$ years), after death the living organic matter is fossilized. When such fossil carbon is transformed into petrochemical products, it is released back into the atmosphere in a much shorter time scale (1-10 years). Due to the disparity between the rate of conversion to fossil and the rate of CO_2 release to the environment at end of life of the product, the CO_2 emitted is more than that is fixed as fossil sources resulting in a total carbon imbalance. On the other hand, by using renewable sources to produce polymers and other products, the rate at which CO_2 is fixed equals the rate at which it is released at the end of life of the product. Therefore, bio-based polymers, i.e. polymers from natural resources, can potentially contribute to reduce carbon dioxide emissions whose uncontrolled increase is the major responsible of the greenhouse effect and of the consequential climate changes.[8]

In Figure 2.4. the carbon cycle with the relative time scales of CO_2 utilization using renewable sources and fossil feedstocks is shown.

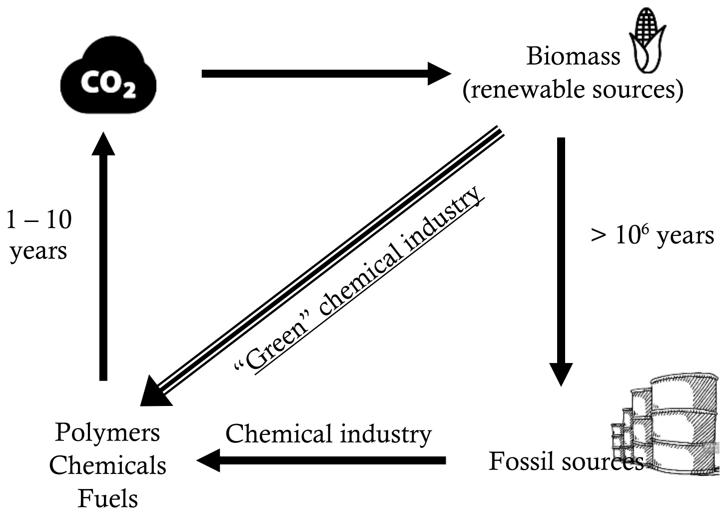

Figure 2.4.: Carbon cycle - time scales of CO_2 utilization using renewable sources (balanced cycle) opposed to using fossil feedstocks (unbalanced cycle).

Secondly, biomasses can be considered as *renewable* carbon sources since their much shorter renewal time. As it can be seen in Figure 2.5., CO_2 and water, thanks to the sun energy, are transformed into biomass, from which raw materials and therefore chemical substances are converted into the final products; these objects, once thrown away, are reconverted into CO_2 and water in short times.

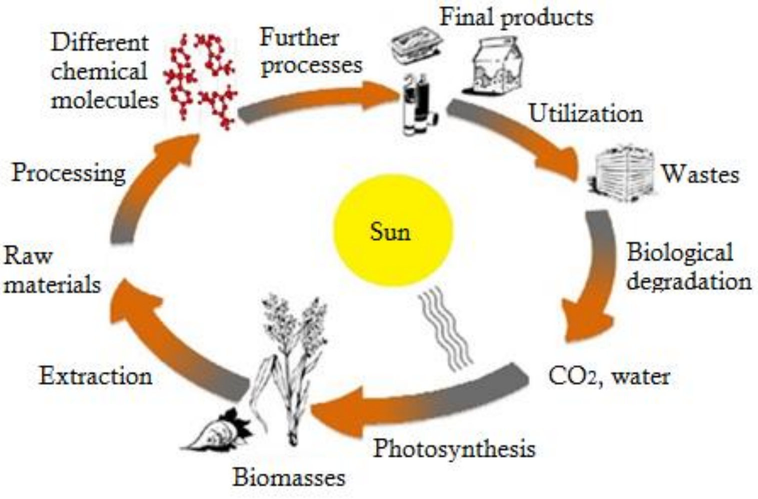

Figure 2.5.: Lifecycle of a final product coming from biomasses.

Other advantages are related to biomass. From it enantiomerically and stereochemically pure molecules can be directly extracted to obtain final products through less processing steps. Furthermore, associating the "bio" term to the final products does undoubtedly increase their added value in terms of market penetration. Even some specific labels to certify the bio-origin of the product exist; they are a form of sustainability measurement directed at consumers, intended to make it easy to take environmental concerns into account when shopping. One of the most important is the EU EcoLabel (Figure 2.6,a), whose functioning is set through a Regulation of the European Parliament and of the Council, but also the labels developed by DIN CERTCO (Germany, Figure 2.6,b) and VINCOTTE (Belgium, Figure 2.6,c).

Figure 2.6.: Some labels certifying the bio-origin of the product (UE EcoLabel, a, DIN CERTCO certification, b, and VINCOTTE certification, c).

Bio-Based Industries Joint Undertaking is a Public-Private Partnership between the EU and the Bio-based Industries Consortium (BBI).[9] This organization predicts that biomasses will, among other things:

- Develop the potential of waste as well as agriculture and forestry residues;
- Diversify and grow farmers' incomes: up to 40% additional margins with existing residues;
- Create a competitive bio-based infrastructure in Europe, boosting job creation, 80% of which will be in rural and underdeveloped areas;
- Reduce CO_2 emissions by at least 50% when new bio-based products will take a step in the market (compared with the emissions due to fossil-based materials).

When biomasses are mentioned, some aspects must be taken into account. It must be underlined that, at the moment, the costs related to the employment of biomasses instead of substances coming from fossil resources are generally higher. It is because the production processes are more recent, and therefore not yet optimized; on the contrary, the ones referring to petrol-chemistry are consolidated and optimized. In this context, a positive note is given by the huge potential and by the fact that the possibilities in this field are many.

An accusation that can be easily moved to the use of biomass for chemistry is represented by the possible "subtraction" of resources to be devoted to human nutrition. In this hypothesis, it is clear that the exploitation of biomass should not only respond to mere market laws, but it should also be regulated according to ethical purposes. Such a contribution can be certainly given by preferring the preparation of chemicals from scrap materials or from by-products of large-scale processes.

2.3. Classification of bio-based polymers

In general, bio-based polymers can be divided into three groups:

- Natural polymers;
- Polymers obtained through microorganisms by fermentation;
- Synthetic polymers from monomers deriving from natural resources.

The polymers belonging to the first group are already available in nature, while for the others polymerization occurs via microorganisms (second group) or through a chemical approach (third group).

Natural polymers

In biochemistry, the term is applied to many polymers that can be found in nature, such as nucleic acids (e.g. DNA), proteins and carbohydrates. Natural polymers can be organic or inorganic,[10] the latter having a skeleton without carbon atoms (e.g. polyphosphazenes, polysilicates, polysulfides and so on).[11]

Among polymers from renewable sources directly extracted and separated from biomass, polymers like starch, cellulose, chitin, chitosan and lignin can be listed.

Cellulose is one of the first natural polymers used by humanity and it still continues to represent a resource. It is a linear polysaccharide in which glucose units are linked by β-1,4-glycosidic bonds (Figure 2.7,a).

Cellulose is the predominant constituent of cell walls of the plants, green algae and of some flagellates, in membranes of most fungi and tunic of sea animals (Tunicatae).[12]

The olecular structure of cellulose determines the characteristic properties of cellulosic materials, such as relative surface reactivity available for chemical modifications, hydrophilicity, chirality, biodegradability.[13-16] Cellulosic materials are used in the polymer industry for a wide range of applications, including laminates, fillers and panel products, composites, alloys and blends, and cellulose derivatives.[17] Some interest is growing in the field of cellulose-reinforced thermoplastics.[17] Furthermore, nanocomposites based on cellulose nanocrystals isolated from different cellulose sources (e.g. wood[18]) have been widely investigated. Outstanding mechanical, optical, barrier properties can be obtained by blending cellulose nanocrystals and a polymer matrix even at low filler loading.[19]

Starch is produced by green plants and, unlike cellulose, it is stored in granules as energy reserve. Starch consists of two macromolecular components: the almost linear amylose with α-(1–4)-linked D-glucose units and branched amylopectin with α-(1–4)- linked D-glucose backbone and side chains linked via a glicosidic bond to the C-6 of the backbone sugar rings (Figure 2.7,b).[20]

Native starch granules are mainly used in plastic applications as rigid fillers,[21] as additives in polymers to enhance their biodegradability due to voids formation and consequentially increasing of matrix porosity when starch degradation takes place.[22, 23] Alternatively, in order to use starch as the main polymer component and to process it as a thermoplastic material, a destructuring treatment called "gelatinization" is adopted in which the starch semi-crystalline granule structure is destroyed. The resulting materials are referred as of thermoplastic starches since they can be processed following conventional plastic processing techniques (injection moulding, extrusion).

Chitin is a structural polysaccharide like cellulose, which is highly abundant in nature and it is the organic constituent of the exoskeleton of insects, of crustacean shells and fungi. The chemical structure of chitin resembles that of cellulose (glucose units linked by β-1,4-glycosidic bonds) except for the presence of an acetamido group at position C-2 instead of an hydroxyl (Figure 2.7,c). It is, for example, used for the preparation of films and fibers for medical and pharmaceutical applications.[24] Chitosan is produced from chitin by fully or partially removing the acetate moieties at C-2 through alkaline or enzymatic hydrolysis (Figure 2.7,d). Such aminopolysaccharide can be used as functional material though chemical and structural modifications to impart desired properties and functions with a wide range of potential applications especially in biomedical sector but also in the cosmetic one due to its biocompatibility, biodegradability and non-toxic properties.[24]

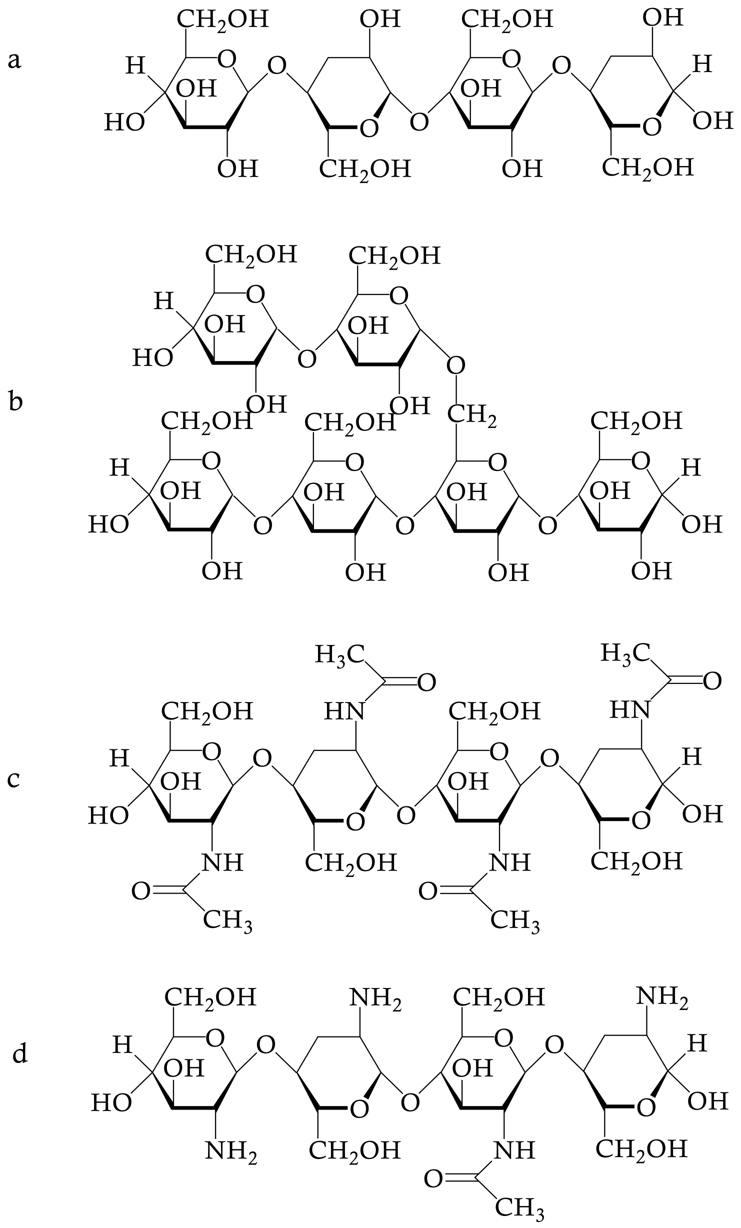

Figure 2.7.: Chemical structure of cellulose (a), starch (b) chitin (c) and chitosan (d).

Lignin is an aromatic polymer that makes up 15–30% of the cell walls of terrestrial plants.[25] It is one of the most promising renewable biomass, possessing some major chemical functional groups such as hydroxy, methoxy, and carbonyl groups (Figure 2.8).

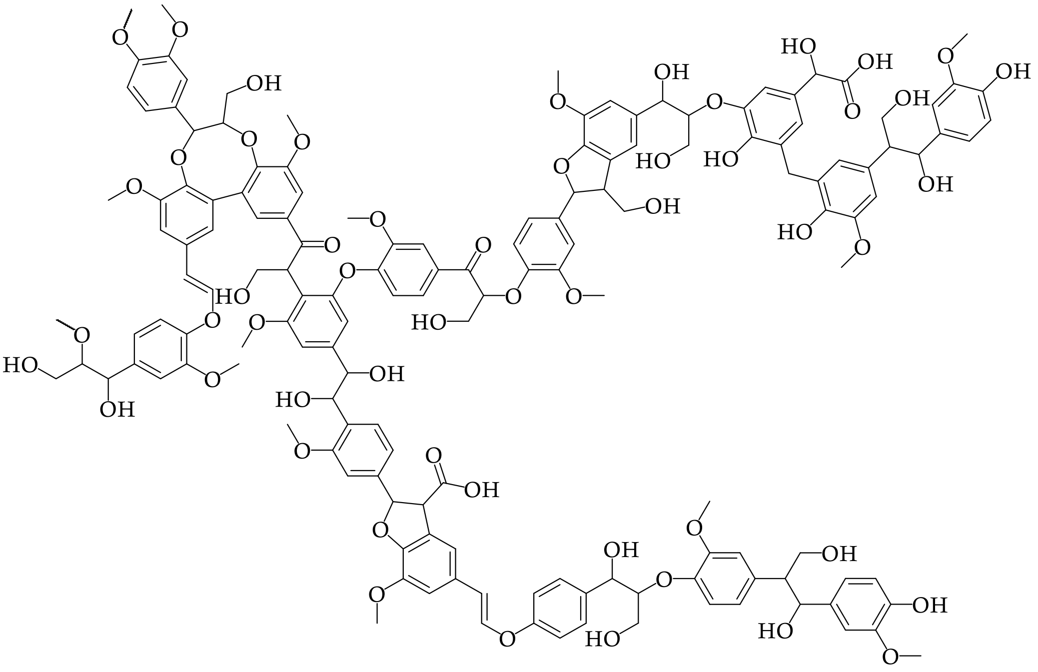

Figure 2.8.: Generic representation of a lignin structure.

Hydroxy and other chemical functional groups have played a major role in the chemical applications of lignin.[26, 27] There are a variety of chemical modifications for the utilization of lignin: low molecular weight degradation products can be also converted to epoxy resins.[28] Other examples for industrial products derived from lignin are reinforcements,[29, 30] adhesives,[31-33] adsorbents,[34-36] flocculants,[37-40] and an antioxidant additive.[41-44]

Polymers obtained through microorganisms by fermentation

In the case of polymers produced by fermentation, the action of some bacteria accumulating polymers inside their cells is exploited. These polymers have been found to be interesting for possible industrial and medical applications.[45] In Figure 2.9,a the chemical formula of polyhydroxyalkanoates (PHAs) is reported; PHAs are polymers synthesized as carbon and energy reserves[46] through fermentation by some bacteria (Figure 2.9,b).[47] Bacteria use different carbon sources to produce PHAs granules in condition of nutrient limitation (nitrogen, phosphorous or oxygen) to prevent starvation and ensuring the cells growth.

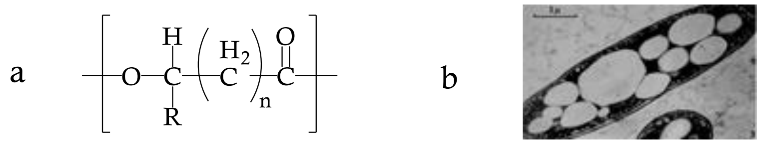

Figure 2.9.: Generic PHAs formula (a) and white PHAs granules within a bacterium (b).

In these polyesters the R group is an alkyl group with a number of carbon atoms ranging from one to fifteen, it can be branched or linear and it can contain various kinds of substituents; PHAs are completely biodegradable, inert, non-toxic and stable to air. Both thermoplastic and elastomeric PHAs are reported in literature.[47]

PHAs are fully bio-based polymers that are also biodegradable in almost all environments including soil and sea water.[48]

In the past, the applications of these polyesters were essentially related to the packaging sector: they were used, for example, for the production of flacons for cosmetics. More recently, because of their high biocompatibility, more interest has been developed towards medical applications; they are therefore used as materials for cardiovascular stents, for replacing tissues, for sutures or for drug delivery systems.[49]

A noteworthy example is given by PHB (poly (R) -3-hydroxybutyrate), wherein the alkyl group R is a methyl group and n = 1.[50] It is the first PHA discovered and it is the most commonly used. PHB is a semicrystalline isotactic stereo regular polymer with 100% R configuration that allows a high level of degradability.[51] Isostatic PHB displays a number of properties comparable to petroleum-based polymers (e.g. polypropylene) such as high melting temperature (175°C) and relatively high tensile strength (30–35 MPa).[52] However, pure PHB has had only limited use mainly because of its intrinsic brittleness and narrow processing window. For such reasons, PHB is commonly blended or copolymerized with longer side chain PHAs to lead to a lower glass transition temperature (T_g) and lower crystallinity.[52]

Synthetic polymers from monomers deriving from natural resources

These materials are obtained through the polymerization of natural monomers or through a synthetic procedure starting from natural sources. Their final properties depend on the chemical structure of such monomers, which can be diverse. These polymers are 100% bio-based if their monomer (or monomers) totally derives (or derive) from renewable sources; whereas they are partially bio-based if both bio- and fossil-derived monomers are used in the polymerization to produce the polymer.

Drop-in bio-plastics are chemically identical to their petrochemical counterparts, but they are at least partially derived from biomass. Here we report a list of some bio-plastics obtained with the drop-in technology. Drop-in polyesters, or more generally, bio-polyesters, are later listed in a specially dedicated chapter.

Bio-based polyethylene (PE): PE (whose chemical structure is depicted in Figure 2.10,a) is one of the most widely used commodity thermoplastics, primarily for packaging purposes (plastic bags, plastic films and so on). Variants are HDPE, LLDPE, and LDPE (high density PE, linear low density PE, and low density PE, respectively). The monomer, ethylene, is commonly made from crude oil. Bio-based PE was first commercialized by Brazilian company Braskem utilizing local sugarcane-derived ethanol/ethylene as feedstock.[53] In September 2010, Braskem started commercial production of bio-based HDPE with a capacity of 200,000 tonnes/year. The material's composition and performance are comparable to those of petroleum-based PE.[53] According to ICIS,[54] the ‘‘green PE’’ has a price premium of around 15–20%, which is possible in selected markets and covers the higher cost of production compared with petrochemical-based plastics. US-based Dow Chemical and Japan's Mitsui completed a 50:50 joint venture for a sugarcane-to-PE project in Brazil. The project will be the world's largest bio-polymers investment. The plant, with capacity of 350,000 tonnes/year, will produce DOWLEX[55] PE resins.[54] The facility will supply the flexible packaging, hygiene and medical markets. The product is expected to be cost-competitive with petrochemical-derived PE as the venture will own and operate the entire value chain, from growing sugarcane to producing the bio-polymer.

Bio-based polypropylene (PP): PP (Figure 2.10,b) is the second most common commodity plastic and its industrial production from natural resources is under development, Braskem is in fact planning an ethanol-based PP, although the construction timeline is currently uncertain.[56] The capacity of the bio-PP plant is projected to be about 30,000 tonnes/year and will produce propylene from ethanol using existing technology via ethylene dimerization followed by metathesis.[56]

A major market for bio-based PP is the automotive industry, as approximately 50% of plastic in cars is PP.

Bio-based polyvinyl chloride (PVC): Company Solvay from Belgium has announced the production of 60,000 tonnes/year of bio-based ethylene for the production of PVC (Figure 2.10,c).[54]

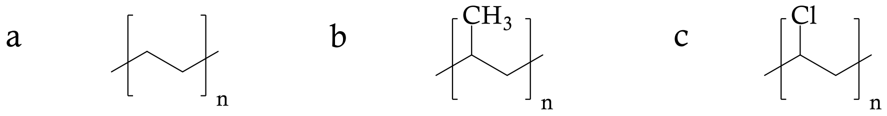

Figure 2.10.: Chemical structure of PE (a), PP (b) and PVC (c).

There are also some examples regarding the production of bio-polymers with new polymeric structures.

Bio-based polycarbonates (PCs): PCs are situated between commodity plastics and engineering plastics, as they exhibit an interesting combination of temperature resistance, impact resistance, and optical properties. Conventional polycarbonates are made from bisphenol A (BPA) and phosgene (Figure 2.11,a). An alternative polycarbonate can partly be made from isosorbide; it is derived from glucose (its hydrogenation gives sorbitol, and isosorbide is obtained by double dehydration of sorbitol). Companies Mitsubishi and Roquette have announced pilot plants for making isosorbide and incorporating it into PCs (Figure 2.11,b).[57] PCs from isosorbide and a diaryl carbonate removes the need to use toxic phosgene and controversial BPA in the process. The bio-based PC, although very promising, is seen as still far from commercialization.[54]

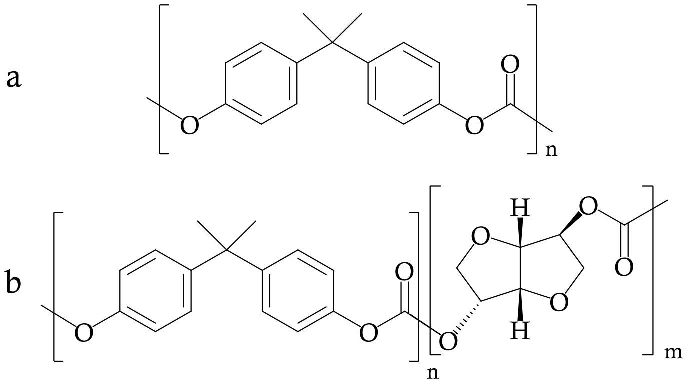

Figure 2.11.: Chemical structure of conventional PCs (a) and of PCs based on isosorbide (b).

Bio-based polyurethanes (PUs): PUs are polymers commonly formed by reacting a di- or polyisocyanate with a polyol (their general structure is reported in Figure 2.12). While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available. Natural oil polyols and sugars, which have long been raw materials for alkyd paints, are now used to make polyurethane foams for automotive applications, while thermoplastic polyurethanes from bio-based polyester polyols find use in sporting goods, particularly shoes, and medical devices.[58]

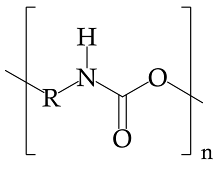

Figure 2.12.: Chemical structure PUs.

2.4.: Bio-polyesters

A huge variety of polyesters whose constituent monomers derive from natural resources can be listed. This is due to the fact that the characteristic features of this type of polymers are very common and easily obtainable in nature; for such reason, many research has been and is still being carried out in order to exploit these functionalities made available by nature in chemical synthesis. It should also be noticed that many studies focus on polyesters because the mechanical properties and the chemical-physical properties they possess make them suitable in a wide range of applications: they are used for packaging applications, in the biomedical field, for the construction of parts of cars, as a basic product for the production of paints, resins and textile fibers.

Certain monomers of natural origin are currently particularly promising for the production of bio-polyesters both from the academic research and the industrial production point of view. Because of their many applications (some of them already realized, other ones potential), tremendous efforts have been performed to ensure that these monomers can best be exploited.

2.4.1.: Polyesters-the importance of aromatic units

Polyester is the general name given to a family of polymers containing the ester group in their constitutional repeating unit. The polyester family is extremely large and exhibits an enormous variety of structures and, therefore, properties and applications. Since the pioneering experiments of Carothers in the 1930s, polyesters have found extensive use in engineering plastics, high performance materials, and recyclable and degradable polymers.

Generally speaking, they can be produced via two methods: (1) step-growth polycondensation of diols and diacid/diesters, or hydroxyacids/hydroxyesters; and (2) ring-opening polymerization of cyclic monomers (lactones, cyclic diesters and cyclic ketene acetals) and cyclic oligomers.

According to the chemical composition of the main chain, polyesters can be classified as aliphatic, semi-aromatic and aromatic.

Completely aliphatic polyesters, made from aliphatic diacid and aliphatic diol components, can be biocompatible and biodegradable; however, in general, they present low glass transition and melting temperatures, and poor hydrolytic stability that make their processing and final properties sometimes poor.

Fully aromatic polyesters have good dielectric strength, excellent mechanical properties and good heat resistance, however they have found very few commercial applications: due to their high crystallinity, they are more difficult to process.

The most interesting polyesters are the semi-aromatic ones: they are composed by aromatic reactants improving their hardness, rigidity and heat resistance, and by aliphatic acids and diols increasing their flexibility, lowering their melting point to improve their processability.

2.4.2.: Bio-polyesters: bio-PET

Polyethylene terephthalate (PET) is the most common thermoplastic polymer belonging to the polyesters family and it is used in fibers for clothing, containers for liquids and foods, thermoforming for manufacturing and in combination with glass fiber for engineering resins. Its chemical structure is reported in Figure 2.13.

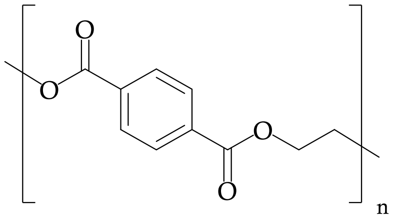

Figure 2.13.: Chemical structure of PET.

Global PET demand stood at 6,472,350 tonnes in 2000, increasing at a compound annual growth rate (CAGR) of 6.9% to reach 12,621,553 tonnes in 2010. This upward trend is expected to continue in the near future, with global PET demand tipped to reach 23,452,281 tonnes by 2020, following a forecast CAGR of 6.4%.[59] PET is produced from ethylene glycol (EG) and terephthalic acid (TPA) or dimethyl terephthalate (TPA dimethyl ester). Both processes lead to the formation of bis-2-hydroxyethyl terephthalate, which is the monomer of polyethylene terephthalate. The reaction, which provides the formation of EG during the process, is catalyzed by antimony trioxide (Sb_2O_3).[60]

Bio-based PET can contain renewable EG, produced for instance from sugarcane-derived ethylene, as being promoted by Coca-Cola under the name Plantbottle.[61, 62] In fact, while EG is largely available from biomasses, its counterpart, TPA, is currently extracted from crude oil. TPA, characterized by a production of approximately 40 million tonnes/year and with an estimated growth of 5% until 2020, is the most widely used aromatic monomer.[63] TPA is prepared on a large scale from p-xylene[64] via p-toluic acid.[65] Recently, different processes have been developed to obtain alternative synthetic routes for a sustainable TPA production. Several patents and papers have described the possibility to obtain TPA from bio-based chemicals,[66] such as isobutanol[67] or limonene (Figure 2.14.)[68] or by exploiting the Diels–Alder reaction (which will be further discussed later) allowing to obtain TPA from muconic acid and ethylene or acrylic acid[69] or p-toluic acid, the TPA precursor, from isoprene and acrylic acid,[70] sorbic acid and ethylene,[71] and sorbic acid and acrylic acid.[72]

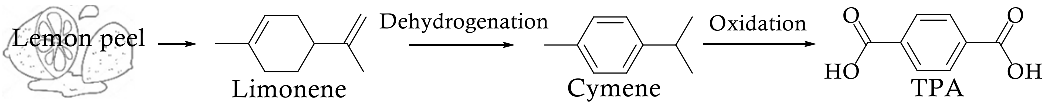

Figure 2.14.: Synthetic synthesis of TPA from limonene.

2.4.3.: Other aromatic bio-polyesters

Bio-based polyesters can be produced by conventional chemical routes from building blocks synthesized using renewable sources. Such polymers are 100% bio-based if their monomer/s totally derive/s from renewable sources, whereas they are partially bio-based if both bio- and fossil-derived monomers are used in the polymerization to produce the polymer.

Polyethylene furanoate (PEF): As already said, great efforts supported by major research centers and big companies are spent today to produce PET from renewable resources, but as well to develop analogous bio-based polymers.[73, 74] PEF is an attractive example of a fully bio-derived material with properties that make it suitable as a substitute for PET in some applications. Although it has not yet been commercialized, pilot-scale production of PEF seems to be under way.[75] It is obtained from 2,5-furandicarboxylic acid (FDCA) and EG (Figure 2.15.).

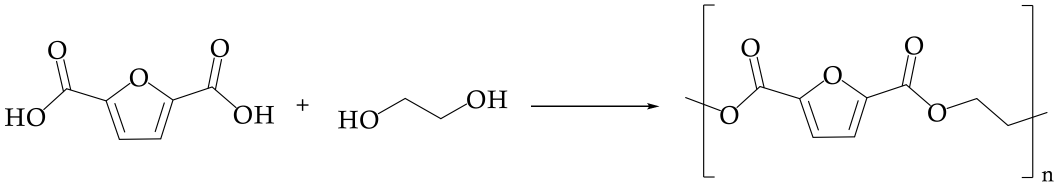

Figure 2.15.: Synthesis of PEF.

FDCA is, in turn, derived from hydroxymethyl furfural (HMF) (produced by the transformation of fructose or glucose through acidification and dehydration reactions).[76] HMF is unstable, which limits the efficiency of the process and results in side products such as levulinic acid. An improved route to HMF ethers, which are more stable and can be oxidized to FDCA, has been reported.[77] Importantly, both the polymerization and oxidation reactions are compatible with

PET manufacturing, and this potential to use existing infrastructure might accelerate the translation and uptake of PEF.[77] PEF has a higher T_g and improved barrier properties, especially with respect to oxygen permeability, than does PET.[77]

Other polymers from FDCA (PBF and PPF): Such promising monomer led to the production of different polyesters, analogues to petroleum-based terephthalates. One of these is polybutylene furanoate (PBF) (Figure 2.16,a), whose mechanical properties, thermal properties and crystal structures are similar to those of the petroleum derived polybutylene terephthalate.[78] Another example is given by polypropylene furanoate (PPF) (Figure 2.16,b); its crystal phase contributes to achieve exceptionally low oxygen transmission rates and also good impermeability to water vapors, making PPF one of the most interesting fully bio-based polyesters for packaging applications.[79]

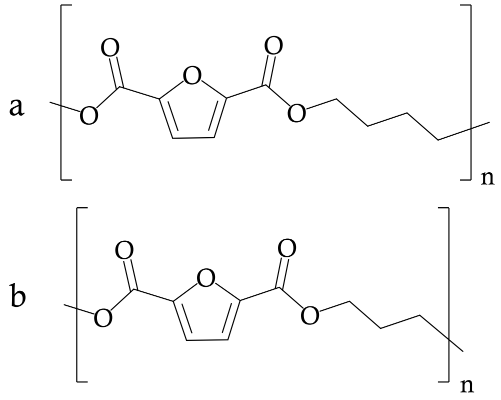

Figure 2.16.: Chemical structure of PBF (a) and PPF (b).

Polybutylene terephthalate (PBT): 1,4-butanediol produced from succinic acid is a raw material for the production of polybutylene terephthalate (PBT) (Figure 2.17,a), an engineering polymer used in automotive, electrical and electronics industries.[80]

Polytrimethylene terephthalate (PTT): PTT (Figure 2.17,b) is produced from 1,3-propanediol, which can be obtained via several renewable routes, and TPA or DMT. Similar to polyethylene terephthalate, the PTT is used to make carpet fibers.[81]

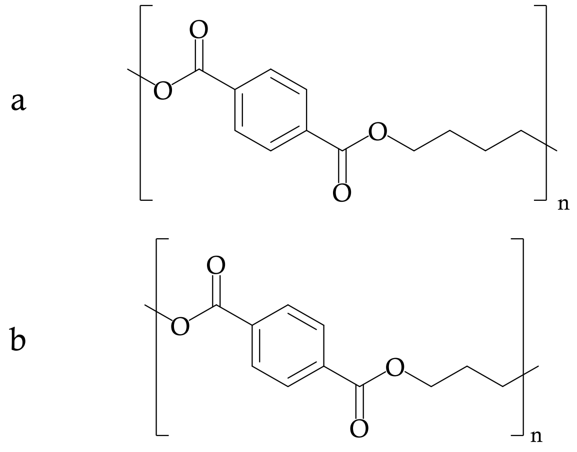

Figure 2.17.: Chemical structure of PBT (a) and PTT (b).

2.4.4.: Aliphatic bio-polyesters

Polylactid acid (PLA): PLA (whose synthetic routes are reported in Figure 2.18.) is an example of a 100% bio-based polymer since it results from the polymerization of lactic acid (2-hydroxypropionic acid), which is produced via bacterial fermentation of carbohydrates from different renewable sources like starch or sugarcane molasses.[82]

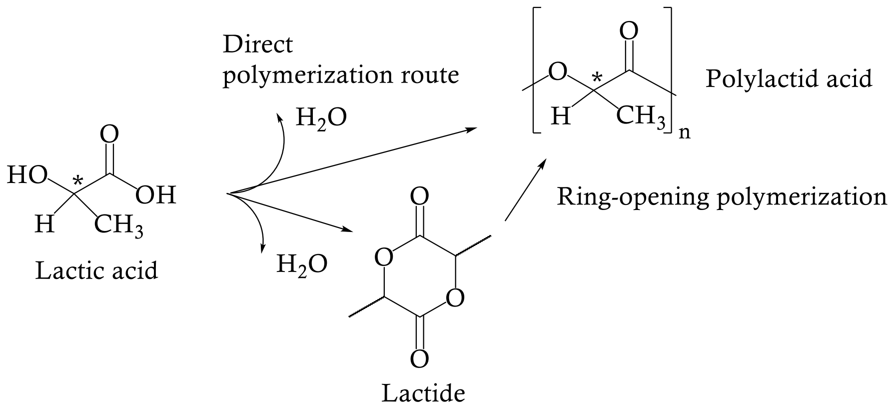

Figure 2.18.: Synthetic routes to PLA.

PLA is produced either by polycondensation of lactic acid or by ring-opening polymerization (ROP) of lactide, the cyclic dimer of lactic acid. Because of some limitations of the polycondensation process (necessity to remove the water generated, long reaction time, high temperature used), especially the fact that only PLA with low molecular weight can be produced, the ROP is the process industrially used to produce this aliphatic polyester with high molecular weight.

The starting lactide monomer is the result of the depolymerization of oligomers which are in turn produced by polycondensation of lactid acid.[83]

PLA can be processed by different routes (injection moulding, blow moulding, fiber spinning, etc.) to be converted in various forms. Currently PLA sectors of application include packaging (cups, bottles, films, trays), textiles (shirts, furniture), electronics (mobile phone housing), agriculture and cutlery.[13, 84, 85] Biodegradability and biocompatibility make PLA suitable also for biomedical applications.[86]

Today PLA is one of the most important bio-based plastics although improvements on downstream processing of lactic acid, material processing and property are still in progress.[13]

Polybutylenesuccinate (PBS): PBS (Figure 2.19.) and its copolymers represent a family of biodegradable polyesters useful in a wide range of applications.[87, 88]

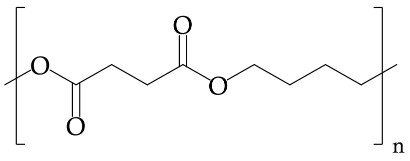

Figure 2.19.: Chemical structure of PBS.

PBS is synthetized from succinic acid and 1,4-butanediol (obtainable in turn by succinic acid). Such dicarboxilic acid traditionally produced from n-butane via chemical synthesis, can be produced via anaerobic fermentation by using various microorganisms and sources like starch and different C5 and C6 sugars.[89]

PHAs: PHAs (polyesters produced in nature by numerous microorganisms as a source of energy and as carbon store) can be either thermoplastic or elastomeric materials. They are characterized by high biodegradability and biocompatibility, making them suitable for applications in the packaging and in the medical field. Such polymers have been deeper discussed in chapter 2.3.-Polymers obtained through microorganisms by fermentation.

2.5. Furans for polymers through Diels-Alder reactions

The interest towards furan derivatives (generally named furans, F) began in the mid-nineteenth century, although it expanded only in the first half of the following century.[90, 91] From this date, a number of publications in this field can be found, particularly in pharmaceutical and fine chemistry, but also in polymers science.[91-94] Furanic heterocycles are particularly interesting due to the possibility of being produced from renewable resources, particularly from carbohydrates, mainly consisting of two types of sugars, pentoses and hexoses. Their dehydration, catalyzed by an acidic substance, leads to the formation of two major derivatives of basic chemistry, namely furfural (Fu), derived from pentoses, especially xylose, and 5-hydroxymethylfurfural (HMF) derived from hexoses, especially glucose and fructose (Figure 2.20.).[92, 95-99]

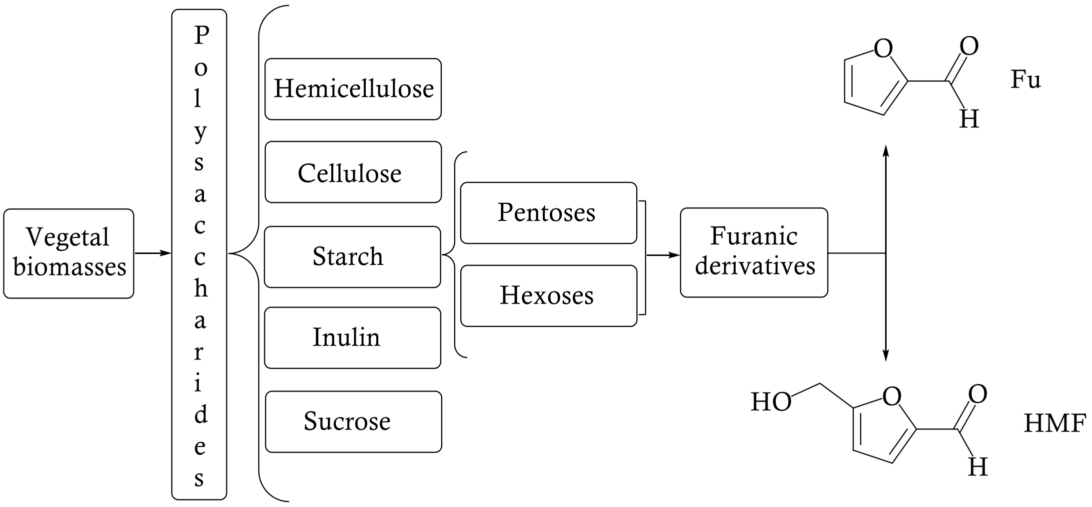

Figure 2.20.: From plant biomass to Fu and HMF.

These two products are then used as precursors of a wide range of furanic structures, including monomers available for each type of polymerization process; these bio-based monomers can virtually replace all the fossil-based counterparts, making the polymers from them derived an attractive alternative to petroleum-based materials.[92, 99-101]

Compared with the thiophene and pyrrole homologues, the furan heterocycle differs substantially in its chemical behavior, because of its pronounced dienic properties, making it and its derivatives very interesting within Diels-Alder (DA) reactions.

The DA reaction was discovered in 1928 by Otto Diels and Kurt Alder, for which work they were awarded the Nobel Prize in Chemistry in 1950.[102] Since its discovery, the reaction has received a great deal of attention, as confirmed by a great number of publications. It is one of the most relevant reactions in organic chemistry since it provides a simple, efficient and clean procedure to form cyclohexenic structures in a single stage. It is, furthermore, one of the few general methods available to produce cyclic molecules.[103] The classical DA reaction is a (4 + 2) cycloaddition between a conjugated diene in the cis form and a second component, called dienophile, to give rise to a stable cyclohexane, i.e. the DA adduct (Figure 2.21.).

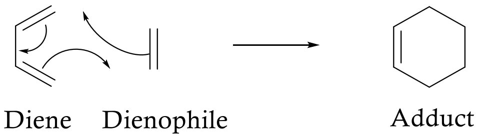

Figure 2.21.: Scheme of a generic DA and retro-DA reaction.

The mechanism of the reaction involves a single, cyclic transition state, with no intermediates generated during the course of the reaction.[104]

The DA reactions regarding F are simple, not involving secondary reactions and easily controllable by tuning temperature. The sum of this aspect together with the fact that furans are bio-based, has given a lot of attention to these synthesis reactions.[99, 105, 106]

The DA reaction can be reversible, which means that the DA adduct breaks giving rise, again, to the diene and to the dienophile. The reverse reaction is called retro-Diels-Alder (retro-DA).[107]

This process can be accomplished spontaneously by heat, through acid or base mediation,[108] or with light.[109] For example, photo-promoted retro-DA can be used in making photosensitive materials, photo patterning, photolithograph or in drug delivery.[109] However, most of retro-DA reactions require heat as a driving force for the reversion or dissociation of the DA adduct, thus generally retro-DA reactions are thermally promoted. It means that the adduct can be converted into its diene and dienophile by simply increasing the temperature. As for practical applications, this reaction is frequently used in organic chemistry, for example to protect a double bond easily subjected to chemical reactions (it can be de-protected with a simple variation of temperature).

F are often coupled with maleimides (M). Maleimide (Figure 2.22,a) is an unsaturated imide which constitutes an important building block in organic synthesis. Maleimides describe a class of derivatives of the parent maleimide where the NH group is replaced with a generic chemical group (X) (Figure 2.22,b). Such group can be an alkyl or aryl group, a small molecule (such as biotin, a fluorescent dye, an oligosaccharide a nucleic acid), a reactive group, or a synthetic polymer. In this work, when the term "maleimides" is used, we are referring to the derivatives of maleimide.

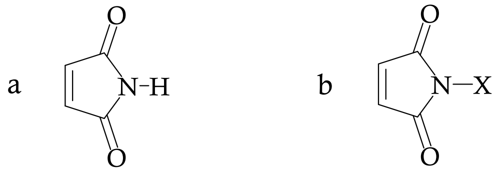

Figure 2.22.: Maleimide and its derivatives, where X is a generic chemical group.

These reactions are also thermally reversible, and low temperatures are required for both the DA and the retro-DA reactions, and guarantee as well high yields (Figure 2.23.).[91, 110, 111]

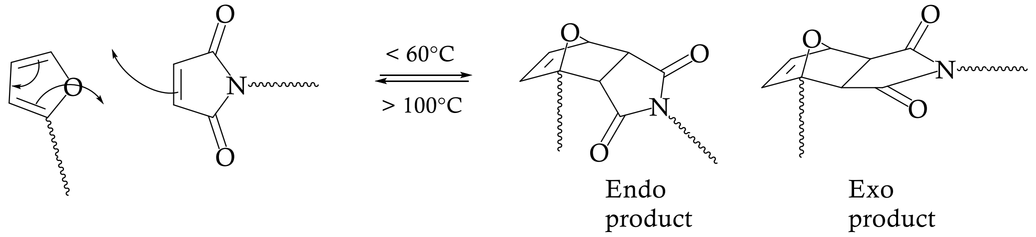

Figure 2.23.: DA reaction between a furan derivative and a maleimide.

Typically, temperatures around 65°C provide a high yield in terms of DA reaction and a negligible amount of remaining reagents. Conversely, around 100°C the adduct undergoes retro-DA leading, again, to the reagents in near-quantitative yields. Also in the specific case of F-M systems, no secondary products are observed and the possibility of repeating cycles more than once with the same results is a particularly interesting feature.[96, 101] The kinetic and thermodynamic aspects of this cycloaddition have been studied extensively, both the endo-adduct and exo-adduct being concurrently formed in a thermally reversible fashion.

The most commonly and widely used diene/dienophile couples in polymer synthesis are anthracene/maleimide, furan/maleimide and butadiene/electron deficient dithioesters.[112]

The application of F-M DA reactions to macromolecular synthesis is essentially aimed to obtain linear and cross-linked polymers.

In the vast majority of cases, the construction of linear polymers involves bifunctional monomers bearing F and M moieties on their extremities. More specifically, linear polymers can be obtained starting from AA and BB monomers, but also from AB monomers (Figure 2.24a and b, respectively).

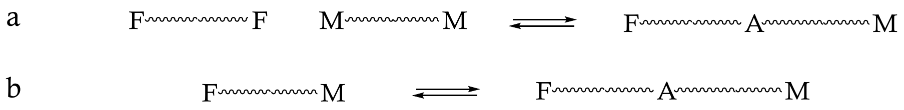

Figure 2.24.: Schematic representation of the synthesis of linear F-M DA polymers from AA and BB monomers (a) and from AB monomers (b). A strands for DA adduct.

The preparation of cross-linked polymers can take place (i) by constructing their backbone through successive DA coupling reactions involving multifunctional complementary monomers, e.g. a tri-furan derivative and a bismaleimide (Figure 2.25,a), either (ii) from linear polymers bearing pendant F and/or M groups (Figure 2.25,b).

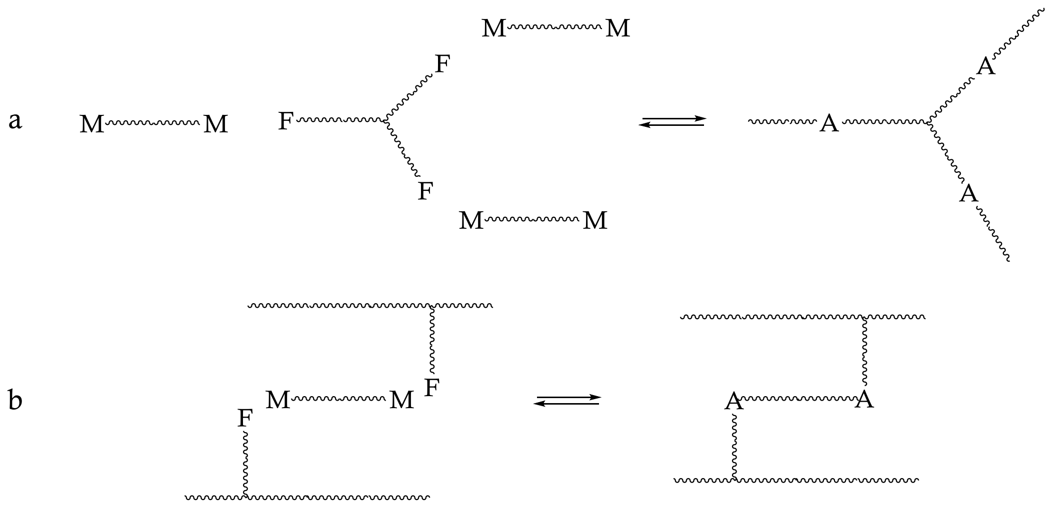

Figure 2.25.: Schematic representation of the synthesis of cross-linked F-M DA polymers through bi- and trifunctional monomers (a) and by linear polymers exhibiting pendant F groups (b).

The application of these DA strategies has also been reported for molecules and macromolecules derived from biomass, more specifically it was applied to plant-oil monomers, starch, natural rubber, cellulose and nanocellulose fibers, chitosan and gelatin.[113]

Beside these widely reported applications, thermally labile dendrimers[114] and star-shaped structures[115] based on the reversible F-M DA reaction were also synthetized.

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3. Research activities

3.1. Towards a fully bio-based PET: a sustainable route to a terephthalic acid precursor

A new synthetic pathway for the production of p-toluic acid, a terephthalic acid precursor, was developed starting from reagents derived from renewable resources. A Diels–Alder (DA) reaction between sorbic and acrylic acids was followed by a combined dehydrogenation/ decarboxylation process, providing p-toluic acid in high yields. This route allows to use milder conditions compared to other DA approaches reported in the literature, and therefore can contribute to a more sustainable terephthalic acid production.

3.1.1. Introduction

Aromatic building blocks are of great interest in polymer science owing to the better mechanical and thermal performances of the aromatic macromolecular backbones, compared to those of aliphatic structures.

Terephthalic acid (TPA) is the most widely used aromatic monomer.[1] The global production of TPA reached 57 million tonnes in 2014[2] and it is expected that it will reach about 65 million tonnes in 2018.[3]

TPA is currently prepared on a large scale, using non-renewable resources, from p-xylene[4] via p-toluic acid (Figure 3.1.1.).[5]

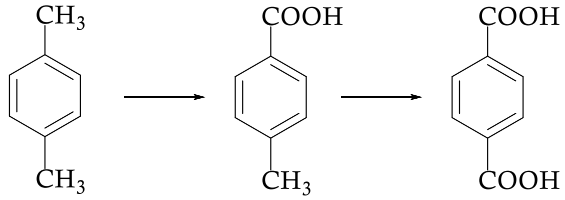

Figure 3.1.1.: Industrial synthesis of TPA from p-xylene (from petroleum), through p-toluic acid.

Some works[2] report the synthesis of p-xylene from bio-ethylene, 5-hydroxymethylfurfural (HMF) and isobutanol, but these synthetic routes currently do not find any industrial application, therefore p-toluic acid is produced on a large scale by exploiting catalytically reformed naphtha and pyrolysis distillates.[2] Several patents and papers have described the possibility to obtain TPA from bio-based chemicals,[2] such as muconic acid,[6] limonene,[7] or isoprene.[8] In particular, the DA reaction constitutes a very promising route for the preparation of cyclic molecules (Figure 3.1.2.).

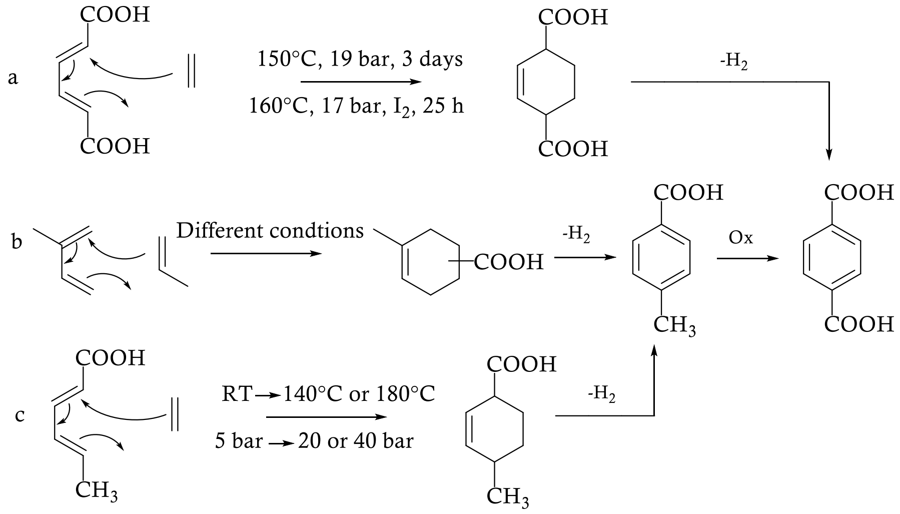

Figure 3.1.2.: TPA synthesis from muconic acid and ethylene (a),[6] isoprene and acrylic acid (b),[8] sorbic acid and ethylene (c).[9]

The Draths corporation developed a system based on the use of DA reactions of muconic acid, which can be produced by yeast fermentation of glucose, with different dienophiles such as ethylene or acrylic acid.[6] However, muconic acid can be obtained only using genetically modified strains and its synthetic process still needs to be optimized.[10] Indeed, dienes other than muconic acid can be used for the preparation of aromatic dicarboxylic acid precursors. Frost et al.[8] developed a method for the synthesis of p-toluic acid that comprises the DA reaction of isoprene with acrylic acid using different catalysts. A mixture of the meta and para isomers was thus obtained, with a 23:1 excess of the para isomer in the case of a reaction performed at room temperature with $TiCl_4$ as catalyst. Then, the two isomers must be separated before aromatization in order to obtain pure TPA. Berard et al.[9] reported the synthesis of p-toluic acid by the reaction of sorbic acid with ethylene.

Sorbic acid is a very promising bio-based DA diene, which can be (i) directly extracted from non-edible berries (e.g., those produced by Sorbus Aucuparia),[11] (ii) synthesized starting from ethanol (via acetaldehyde and sorbaldehyde),[11] or (iii) prepared from triacetic acid lactone,[12] a compound enzymatically derived from glucose.[13] Its market demand has increased consistently during the last several years, with a current production of 30,000 tonnes/year.[9] The DA reaction between sorbic acid and ethylene displays a high selectivity, but needs more than 40 hours to reach high conversions.[9] Moreover, a high pressure of ethylene (40 bar) is required and toluene has to be used as solvent, in combination with a high temperature (180°C). The second step of aromatization also needs significant improvements as a selectivity in p-toluic acid of only 41% was obtained.[9]

It follows that a process that requires milder conditions and provides higher yields with respect to the results previously reported[9] would be welcome.

Alder et al.[14] studied the reaction between sorbic acid and acrylic acid in 1950. The reaction led to two isomers consisting of six-membered aliphatic rings, which were dehydrogenated using sulfur. This aromatization process led to an isophthalic acid-like and a phthalic acid-like molecule.[14]

3.1.2. Aim of the work

The aim of this work consisted in setting up a modern adaptation of Alder's route exploiting the DA reaction between sorbic acid and acrylic acid followed by a concerted aromatization/selective decarboxylation process for the production of p-toluic acid in high yields.

More into detail, a green and sustainable DA reaction was tuned; it led to a mixture of cyclic aliphatic structures that were deeply characterized through mono and bi-dimensional ^{1}H-NMR analysis. An aromatization step characterized by a selective decarboxylation of the carboxylic groups present on the cycloadduct belonging to the DA products was set up. This procedure led, subsequently, to p-toluic acid in high yelds. This approach differs from Alder's work[14] in the final products. It must be underlined that acrylic acid is, as sorbic acid, a bio-based reagent, as it can be easily obtained from renewable resources such as lactic acid[15, 16] or 3-hydroxypropionic acid,[17] which can be prepared from glycerol.[18]

3.1.3. Results and discussion

Diels-Alder reaction

The DA reaction was carried out starting from acrylic and sorbic acids or the corresponding esters (Figure 3.1.3.).

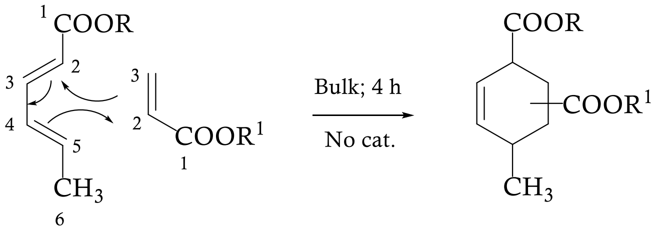

Figure 3.1.3.: Diels–Alder reaction between sorbate and acrylate.

The reaction temperature was chosen according to the type of reactant used. In particular, in the case of sorbic acid, the reaction had to be performed above its melting temperature (138°C), whereas for reactions performed using the methyl ester of acrylic acid, the temperature had to be kept below its boiling temperature (80°C). In all of these cases, an excess of the dienophile (2 equivalents with respect to sorbic acid or its ester) was used. A purification step to remove the resulting excess was not necessary, because its presence did not influence the second step of the process (aromatization). Furthermore, in an industrial process, acrylic acid or its methyl ester could be easily recovered by distillation from the reaction mixture. Table 3.1.1. gives the reaction conditions in terms of reagents, temperature and time, as well as the corresponding product yields.

R	R^1	Catalyst	T (°C)	Reaction time (h)	Conversion (%)	ortho/meta ratio
CH_3	H	/	RT	4	0	-
CH_3	H	CH_3COOH	RT	4	3	n.c
CH_3	H	$LiClO_4$	RT	4	7	n.c
CH_3	CH_3	/	RT	4	0	-
CH_3	CH_3	/	80	40	0	-
CH_3	H	/	80	4	79	64/36
CH_3	H	/	140	4	100	64/36
H	H	/	140	4	100	61/39

Table 3.1.1.: Reaction conditions, conversion, and ortho/meta ratio of the DA reactions.

The reactions between methyl sorbate and acrylic acid and between methyl sorbate and methyl acrylate were performed at room temperature. In both cases no conversion was observed. The use of 10 mol% of catalysts (Table 3.1.1.) did not significantly improve the conversion that was very limited even after 4 hours of reaction. For this reason, the reactions were performed at higher temperatures. In particular, the reaction between the two esters at the boiling temperature of methyl acrylate (80°C), using an excess of 2 equivalents of acrylate, did not show any conversion even after 40 hours. On the contrary, the reaction between methyl sorbate and acrylic acid at the same temperature afforded the cycloadduct with a 79% conversion of methyl sorbate (calculated by ^{1}H-NMR analysis on the crude product). The reaction between methyl sorbate and acrylic acid was also conducted at 140°C obtaining a complete conversion of the limiting reagent. Notably, a complete conversion into the DA adduct was also obtained using sorbic acid and acrylic acid at 140°C. These results suggested an acid-promoted mechanism because carboxylic acids appeared to be directly responsible for the activation of acrylates, increasing their dienophilic character toward cycloaddition reactions. Indeed, acidic species can lower the energy of the lowest unoccupied molecular orbital (LUMO) level of the dienophile increasing its tendency to react with the diene.[19]

DA products characterization

The DA reaction could lead to different isomers, two structural isomers (ortho and meta diacids), each of which comprised two different diastereoisomers. These isomers, resulting from the reaction between sorbic and acrylic acid, are shown in Figure 3.1.4.

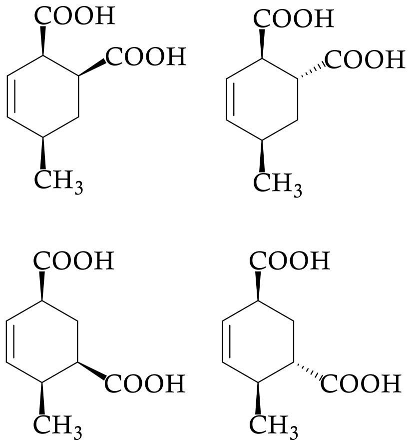

Figure 3.1.4: Structure of the isomers formed by the DA reaction of sorbic acid with acrylic acid.

^{1}H-NMR bidimensional analysis conducted on the products obtained from a selective precipitation[14] permitted to evaluate the composition of the isomeric mixture. In particular, the ortho isomers were separated from the meta isomers by exploiting their different tendencies to precipitate in acetonitrile. The first white solid, obtained from the acetonitrile solution after 3 days, was crystallized in ethyl acetate. A comparison between the ^{1}H-NMR of the crude mixture and the one of the ortho isomer obtained from the first precipitation process in acetonitrile and crystallization in ethyl acetate is reported in Figure 3.1.5.

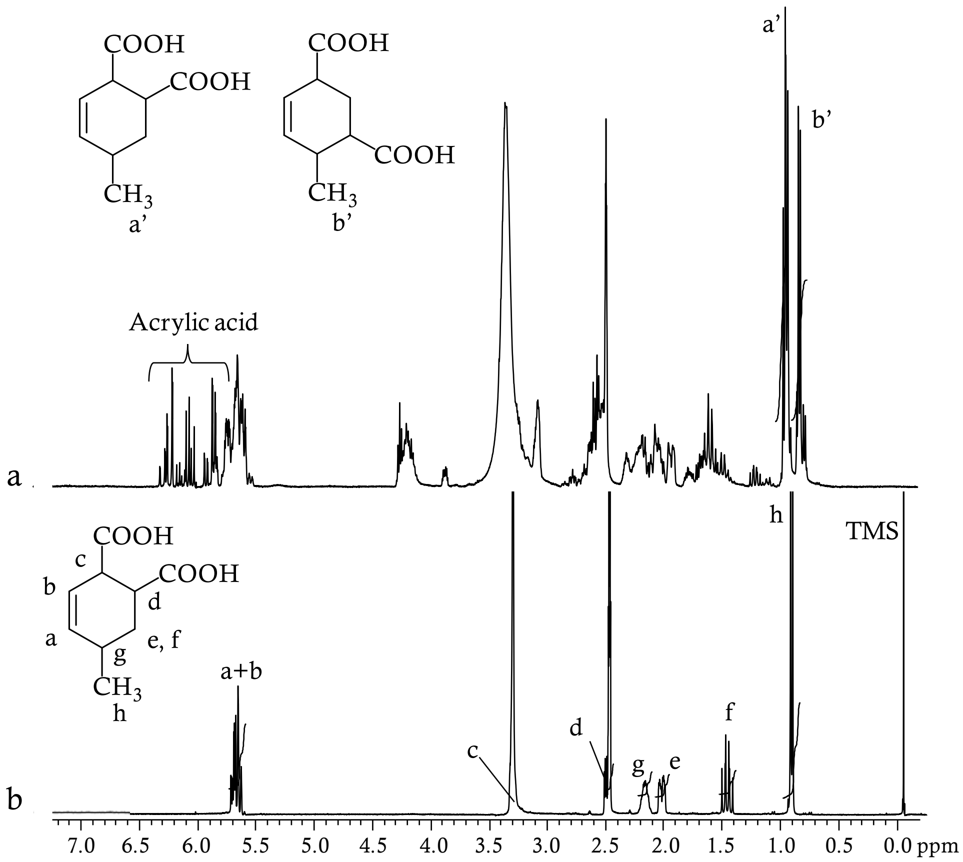

Figure 3.1.5.: ^{1}H-NMR of the crude mixture (a) and the of the ortho isomer obtained from the first precipitation process in acetonitrile and crystallization in ethyl acetate (b).

Bidimensional g-COSY ^{1}H-NMR spectroscopy showed that this product corresponded to the ortho isomer. The second white solid, precipitated at longer times, showed NMR peaks ascribable to both ortho and meta isomers. The ortho/meta ratios reported in Table 3.1.1. were determined on the basis of signals intensity of the methyl groups of two isomers ($H_{a'}$ and $H_{b'}$). The reaction mixture based on acrylic and sorbic acid had a molar ratio of ortho/meta of 61/39, whereas the reaction mixture based on acrylic acid and methyl sorbate led to an ortho/meta molar ratio of 64/36. Such preferential formation of the ortho diacids could be explained by a slightly more effective orbital overlapping of the electron-poor C3 of acrylic acid with the electron-rich C5 of sorbic derivative. NOESY experiments permitted to assign the proton signals of the regio- and stereoisomers.

Aromatization step

The crude mixture afforded after the DA reaction was used to obtain an aromatic compound. The procedure developed here (Figure 3.1.6.) involved the addition of concentrated sulfuric acid at 60°C before gradually increasing the temperature to 90°C during 20 minutes and then to 130°C for an additional 5 minutes.

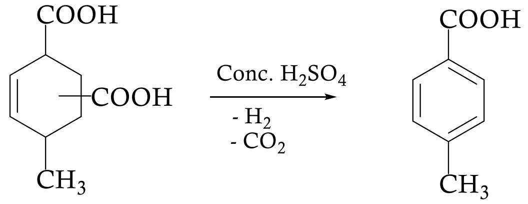

Figure 3.1.6.: Aromatization reaction of the DA adduct.

A strong effervescence was observed when the temperature reached 100°C. The reaction mixture was kept at 130°C for 15 minutes until the end of the effervescence and then quenched in ice before filtering and drying, affording p-toluic acid in a high yield (86 %), as confirmed by ^{1}H-NMR analysis. Moreover, a melting point analysis (T_m=178°C, reported 178–180°C[20]) confirmed that the final reaction mixture was composed of p-toluic acid. This result indicated that the selective decarboxylation of both carboxylic acids, at the ortho or meta position with respect to the methyl group, occurred during the aromatization process and therefore no intermediate separation or purification of the DA reaction products was needed. The ^{1}H-NMR spectrum of the synthetized p-toulic acid is reported in Figure 3.1.7.

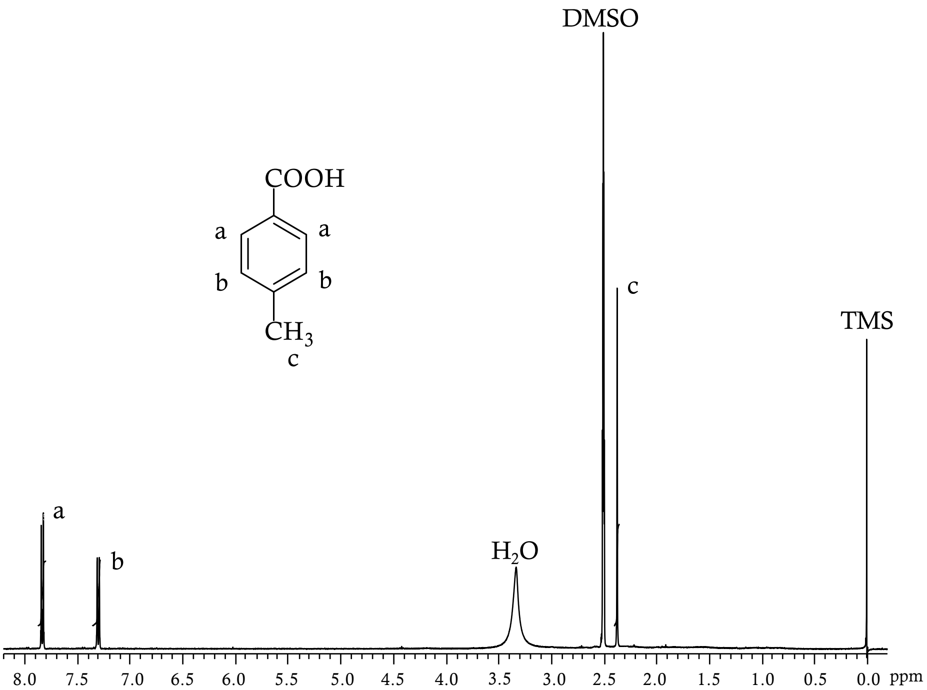

Figure 3.1.7.: ^{1}H-NMR of the p-toluic acid obtained from the crude mixture of the DA reaction after the H_2SO_4 aromatization process.

The proposed mechanism is below reported (Figure 3.1.8.).

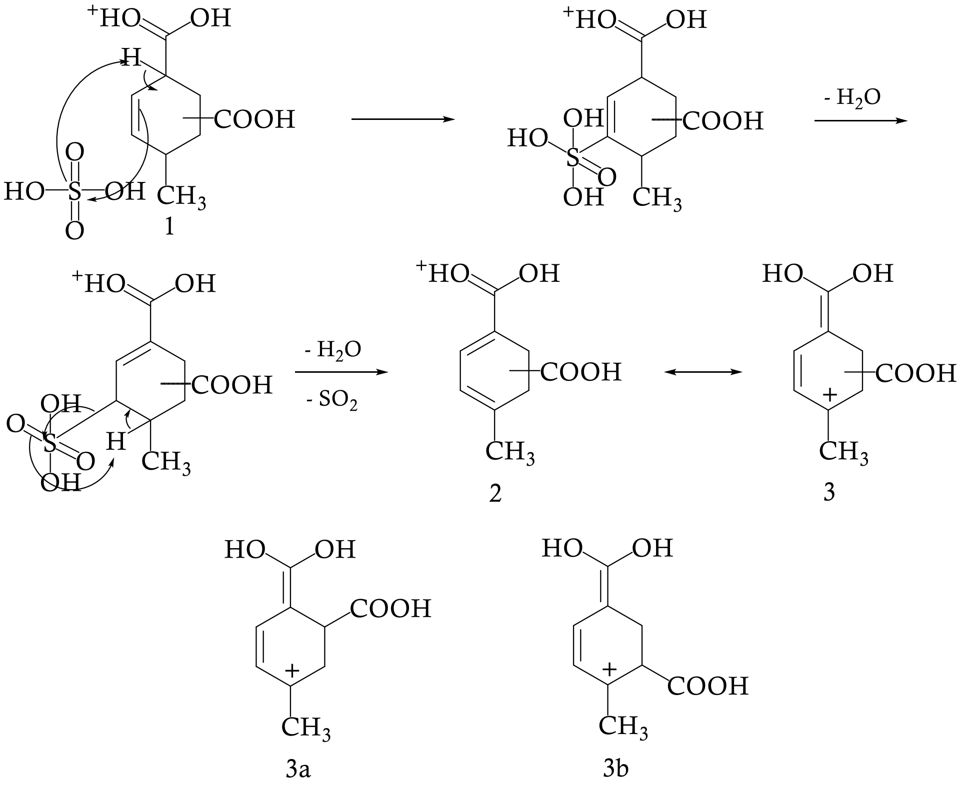

Figure 3.1.8.: Proposed oxidation mechanism.

According to the mechanism proposed by Wang and Tong,[21] the dehydroaromatization of cyclohexene dicarboxylic acid consisted in the formation of oxonium ion by H_2SO_4 protonation (1). Through the ene-reaction, the cation eliminated water and sulfurous anhydride (2). The resulting cyclohexadiene was characterized by a stable resonance structure (3) where the positive charge was located in α position with respect to the methyl group. The resonance structure of both ortho (3a) and meta (3b) isomers showed that the decarboxylation of the acidic group coming from sorbic acid could not occur because of the presence of the double bond on the aliphatic ring. Then, the repeated proton extraction due to sulfuric acid should gave rise to a simultaneous decarboxylation/aromatization process in both isomers, finally leading to p-toluic acid.

When using a less-concentrated sulfuric acid (47.6% w/w), a complete conversion was achieved in 40 minutes, whereas neither aromatizations nor other reactions were observed when using solutions with even lower concentrations of sulfuric acid (30.2% w/w and 14.2% w/w).

The approach was similar to those of Frost et al.[8] and Wang et al.[21] to produce toluic acid. Both Frost[8] and Wang[21] focused on monocarboxylic cyclohexene acids, and in both studies decarboxylation reactions were not observed during the aromatization process. Wang[21] observed a partial decarboxylation only when dealing with maleic anhydride cyclohexene derivatives. In agreement with the here-reported results, p-toluic acid was obtained in that case, also.[21] Here the process offers the advantage of combining the aromatization of the cyclohexene ring with the selective decarboxylation of the carboxylic acid group that is either at ortho or meta position with respect to the methyl group.

3.1.4. Conclusions

A green and substainable synthetic procedure for the preparation of p-toluic acid, the most-often-used precursor for the preparation of TPA, starting from renewable resources (sorbic and acrylic acids), was tuned. This route allowed milder conditions as compared to DA approaches previously reported in the literature, and therefore contributed to a more sustainable production of TPA. More into detail, the process involved two steps: (i) a DA reaction between sorbic acid and acrylic acid in mild conditions followed by (ii) a combined dehydrogenation/decarboxylation reaction that afforded p-toluic acid in high yields. The products obtained during the first step were deeply characterized through mono- and bidemensional ^{1}H-NMR analysis. Notably, these products can be also used for the production of other diacids such as isophthalic-like acids.

3.1.5. Experimental

Materials

Sorbic acid (hexa-2,4-dienoic acid), acrylic acid and methyl acrylate were supplied from Sigma-Aldrich; concentrated sulfuric acid was purchased by Carlo Erba.
All the reagents were purchased in high purity and therefore used without further purification.
Methyl sorbate was synthetized from the purchased sorbic acid.

Diels-Alder reaction

General procedure: 5.00 g (0.0446 mol) of sorbic acid and 6.1 mL (0.089 mol, 2 eq) of acrylic acid were charged into a three-necked round bottom flask equipped with a magnetic stirrer and a bubble condenser. The mixture was heated under a nitrogen atmosphere at 140°C for 4 hours. Conversion of sorbic acid: 100%.
The other reactions were carried out changing some parameters of the general procedure:

- Reaction between methyl sorbate and methyl acrylate at 80°C:
  Methyl sorbate and methyl acrylate instead of sorbic acid and acrylic acid were employed.
  1.77 g (0.0140 mol) of methyl sorbate and 2.5 mL (0.028 mol, 2 eq) of methyl acrylate were used.
  The temperature was kept at 80°C.
  No conversion of the limiting reagent was observed.
- Reaction between methyl sorbate and acrylic acid at 80°C:
  Methyl sorbate instead of sorbic acid was employed.
  9.26 g (0.0734 mol) of methyl sorbate and 10 mL (0.15 mol, 2 eq) of methyl acrylate were used.
  The temperature was kept at 80°C.
  Conversion of the limiting reagent after 4 hours: 79%.
- Reaction between methyl sorbate and acrylic acid at 140°C:
  Methyl sorbate instead of sorbic acid was employed.

6.65 g (0.0527 mol) of methyl sorbate and 7.2 mL (0.11 mol, 2 eq) of methyl acrylate were used.

Conversion of the limiting reagent after 4 hours: 100%.

Isomers isolation

The isolation of the isomers obtained from the reaction between sorbic acid and acrylic acid at 140°C was achieved by exploiting the different tendency of the ortho and meta isomers to precipitate in acetonitrile.

First, 20 mL of acetonitrile were added to the crude mixture obtained from the DA reaction. After three days the formation of a filterable white solid was observed. This latter solid was crystallized in ethyl acetate in order to improve its purity. The crystallized product consisted of the ortho isomer.

After some further days, the formation of a new white precipitate was observed from the original acetonitrile solution. This new-formed solid was filtered and analysed by NMR, which indicated the presence of both ortho and meta isomers.

Aromatization to p-toluic acid

General procedure: the reaction was carried out in the same round bottom flask in which the first reaction step took place. The flask was still equipped with a magnetic stirrer but no bubble condenser was used.

The mixture obtained from the DA reaction was progressively heated from 60°C to 130°C within about 25 minutes in air and kept at this temperature for 15 minutes. 25 mL of concentrated sulfuric acid were added dropwise, while the temperature ranged from about 60°C to approximately 90°C. Starting from about 100°C a vigorous gas formation was observed.

The reaction was carried out until the gas formation completely ceased.

The flask contents were slowly dropped in approximately 400 g of ice. While the addition occurred, the formation of a tan-colored precipitate was observed.

The precipitate was filtered using filter paper.

^{1}H-NMR analysis confirmed that the precipitate was p-toluic acid.

The yield, calculated on the vacuum-dried product, was 86%.

Other aromatization experiments were carried out according to the same general procedure; the concentration of the sulfuric acid was the only parameter that was changed. Working with 30.2% wt/wt and 14.2% wt/wt H_2SO_4 neither aromatization, nor other reactions were observed. On the other hand, a 47.6% wt/wt H_2SO_4 led to complete conversion in p-toluic acid in 40 minutes.

Chemical characterization of Diels-Alder reaction products and p-toluic acid

All the ^{1}H-NMR analyses were performed at room temperature using a Varian Mercury 400 spectrometer operating at 400 MHz. The analyses were carried out on samples dissolved in deuterated dimethyl sulfoxide when dealing with acids and with the adduct obtained from methyl sorbate and acrylic acid and in deuterated chloroform when dealing with the esters.

3.1.6. References

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3.2. Novel aromatic polymeric and copolymeric structures derived from vanillic acid

Due to the need to prepare renewable aromatic polyesters, polyethylene vanillate (PEV), a polyethylene terephthalate (PET)-like polyester, was synthetized through an innovative and sustainable route, not involving solvents and purification steps and using only bio-based reagents. Vanillic acid (VA), the starting material, can be recovered by biomass and bio-waste. The poor reactivity of the fenolic –OH group of VA has been overcome by etherification reactions with ethylene carbonate. The PEV obtained is characterized by high thermal transitions and a notable level of crystallinity, making it very close to PET. However, probably due to its low molecular weight, the material is brittle. In order to solve such problems and to exploit the aromatic structure of PEV to enhance the properties of aliphatic polyesters, new copolymers based on PEV and poly-ε-caprolactone and ricinoleic acid were prepared. The new materials are characterized by tunable thermal properties and by the presence of an ethylene-vanillate crystalline phase, according to the composition.

3.2.1. Set up of a green and sustainable synthesis of polyethylene vanillate (PEV)

3.2.1.1. Introduction

Great efforts are applied today, to produce PET from renewable resources or to develop analogous bio-based polymers.[1] Within such a framework, vanillin (4-hydroxy-3-methoxybenzaldehyde) could play a key role as it is an aromatic molecule industrially available from lignin, which is the second most abundant polymer on earth (making up roughly 25% of vascular plants) and represents an inexhaustible resource of monomers and polymers.[2, 3] Although vanillin is currently mainly produced through the petroleum-based catechol–guaiacol process by Solvay-Rhodia, significant advances in the lignin-to-vanillin process, in terms of a better knowledge of lignin depolymerization mechanisms, improving yields, separation and purification techniques, have promoted vanillin as one of the most interesting, industrially produced aromatics. Its advantages are sustainability, economic relevance, and potentiality as renewable building blocks.[4-8] For these reasons, the development of bio-based aromatic compounds, polymers and copolymers, starting from vanillin and some of its derivatives, is in progress. For example, three vanillin derivatives, in different oxidation states, were studied by Fache et al. as starting materials to obtain monomers by functionalization with epoxy, cyclic carbonates, allyl, amine, alcohol and carboxylic acid moieties.[4-6] Moreover, new vanillin-based macromolecular structures have been studied. For example, Mialon et al. used vanillin to prepare acetylferulic acid that was reduced and polymerized to lead to a vanillin-based polyester, polydihydroferulic acid, characterized by a glass transition temperature (T_g) of 73°C and a melting temperature (T_m) of 234°C. This represents a first attempt to prepare a PET mimic.[9] In a subsequent paper the same authors describe the reaction between VA and several chloroalkanols or oxirane ring-containing compounds to obtain hydroxy acids and then, through polycondensation reactions, polyalkylene vanillates.[10] A direct condensation polymerization of VA or methyl vanillate was unsuccessful, resulting in a low-molecular weight and insoluble material. PEV has been prepared through the synthetic pathway described in Figure 3.2.1.[10]

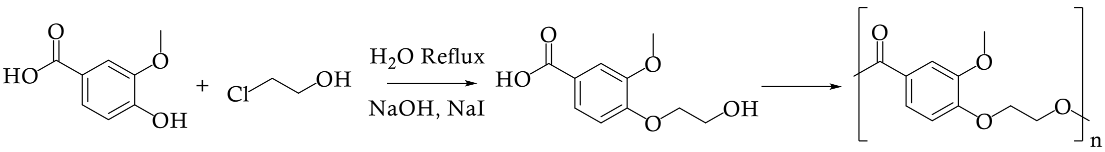

Figure 3.2.1.: Modification of VA with chloroethanol and synthesis of PEV.[10]

Due to the low reactivity of the phenolic –OH groups, it was necessary to react the phenolic functionality in order to obtain an aliphatic primary alcohol suitable for a further polyesterification reaction. Although this approach produced a partially bio-based semiaromatic material presenting a PET-like structure with high temperature thermal transitions (a T_g of 71°C and a T_m of 239°C), the process required non-sustainable reaction conditions and petroleum-based reagents, such as chloroethanol. Furthermore, a purification step, with a final yield of 79%, was necessary, and a molecular weight (M_w) of 14,500 g mol^{-1} was obtained.

PEV has already been obtained by Lange et al. from VA and ethylene oxide.[11, 12] In particular, sodium vanillate was reacted in a water solution with ethylene oxide in the presence of a sodium hydroxide.[12] However, the use of ethylene oxide required apparatus suitable for the treatment of toxic and explosive gases. Although the reaction provided complete conversion, the desired hydroxy-acid was obtained after precipitation with sulfur dioxide, followed by sublimation and crystallization with a mixture of methanol and ethyl acetate. PEV was finally obtained by reacting the corresponding hydroxyl-acid at high temperature (up to 280°C) to produce a brittle material with high melting temperature (T_m = 235°C) although no indications of the molecular weight of the polymer obtained are reported.

3.2.1.2. Aim of the work

Given the interest in finding PET-like polymers and due to some limitations in PEV preparation, the aim of the work consisted in developing a new and fully eco-friendly synthetic route to produce PEV. Bio-based ethylene carbonate (EC) was used to perform etherification reactions in order to overcome the poor reactivity of the fenolic –OH group of VA: this procedure converted the aromatic OH group into an aliphatic one, which was more suitable to take part in polycondensation reactions. A complete molecular and thermal characterization was performed on the synthetized polymer.

3.2.1.3. Results and discussion

A more sustainable synthetic route for PEV, with respect to the ones already proposed,[10-12] was set up by exploiting an eco-friendly way to improve the reactivity of the phenolic functionality, i.e. etherification reactions of phenolic compounds using K_2CO_3 as a catalyst.[13-15] By applying this strategy, a completely new sustainable synthetic pathway, which avoided solvents and purification steps and which substituted chloroethanol with bio-based EC, was developed, according to Figure 3.2.2.

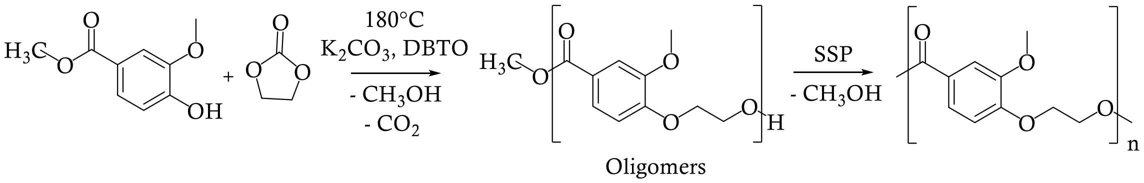

Figure 3.2.2.: A new sustainable reaction pathway for the synthesis of PEV starting from methyl vanillate and EC.

This one-pot procedure featured a first step in which methyl vanillate reacted with EC in the presence of K_2CO_3 providing methyl 4-(2-hydroxyethoxy)-3-methoxybenzoate (EV).

Methyl vanillate was chosen as a starting monomer instead of VA, because VA, under these conditions, could react with EC to produce a hydroxyl ester group, interfering with the reaction between EC and the phenolic functionality. Then, as soon as EV was formed, the transesterfication process occurred in the presence of DBTO and PEV oligomers were produced. These low molecular weight polyesters were characterized by a melting point of 264°C.

Then, since the oligomers tended to be in the solid state at the moment of their formation, for the second polycondensation step a solid state polymerization process, under nitrogen flux, was chosen. Finally, a brittle and highly crystalline material was obtained. Its ^{1}H-NMR spectrum is reported in Figure 3.2.3.

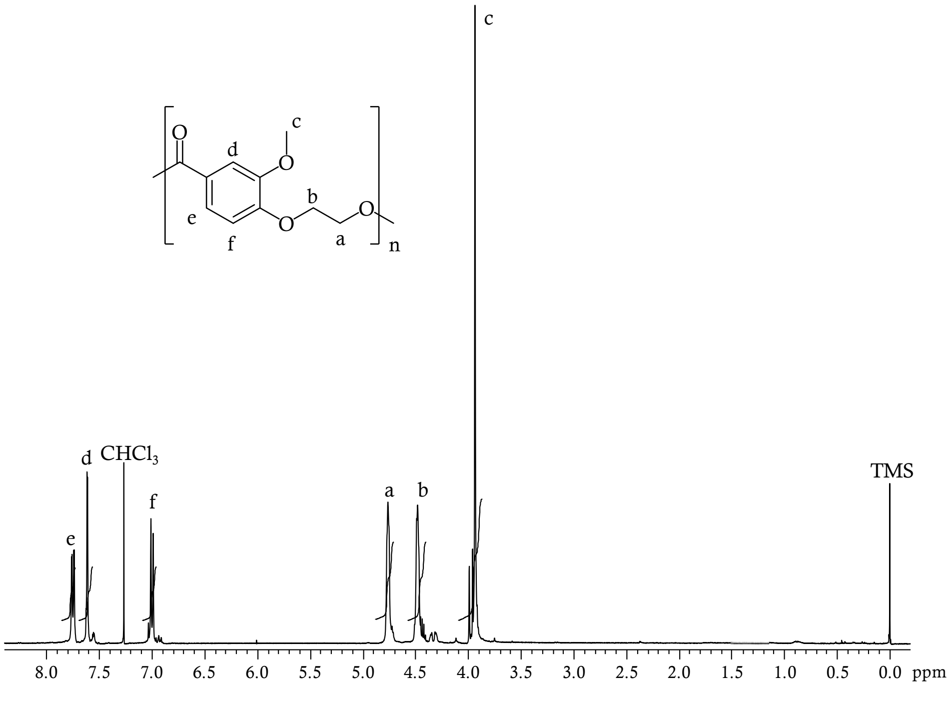

Figure 3.2.3.: ^{1}H-NMR spectrum of the synthetized polymer.

The NMR spectrum showed that the obtained molecular structure corresponded to the expected one.

Molecular weight was analyzed by ^{1}H-NMR as PEV was insoluble in the GPC solvent. It was calculated by dividing the average of the intensity of the polymer signals peaks over the average of the intensity of the corresponding terminal groups and by multiplying the result by 2 and by the molecular weight of the repeating unit.

The obtained number average molecular weight was equal to 4,700 g mol^{-1}; it indicated that EV units were characterized by a low reactivity probably due to the high viscosity of the system.

Concerning the thermal stability, the PEV T_D value, i.e. the temperature of the maxima of the differential thermogravimetric curves (measured by TGA in nitrogen at 10°C min^{-1}), corresponded to 406°C, and therefore to a remarkable stability up to high temperatures. The degradation process occurred through a single step, ending in a complete weight loss. It is noteworthy that the T_D of PEV is 30°C lower than that of PET (T_D = 436 °C),[16] probably due to the presence of methoxy[10] and ethoxy substituents in the aromatic ring. Indeed, the presence of ether bonds is generally described as weak points for the thermal stability, as observed for DEG groups in PET.[17] Moreover, the low molecular weight value of the PEV sample could contribute to the relatively lower thermal stability of PEV as compared to PET. In fact, the influence of molecular weight on the final thermal stability is known in the literature.[18]

The thermal data of PEV registered during a cooling and subsequent second heating scans through DSC analysis are in reported Table 3.2.1.

Sample	**T_c (°C)**	**ΔH_c (J g^{-1})**	**T_m (°C)**	**ΔH_m (J g^{-1})**	**T_g (°C)**
PEV	156	61	264	68	74

Table 3.2.1.: DSC characterization of PEV.

T_c (temperature of crystallization) and ΔH_c (enthalpy of crystallization) were measured during the cooling scan at 20°C min^{-1}. T_m and ΔH_m (enthalpy of melting) were measured during the 2nd heating scan at 20°C min^{-1}, while T_g was measured during the 2nd heating scan at 20°C min^{-1} after a quenching in liquid nitrogen of the molten sample.

PEV presented high values of crystallization temperature (156°C) and enthalpy (61 J g^{-1}), confirming the ability of the polymer to reach a state of high order when cooled from the melt. In the following heating scan, PEV exhibited a very high melting temperature (264°C), higher than that reported by Mialon et al. (239°C)[10] and more in agreement with Lange (254°C).[11] The T_m of PEV was very close to that observed for PET (T_m = 260°C at 20°C min^{-1} (ref. 19) and T_m = 252°C at 10°C min^{-1} (ref. 20)), showing a certain similarity in thermal behavior between these two aromatic polyesters.

However, the melting enthalpy of PEV (68 J g^{-1}) was higher than that observed for other aromatic polyesters (ΔH_m PET = 42 J g^{-1} (ref. 19) and ΔH_m PBT = 43 J g^{-1} (ref. 21)). Such a behavior could be justified by considering a higher mobility of the PEV chain around the rigid aromatic rings with respect to the terephthalic units in PET. Indeed, in terephthalic units the sp^2 hybridization of the carbon atoms of the two carbonyl groups induces coplanarity between carbonyl and phenyl groups, restricting the rotational angles about C_{phenyl}–CO to 0 and 180°.[20, 22] A similar high rigidity was not present in PEV, where one carboxylic group was substituted by an ether unit, which conferred more mobility to the chain and could impart a higher chain folding capability. This chain flexibility could probably overcome the hindrance to crystallization due to the presence of a side methoxy group.

The T_g of PEV (74°C) corresponded to the one of PET registered at 20°C min^{-1} [19] and it was very similar to the one previously reported (73°C).[9]

3.2.1.4. Conclusions

A new synthetic method to exploit building blocks obtainable from biomass and, in particular, from lignin was set up. More into detail, VA was the bio-based monomer successfully used to build a polyester, PEV, by a fully sustainable synthetic pathway. PEV was characterized by high T_g and T_m values and by a high level of crystallinity and can be considered to be a bio-based PET mimic.

3.2.2. Copolymerization of PEV with ε-polycaprolactone

3.2.2.1. Introduction

PEV was characterized by high brittleness and its molecular weight had difficulty in increasing.

On the other hand, it is in known that aliphatic polymers do not exhibit high mechanical and thermal properties. One of the most diffused aliphatic polymers is given by ε-polycaprolactone (PCL) which is prepared by ring opening polymerization of ε-caprolactone (CL). It is commercially available and non-toxic, however it is characterized by low transition temperatures that strongly limit its applications.

3.2.2.2. Aim of the work

The aim of this work consisted in improving the low molecular weight and brittleness of PEV and in increasing the bio-based content in petroleum-derived polymers, maintaining or improving specific performances, by copolymerizing it with PCL for the preparation of new random copolymers. Different combinations of rigid aromatic segments derived from VA with the flexible units of PCL were studied and their thermal properties determined in order to find out how the final material properties could be successfully tailored to match those of petroleum-based traditional aromatic polyesters.

3.2.2.3. Results and discussion

In order to improve the PEV properties and to synthetize a series of copolymers starting from it and PCL, the optimized one-pot procedure for the synthesis of PEV was modified by introducing different amounts of CL along with methyl vanillate and EC (Figure 3.2.4.).

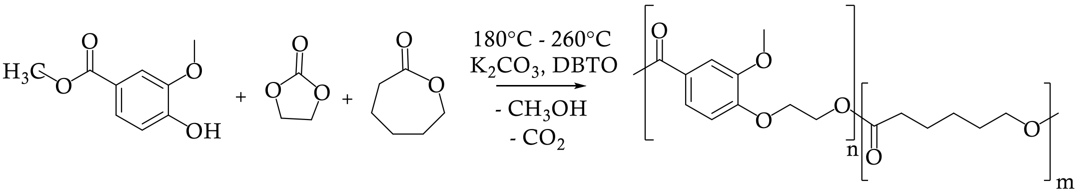

Figure 3.2.4.: Synthesis of the copolyesters containing repeating units derived from EV and CL.

In this case, thanks to the enhanced mobility of the oligomeric chains and the progressive decrease of their melting point, a typical two-step melt polycondensation could be performed.

Copolymers were prepared by using the 80/20, 50/50 and the 20/80 EV:CL ratios. They were named P(EV-*co*-CL)-X/Y, where EV indicated the units derived from methyl 4-(2-hydroxyethoxy)-3- methoxybenzoate and CL indicates the units derived from ε-caprolactone. X/Y was the molar feed ratio of methyl vanillate to ε-caprolactone.

The structural analysis of PEV and its copolymers was carried out by ^{1}H-NMR and ^{13}C-NMR. As an example, Figure 3.2.5. displays the full ^{1}H-NMR spectrum of the P(EV-*co*-CL)-20/80 specimen and the possible diads present in the P(EV-*co*-CL) copolyesters.

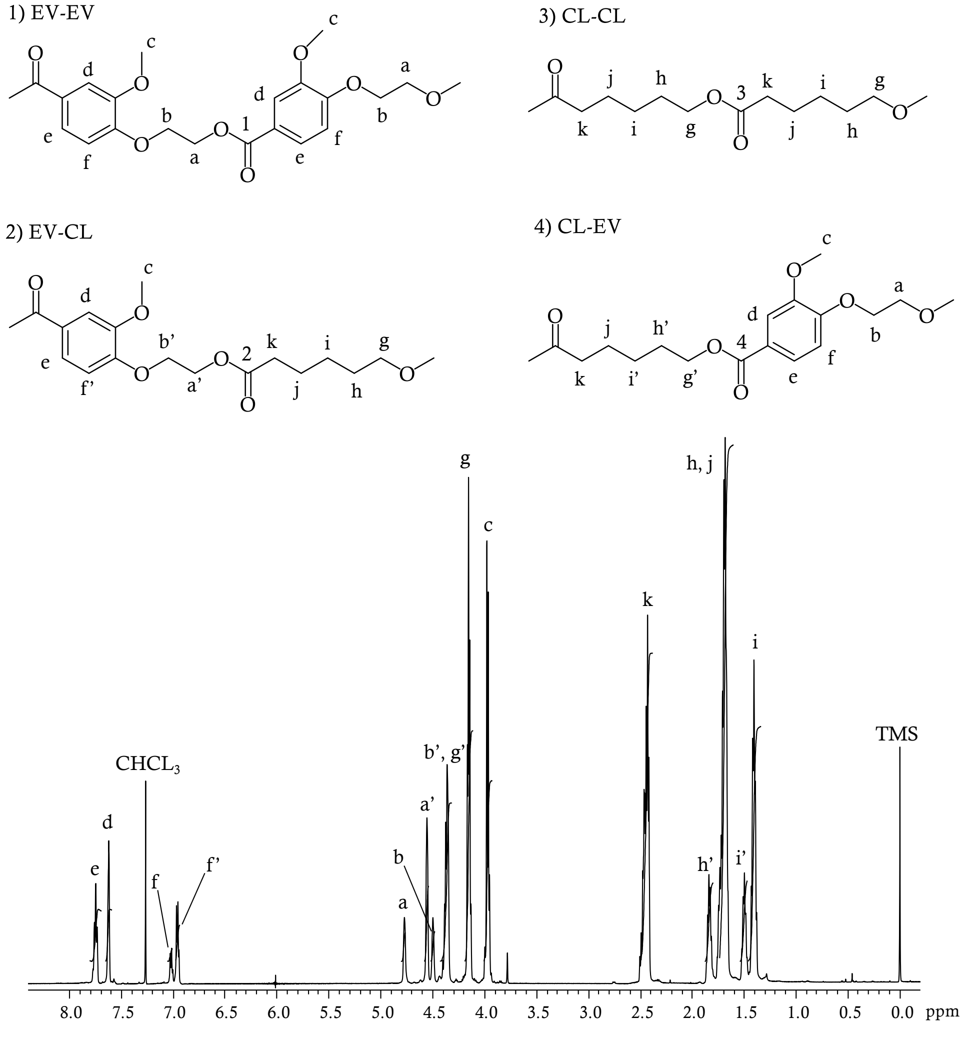

Figure 3.2.5.: ^{1}H-NMR spectrum of the P(EV-*co*-CL)-20/80 sample and the letters assigned to peaks in the spectrum.

Peak assignments, reported in Figure 3.2.5., were based on the spectra recorded for PEV and PCL homopolymers, and on the literature for copolymers.[21]

Four different diads could be identified in the copolyester chains:

1) EV–EV sequence, obtained from the reaction between carboxylic and hydroxylic groups of the EV group;
2) EV–CL sequence, obtained from the reaction between hydroxylic groups of the EV units and carboxylic groups derived from caprolactone;
3) CL–CL sequence, obtained from the reaction between the carboxylic and hydroxylic groups derived from caprolactone;
4) CL–EV sequence, obtained from the reaction between hydroxylic groups derived from caprolactone and carboxylic groups derived from EV units.

The ^{1}H-NMR spectra of the synthesized copolymers were consistent with the ones expected according to the copolymer structures.

For the aromatic H_d proton, a singlet centred at 7.62 ppm was observed: its position was independent of the neighbouring groups, EV or CL. This meant that only one signal for the H_d proton could be observed if the hydroxylic functionality of EV reacted with the carboxylic functionality of EV or CL and if the carboxylic functionality of EV reacted with the hydroxylic functionality of EV or CL. On the other hand, the signal centred at 7.76 ppm, due to the aromatic H_e proton, changed its multiplicity with respect to the signal recorded for the homopolymer, thus indicating a weak influence of the neighbouring atoms. The last aromatic H_f proton, instead, was strongly influenced by the neighbouring unit (EV or CL) and two multiplets could be observed at 7.02 (proton H_f) and 6.95 ppm (proton $H_{f'}$), according to sequences at the diad level (EV–EV and EV–CL, respectively). The aliphatic H_a proton (in α to the ester oxygen atom) and H_b proton (linked to the ether group) were also influenced by the neighboring units, according to the EV–EV and EV–CL diads in Figure 3.2.5. (H_a centered at 4.77 ppm, $H_{a'}$ at 4.55 ppm, H_b at 4.49 ppm and $H_{b'}$ at about 4.36 ppm). Only the signal of H_a was well resolved, while the $H_{a'}$, H_b and $H_{b'}$ signals partially overlapped with other signals. The H_g (4.14 ppm), H_h and H_j (1.63–1.77 ppm), H_i (1.40 ppm) and H_k (2.46 ppm) protons, due to the CL-unit, were observed in the spectrum, according to the signals recorded for the PCL sample. CL-unit protons in α, β, and γ to the ester oxygen atom (H_g, H_h and H_i) were all influenced by the neighboring unit (CL or EV) (see CL–CL and CL–EV diads in Figure 3.2.5.) and the signals due to $H_{g'}$ (at about

4.36 ppm), $H_{h'}$ (1.83 ppm) and $H_{i'}$ (1.50 ppm) could also be observed in the spectrum, even if the signal of the $H_{g'}$ proton overlapped with that of the $H_{b'}$ proton. The H_k and H_j protons, in α and β to the ester carbonyl moiety in the CL unit, appeared to be weakly influenced by whether the neighbouring group is a CL or EV-unit and only a change in the multiplicity of the signals was observed.

To determine the molar fractions of copolymer units, the signals at 7.63 ppm (proton H_d of EV-unit) and at 2.46 ppm (proton H_k of CL-unit) were chosen, because independently of the molar composition such signals maintained their chemical shifts and did not show any splitting, thus assuring a minimal error in the integration evaluation. Therefore, the molar fractions of EV (F_{EV}) and CL (F_{CL}) units were calculated by means of the equations:

$$F_{EV} = \frac{I_d}{I_d + \frac{I_k}{2}} \qquad (1)$$

$$F_{CL} = \frac{\frac{I_k}{2}}{I_d + \frac{I_k}{2}} = 1 - F_{EV} \qquad (2)$$

where I is the integration intensity of signals.

Values of F_{EV} and F_{CL} are listed in Table 3.2.2., together with molecular weights from the bulk condensation polymerization of PEV, PCL and their copolyesters.

Sample	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**	**F_{EV}**	**F_{CL}**
PEV	4.7	-	1	-
P(EV-*co*-CL)-80/20	2.7	7.2	0.81	0.94
P(EV-*co*-CL)-50/50	6.0	18.0	0.56	0.44
P(EV-*co*-CL)-20/80	8.0	24.0	0.26	0.74
PCL	25.0	60.0	-	1

Table 3.3.2.: Molecular weights and molar fractions (F) of EV and CL units of the PEV and PCL homopolymers and P(EV-*co*-CL) copolyesters.

All molecular weights, except for PEV homopolymer, were determined by GPC. F_{EV} and F_{CL} were determined by equations 1 and 2.

Molecular weights tended to increase with the amount of CL units, indicating that EV units were characterized by a lower reactivity probably due to the high viscosity of the system. Comonomer molar feed ratios (X/Y) and the corresponding copolyester compositions were in good agreement, even if CL units were in general in lower amount with respect to the feed quantity, probably due to the higher volatility of CL with respect to EV.

The analysis of the chemical sequences present in the samples was carried out by using the signals due to H_f and $H_{f'}$ protons for the EV-unit and due to H_i and $H_{i'}$ protons for the CL-unit, whose intensities depended on the neighboring groups.

By applying the method developed by Devaux,[23] the molar fractions of diads, the average sequence lengths of EV–EV and CL–CL diads (L_{EV-EV} and L_{CL-CL}) and the randomness degree (B) could be calculated on the basis of the integration intensities of the corresponding ^{1}H-NMR signals by means of equations 3, 4, 5 and 6, which are following reported.

$$F_{EV-EV} = \frac{I_f}{I_f + I_{f'}} \qquad (3)$$

$$F_{EV-CL} = \frac{I_{f'}}{I_f + I_{f'}} \qquad (4)$$

$$F_{CL-CL} = \frac{I_i}{I_i + I_{i'}} \qquad (5)$$

$$F_{CL-EV} = \frac{I_{i'}}{I_i + I_{i'}} \qquad (6)$$

Table 3.2.3. lists the average sequence lengths and B values obtained for the P(EV-*co*-CL) copolyesters.

Sample	L_{EV-EV}	L_{CL-CL}	B
P(EV-*co*-CL)-80/20	4.1	1.5	0.91
P(EV-*co*-CL)-50/50	2.2	1.7	1.04
P(EV-*co*-CL)-20/80	1.4	3.7	0.98

Table 3.2.3.: Average block lengths (L) and randomness degree (B) of P(EV-*co*-CL) copolyesters determined by ^{1}H-NMR.

The data showed that the sequence distribution of copolymers was best approximated as random and the sequence lengths varied following the random copolymer model as would be expected with changes in composition.

The structure of copolyesters was also studied by means of ^{13}C-NMR analysis. As an example, Figure 3.2.6. displays the ^{13}C-NMR carbonyl region (165–180 ppm range) of the P(EV-*co*-CL)-80/20 specimen used for the calculation of average molar fractions, block lengths and randomness degree.

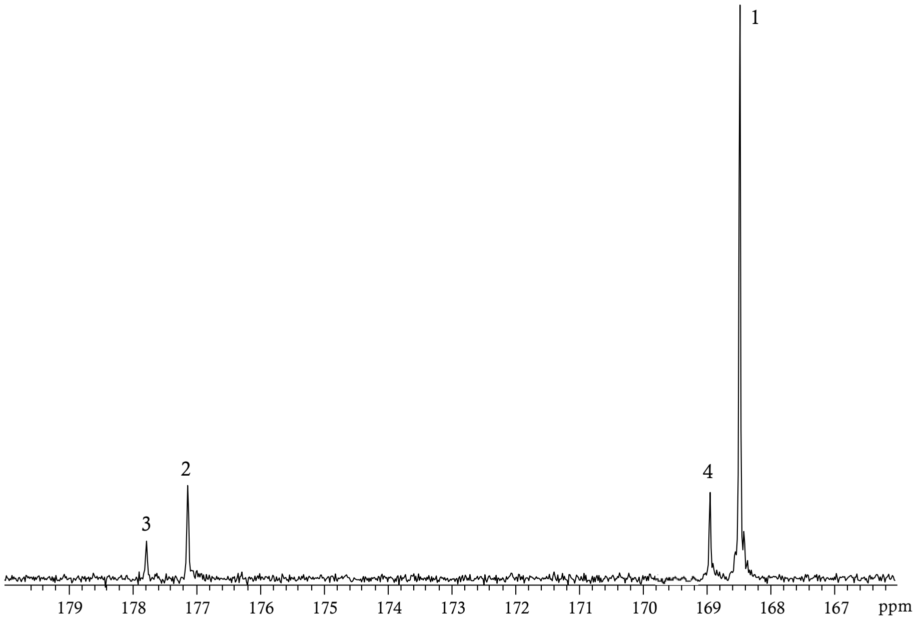

Figure 3.2.6.: ^{13}C-NMR spectrum of copolymer poly(ethylene vanillate-*co*-caprolactone) P(EV-*co*-CL)-80/20.

Four peaks due to the different carbonyl groups could be detected in this region. Peaks assignments referred those of the diads reported in Figure 3.2.5. Based on the ^{13}C-NMR spectra of the homopolymers, the following peak assignments could be made: C_1 at 168.7 ppm (EV–EV diad), C_4 at 169.1 ppm (EV–CL diad), C_2 at 177.4 ppm (CL–EV diad) and C_3 at 177.9 ppm (CL–CL diad).

As reported in the literature,[24-26] the analysis of the chemical sequences present in the samples could be performed by using the signals due to C_1–C_4 carbonyl groups. The results of the molar fractions, the average block lengths and randomness degree, calculated from the intensities of the corresponding ^{13}C-NMR signals and using Devaux's approach,[23] are listed in Table 3.2.4.

Sample	**L_{EV-EV}**	**L_{CL-CL}**	**B**
P(EV-*co*-CL)-80/20	6.7	1.4	0.86
P(EV-*co*-CL)-50/50	1.8	1.8	1.11
P(EV-*co*-CL)-20/80	1.4	4.1	0.96

Table 3.2.4.: Average block lengths (L) and randomness degree (B) of P(EV-*co*-CL) copolyesters determined by ^{13}C-NMR.

The equations used for the quantitative determination of these parameters and the ones for the determination of the molar fraction of the diads (7, 8, 9, 10, 11, 12, 13) are below reported.

$$F_{EV-EV} = \frac{I_1}{I_1 + I_2} \qquad (7)$$

$$F_{EV-CL} = \frac{I_2}{I_1 + I_2} \qquad (8)$$

$$F_{CL-CL} = \frac{I_3}{I_3 + I_4} \qquad (9)$$

$$F_{CL-EV} = \frac{I_4}{I_3 + I_4} \qquad (10)$$

$$L_{EV-EV} = \frac{F_{EV-EV}}{F_{EV-CL}} + 1 \qquad (11)$$

$$L_{CL-CL} = \frac{F_{CL-CL}}{F_{CL-EV}} + 1 \qquad (12)$$

$$B = \frac{1}{L_{EV-EV}} + \frac{1}{L_{CL-CL}} \qquad (13)$$

The data obtained by ^{1}H and ^{13}C-NMR analyses were in perfect agreement.

Concerning the thermal properties of the synthetized homopolymers and copolymers, Figure 3.2.7. shows their DSC cooling and subsequent second heating scans, while Table 3.2.5. reports the corresponding thermal data and their T_D values, corresponding to the temperatures of the maxima of the differential thermogravimetric curves.

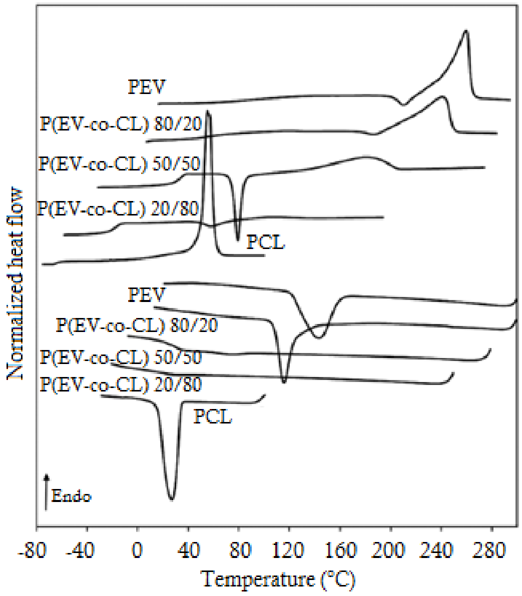

Figure 3.2.7.: DSC scans (20 °C min^{-1}) of PEV, PCL and P(EV-*co*-CL) copolyesters.

Sample	**T_D (°C)**	**T_c (°C)**	**ΔH_c (J g^{-1})**	**T_{cc} (°C)**	**ΔH_{cc} (J g^{-1})**	**T_m (°C)**	**ΔH_m (J g^{-1})**	**T_g (°C)**
PEV	406	156	61	-	-	264	68	74
P(EV-*co*-CL)-80/20	402	116	44	-	-	241	52	59
P(EV-*co*-CL)-50/50	403	74	2.4	79	23	181	32	35
P(EV-*co*-CL)-20/80	409	-	-	58	4	104	6	-18
PCL	411	27	66	-	-	55	66	-63

Table 3.2.5.: TGA and DSC characterization of P(EV-*co*-CL) copolyesters and the corresponding homopolymers.

T_D was measured by TGA in nitrogen at 10°C min^{-1}. T_c (temperature of crystallization) and ΔH_c (enthalpy of crystallization) were measured during the cooling scan at 20°C min^{-1}. T_{cc} (cold crystallization temperature), ΔH_{cc} (cold crystallization enthalpy), T_m and ΔH_m (ethalpy of fusion) were measured during the 2nd heating scan at 20°C min^{-1}, while T_g was measured during the 2nd heating scan at 20°C min^{-1} after a quenching in liquid nitrogen of the molten sample.

As far as the PCL sample is concerned, it presented a notably high T_D value, as confirmed by the literature where it is reported that PCL has a higher thermal stability compared to other polyhydroxy acids, such as polyglycolic acid and polylactic acid,[27] or aliphatic polyesters, such as polybutylene succinate.[28] Data reported in Table 3.2.5. for the copolymers showed that the thermal stability of PCL decreased slightly with the insertion of EV units, according to the composition. The values observed for 80/20 and 50/50 samples could suffer from low molecular weight. In conclusion, copolymers derived from VA and PCL were characterized by good thermal stability, which is a very important parameter for their processability.

From the observation of the cooling thermograms, it was evident that PEV and PCL and 80/20 and 50/50 copolymers showed a crystallization process, with different characteristics according to the composition. In fact, T_c and ΔH_c values varied over a wide range with copolyester composition.

High crystallinity was evident both for PEV and PCL, but in this case T_c was very low (27°C).

The 80/20 copolymer maintained the crystallizability of the PEV homopolymer, the 50/50 sample showed a very low value of crystallization enthalpy, suggesting a significant reduction in the ability to crystallize, and the sample 20/80 did not crystallize from the melt under the conditions used.

In the following heating scan, all the samples presented a melting transition, even if the processes were very different depending on the composition. PEV exhibited a very high melting temperature (264°C), the 80/20 sample maintained a very high melting temperature (241°C) and enthalpy (52 J g^{-1}), in agreement with similar results previously obtained on aliphatic–aromatic random copolyesters.[21, 29] The presence of CL units did not affect its amount of crystallinity, but only caused a poorer level of crystal perfection, as indicated by the lower T_m value with respect to PEV. The P(EV-*co*-CL)-50/50 copolymer mainly crystallized during the heating scan with a sharp crystallization peak at 79°C: in this case the average sequence of two EV units in the macro macromolecular structure hindered an important crystallization process during the cooling step from the melt, but promoted a fast formation of crystals during the subsequent heating scan. The melting process occurred with a broad endothermal process, indicating a low level of crystal perfection, due to the high percentage of CL units. The high T_m value of 181°C suggested that the crystal phase present was that of PEV; the amount of crystalline phase was comparable with that of the PEV homopolymer, by considering the copolymer composition. These results confirmed the high tendency of EV units to crystallize, although the copolymer was rich in CL units (50 mol%) and the average EV blocks were formed by only two sequences. Analogous aliphatic–aromatic systems, based on PBT,[21, 29] differed in crystallization behavior and presented poorly organized crystalline phases when the two comonomeric units were present in similar amounts.

The copolyester rich in CL units, the P(EV-*co*-CL)-20/80 sample, showed a weak crystallization process at 58°C, during the second heating scan. This was a temperature higher than the T_m of PCL. Therefore, a crystalline EV phase tended to be formed even when EV sequences were very short. The subsequent melting process, at about 104°C, was very difficult to detect for the wide temperature range in which it occurs. It is notable that a crystalline phase of CL was not evident, although the CL sequences in this material were significantly long ($L_{CL\text{–}CL}$ was equal to about 4, Table 3.2.3.). Considering that in a copolymer the crystallization process should have taken place at temperatures lower than that of the corresponding homopolymer, due to the presence of co-units that hindered the rearrangement towards an ordered lattice, CL crystals should grow at very low temperatures, lower than 27°C (T_c of PCL), during the cooling scan from the melt. Under such conditions, the 20/80 copolymer could have been characterized by a very low chain mobility, which prevented PCL crystal phase formation.

Further details of trends in T_m and ΔH_m as a function of the copolyester composition are given in Figure 3.2.8.

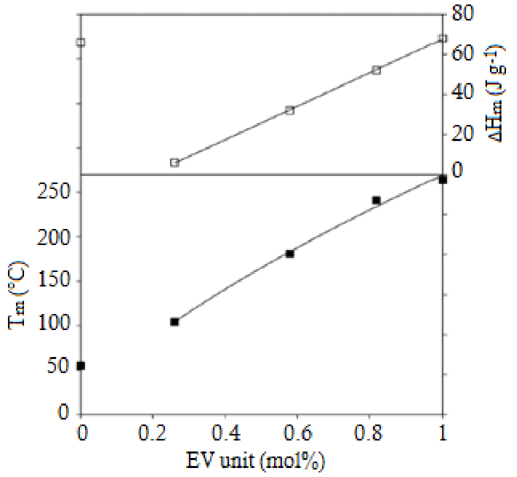

Figure 3.2.8.: Trends of melting enthalpy (ΔH_m) and melting temperature (T_m) vs. EV mol% for P(EV-*co*-CL) copolyesters.

It is interesting to note that the melting enthalpy and the melting temperature decreased linearly with the composition up to the 20/80 sample.

With regard to the amorphous phase, only one glass transition was observed for the whole range of compositions, for both semicrystalline and fully amorphous samples, obtained after quenching from the melt. In particular, Figure 3.2.9. shows the variation of the T_g of the amorphous copolymers versus composition, which fits well the Fox equation.[30]

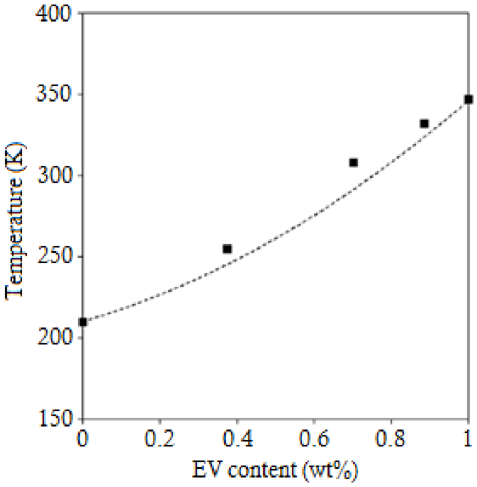

Figure 3.2.9.: Dependence of the T_g of the amorphous samples (measured at 20°C min^{-1} after quenching from the melt) on their composition from DSC. The dotted line was calculated using the Fox equation.

Therefore, it is reasonable to claim that the amorphous phase was homogeneous and this behaviour was surprising given the different structure of the two homopolymers. Probably, the random distribution of the comonomeric units in the chain did not allow the formation of separate domains.

3.2.2.4. Conclusions

VA was used for the preparation of new random copolyesters based on PEV and PCL, whose final properties depended on the material compositions.

3.3.1. Copolymerization of PEV with ricinoleic acid

3.2.3.1. Introduction

Plant oils are the most promising candidates as economical and renewable source of many monomers for bio-polymers production. Castor oil, derived from the beans of the castor plant, *Ricinus Communis*, of the *Euphorbiaceae* family, contains approximately 85–90 wt% of triglycerides of ricinoleic acid (RA). RA could be a precursor for the synthesis of functional materials thanks to the presence of hydroxyl and carboxyl groups, as well as a Δ9 unsaturation. The self-polycondensation of ricinoleic acid produces an amorphous polyester (PRA), presenting a remarkable biocidal activity.[31, 32] Unfortunately it is characterized by a low T_g, that strongly limits its applications. To overcome this limit, copolymerization can be the synthetic pathway that allows PRA to enhance its poor mechanical properties. To perform copolymerization PEV was used since, as already demonstrated, it is characterized by high brittleness.

3.2.3.2. Aim of the work

The aim of this work consisted in copolymerizing PRA with VA by overcoming its phenolic –OH group poor reactivity by etherification reactions with bio-based EC. This procedure allowed to improve the PRA properties by keeping at the same time its remarkable biocidal activity by copolymerization. It has already been observed that PRA maintains its antimicrobial activity when copolymerized with PBS.[31]

Different ratios of aromatic rigid units from VA and soft units derived from RA were combined with the aim of finding a correlation between structure and final properties.

3.2.3.3. Results and discussion

The preparation of PEV and PRA copolymers was carried out considering the already optimized one-pot synthesis of PEV, and therefore this procedure was modified by introducing, besides VA and EC, different amounts of RA (Figure 3.2.10.).

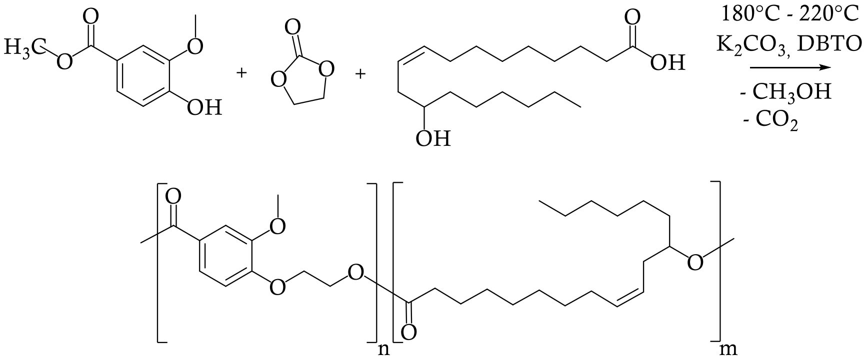

Figure 3.2.10.: Synthesis of the copolyesters containing repeating units derived from EV and RA.

The prepared copolymers, resulting from the 70/30, 50/50 and 15/85 EV:RA ratios, were named P(EV-*co*-RA)-X/Y, where EV indicated the units derived from methyl 4-(2-hydroxyethoxy)-3-methoxybenzoate and RA indicated the units derived from ricinoleic acid. X/Y was the molar feed ratio of methyl vanillate to ricinoleic acid. PRA homopolymer was previously synthetized in our laboratories by a procedure described in ref. 31.

All of these products were analyzed through ^{1}H-NMR and ^{13}C-NMR analysis. Figure 3.2.11. reports all the units present in the P(EV-*co*-RA) systems and the ^{1}H-NMR spectrum of the P(EV-*co*-RA)-50/50 specimen.

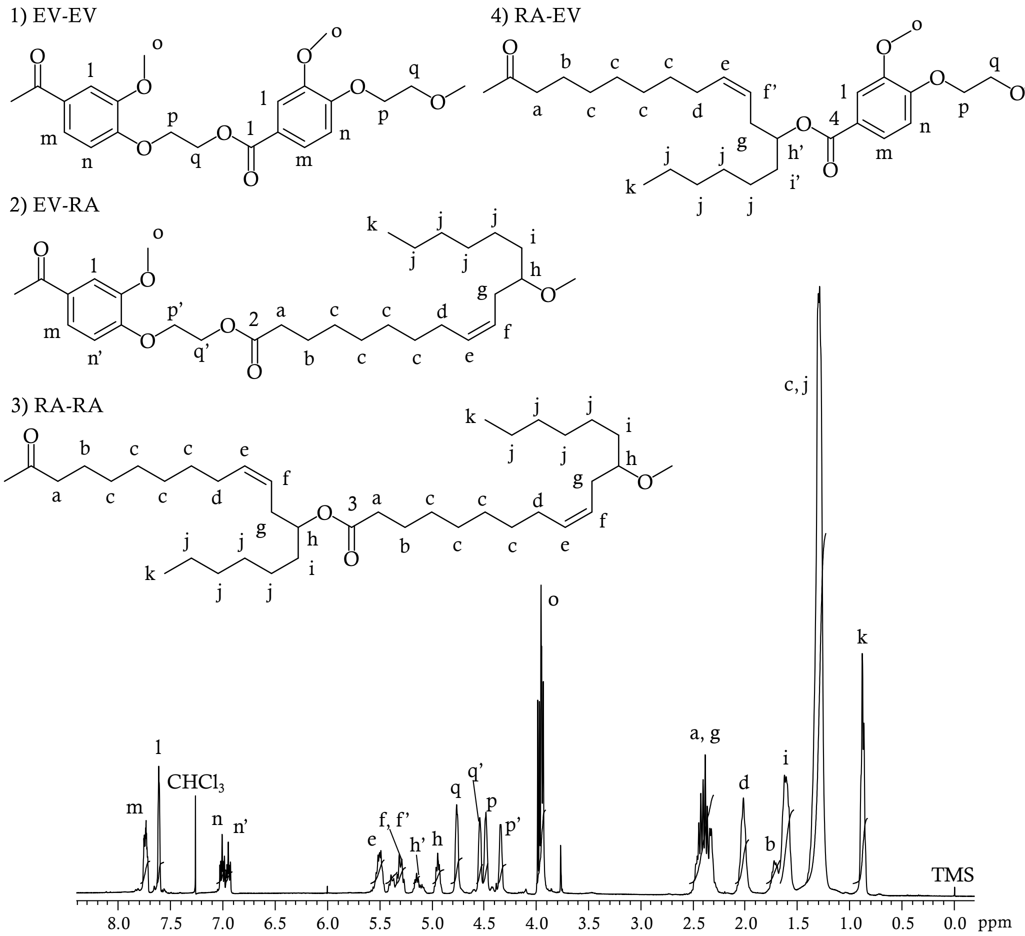

Figure 3.2.11.: ^{1}H-NMR spectrum of the P(EV-*co*-RA)-50/50 sample and all the possible diads.

Peaks assignments, reported in Figure 3.2.11., were based on the spectra recorded for PEV (Figure 3.2.3.) and PRA homopolymers.[31]

Four different diads could be identified in the copolyester chains:

1) EV–EV sequence, obtained from the reaction between carboxylic and hydroxylic groups of the EV group;
2) EV–RA sequence, obtained from the reaction between hydroxylic groups of the EV units and carboxylic groups derived from RA;
3) RA-RA sequence, obtained from the reaction between the carboxylic and hydroxylic groups derived from RA;
4) RA–EV sequence, obtained from the reaction between hydroxylic groups derived from RA and carboxylic groups derived from EV units.

The ^{1}H-NMR spectra of the synthesized copolymers were consistent with the ones expected according to the copolymer structures.

To determine the EV/RA composition, and therefore the molar fractions of EV (F_{EV}) and RA (F_{RA}), one signal for each unit had to be taken into account; these signals had to be as close as possible to each other, in order to avoid timing errors. These would then necessarily have been H_h (4.95 ppm) and H_q (4.77 ppm). However, each one of them splitted since they were probably affected by the surrounding system. At this point, two other signals had to be chosen. In this case, H_m (7.72-7.78 ppm) or H_l (7.62 ppm) could be considered for PEV and H_d (1.96-2.10 ppm) or H_k (0.88 ppm) for PRA. H_m was the best choice for PEV, because of the satellite signals affecting H_l intensity value, while H_k had to be considered for PRA (double bond signals had to be avoided since they could be subjected to cis-trans isomerization, making quantification difficult). Therefore, F_{EV} and F_{RA} units were calculated by means of the equations 1’ and 2’ where I indicates the intensity of the signals:

$$F_{EV} = \frac{I_m}{I_m + \frac{I_k}{3}} \qquad (1')$$

$$F_{RA} = \frac{\frac{I_k}{3}}{\frac{I_k}{3} + I_m} = 1 - F_{EV} \qquad (2')$$

Signals due to protons H_m and H_k did not change their chemical shift and did not show any splitting by way of the molar composition, making errors in the integration evaluation minimal.

F_{EV} and F_{RA} values and molecular weights of the synthetized homopolymers and copolymers are reported in Table 3.2.6.

Sample	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**	**F_{EV}**	**F_{RA}**
PEV	4.7	-	1	-
P(EV-*co*-RA)-70/30	4.0	12.5	0.70	0.30
P(EV-*co*-RA)-50/50	2.0	6.8	0.49	0.51
P(EV-*co*-RA)-15/85	3.0	8.0	0.15	0.85
PRA	2.7	8.0	-	1

Table 3.2.6.: Molecular weights and molar fractions (F) of EV and RA units of the PEV and PRA homopolymers and P(EV-*co*-RA) copolyesters.

All molecular weights, except for PEV homopolymer, were determined by GPC. F_{EV} and F_{CL} were determined by equations 1' and 2'.

It resulted that the molar feed well corresponded to the copolymers composition. Concerning the molecular weight, it could be noted that the final M_n values were lower for PRA and copolymers than for PEV: RA contained a secondary –OH group and a lateral aliphatic chain, with a notable steric hindrance: these two characteristics made the reactivity of ricinoleic acid toward esterifications significantly low. However, a classical two-stage polycondensation was used for the preparation of PRA,[31] and a higher molecular weight was obtained in shorter times compared to those reported in the literature.[33, 34]

In order to identify the molar fraction of diads, the average sequence lengths of EV-EV and RA-RA units (L_{EV-EV} and L_{RA-RA}) and the randomness degree (B), some considerations regarding the NMR signals had to be made. The individual signals had to be analyzed to identify which of them was affected by copolymerization. Regarding PRA, H_f (5.31 ppm) and H_h were strongly subjected to splitting, and H_f was not completely resolved. Also H_g and H_a were influenced by copolymerization, but they partially overlapped. Finally also H_i (1.61 ppm) splitted, but $H_{i'}$ overlapped with H_b. In the view of these options, H_h was indubitably the best proton to consider for PRA.

Regarding PEV, H_p (4.49 ppm), H_q (4.34 ppm) and H_n (7.01 ppm) splits could be well identified, however $H_{q'}$ and H_p chemical shifts were very close, therefore it was better taking into consideration H_n intensity.

The method reported by Deveaux[23] allowed to calculate the molar fractions of diads (equations 3', 4', 5' and 6'), average sequence lengths of EV-EV and RA-RA units (equations 7'and 8') and randomness degree (equation 9') .

$$F_{EV-EV} = \frac{I_n}{I_n + I_{n'}} \qquad (3')$$

$$F_{EV-RA} = \frac{I_{n'}}{I_{n'} + I_n} \qquad (4')$$

$$F_{RA-RA} = \frac{I_h}{I_h + I_{h'}} \qquad (5')$$

$$F_{RA-EV} = \frac{I_{h'}}{I_{h'} + I_h} \qquad (6')$$

$$L_{EV-EV} = \frac{F_{EV-EV}}{F_{EV-RA}} + 1 \qquad (7')$$

$$L_{RA-RA} = \frac{F_{RA-RA}}{F_{RA-EV}} + 1 \qquad (8')$$

$$B = \frac{1}{L_{EV-EV}} + \frac{1}{L_{RA-RA}} \qquad (9')$$

Table 3.2.7. reports the average sequence lengths and B values obtained for the P(EV-*co*-RA) copolyesters.

Sample	**F** $_{EV-EV}$	**F** $_{EV-RA}$	**L** $_{EV-EV}$	**F** $_{RA-RA}$	**F** $_{RA-EV}$	**L** $_{RA-RA}$	**B**
P(EV-*co*-RA)-70/30	0.74	0.27	3.8	0.51	0.50	2.0	0.8
P(EV-*co*-RA)-50/50	0.54	0.46	2.2	0.64	0.36	2.8	0.8
P(EV-*co*-RA)-15/85	0.27	0.73	1.4	0.88	0.12	8.3	0.9

Table 3.2.7.: Molar fraction of diads (F), average sequence lengths (L) of EV-EV and RA-RA units and randomness degree (B).

It could be noticed that B increased as the content of PRA was higher.

By comparing the theoretical and the calculated data (Table 3.2.8.) the fact that the experimental average sequence lengths were longer compared to the theoretical ones is highlighted.

Sample	**Δ ($L_{EV\text{-}EV\ exp} - L_{EV\text{-}EV\ theor}$)**	**Δ%**	**Δ ($L_{RA\text{-}RA\ exp} - L_{RA\text{-}RA\ theor}$)**	**Δ%**
P(EV-*co*-RA)-70/30	0.5	13	0.6	41
P(EV-*co*-RA)-50/50	0.2	13	0.7	33
P(EV-*co*-RA)-20/80	0.2	18	1.2	17

Table 3.2.8.: Comparison between theoretical and experimental data.

In particular, the difference between experimental and theoretical data was higher for $L_{RA\text{-}RA}$ and it indicated that a higher number of RA-RA sequences than expected could be found. It probably meant that RA tended to react preferably with itself. However, the percentage difference between measured and theoretical data for $L_{RA\text{-}RA}$ did decrease when the RA amount increased, making the copolymers closer to the random situation. While the formation of PEV was taking place, PEV tended to crystallize and PRA to react with itself since PEV was no more present in the reaction mixture. Of course, in copolymers where the RA content was higher, the PEV segregation phenomenon was less evident and therefore the discrepancy between experimental and theoretical data was lower.

^{13}C-NMR technique was also considered to study the copolymers structures. More into detail, the peaks taken into account for the calculation of average molar fractions, block lengths and randomness degree are the ones belonging to four different carbonyl groups. It is reported in the literature[24-26] that the following carbonyl groups can be used to calculate the chemical sequences: C_1 (168.5 ppm, EV-EV diad), C_4 (168.6 ppm, EV-RA diad), C_3 (177.7 ppm, RA-RA didad) and C_2 (178.2 ppm, RA-EV diad). Peaks numbering refers to diads reported in Figure 3.2.11.

Table 3.2.9. lists the results of molar fractions, average block lengths and randomness degree calculated using the Devaux approach[23] thanks to the intensities of the ^{13}C-NMR signals.

Sample	F $_{EV\text{-}EV}$	F $_{EV\text{-}RA}$	L $_{EV\text{-}EV}$	F $_{RA\text{-}RA}$	F $_{RA\text{-}EV}$	L $_{RA\text{-}RA}$	B
P(EV-*co*-RA)-70/30	0.83	0.17	5.9	0.35	0.65	1.5	0.8
P(EV-*co*-RA)-50/50	0.64	0.37	2.7	0.55	0.45	2.2	0.8
P(EV-*co*-RA)-15/85	0.27	0.73	1.4	0.87	0.13	7.9	0.9

Table 3.2.9.: F (molar fractions), L (average block lengths) and B (randomness degree) calculated through ^{13}C-NMR.

These values were calculated referring to equations 10'-16':

$$F_{EV-EV} = \frac{I_1}{I_1 + I_2} \qquad (10')$$

$$F_{EV-RA} = \frac{I_2}{I_1 + I_2} \qquad (11')$$

$$F_{RA-RA} = \frac{I_3}{I_3 + I_4} \qquad (12')$$

$$F_{RA-EV} = \frac{I_4}{I_3 + I_4} \qquad (13')$$

$$L_{EV-EV} = \frac{F_{EV-EV}}{F_{EV-RA}} + 1 \qquad (14')$$

$$L_{RA-RA} = \frac{F_{RA-RA}}{F_{RA-EV}} + 1 \qquad (15')$$

$$B = \frac{1}{L_{EV-EV}} + \frac{1}{L_{RA-RA}} \qquad (16')$$

The data calculated through ^{1}H-NMR and ^{13}C-NMR were consistent with each other.

The thermal properties of the synthetized homopolymers and copolymers were studied. Figure 3.2.12. reports the registered DSC thermograms, while Table 3.2.10. all the T_D values and the temperatures and the enthalpies values resulting from DSC analysis.

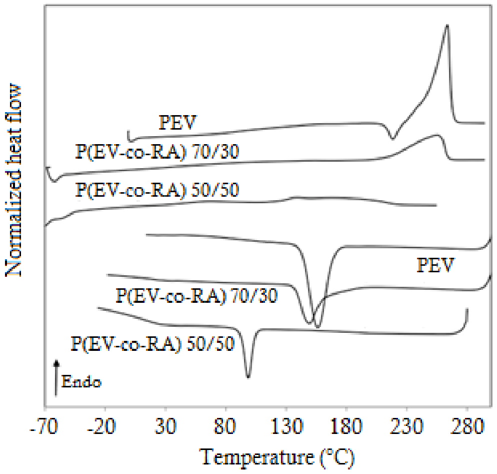

Figure 3.2.12.: DSC scans of PEV and the semicrystalline P(EV-*co*-RA) copolymers.

Sample	**T_D (°C)**	**T_c (°C)**	**ΔH_c (J g^{-1})**	**T_m (°C)**	**ΔH_m (J g^{-1})**	**T_g (°C)**
PEV	406	156	61	264	68	74
P(EV-*co*-RA)-70/30	366, 410	149	35	255	35	-18
P(EV-*co*-RA)-50/50	362, 408, 453	99	18	135-172	20	-44
P(EV-*co*-RA)-15/85	361, 448	-	-	-	-	-60
PRA	360, 450	-	-	-	-	-67

Table 3.2.10.: Degradation temperature (T_D) and DSC characterization of P(EV-*co*-RA) copolyesters and corresponding homopolymers.

T_D was measured by TGA in nitrogen at 10°C min^{-1}. T_c (temperature of crystallization) and ΔH_c (enthalpy of crystallization) were measured during the cooling scan at 20°C min^{-1}. T_m and ΔH_m (ethalpy of fusion) were measured during the 2nd heating scan at 20°C min^{-1}, while T_g was measured during the heating scan after a quenching in liquid nitrogen of the molten sample.

The degradation of PRA occurred at temperatures lower than those of PEV. With the increasing of PEV content in the copolymers the first degradation process shifted towards that of PEV. However, all the materials showed a good thermal stability and for PRA and all the copolymers a multi-step degradation process could be observed.

PRA was an amorphous polymer, with T_g equal to -67°C, therefore PRA chains did not have the capacity of reaching an ordered arrangement. Such behavior could be ascribed to the peculiar chemical structure of the polymer characterized by the presence of cis double bonds, which cause kinks and disturb the symmetry of the chains. Moreover the long lateral sequence of six methylene groups for each monomeric unit strongly contributed to hinder the chain packing. PRA chains had a high level of flexibility, as indicated by a very low value of T_g.

The DSC data of copolymers showed that the materials were semicrystalline at high PEV content, with crystallization and melting temperatures that tended to those of PEV as a function of composition.

As already pointed out, PEV showed a crystallization process, and the same happened for P(EV-*co*-RA)-70/30 and P(EV-*co*-RA)-50/50, while sample 15/85 did not crystallize from the melt under the conditions used.

T_c and ΔH_c values varied over a wide range with copolyester composition. The capability of crystalizing was particularly evident for P(EV-*co*-RA)-70/30, suggesting that it was maintained by the high content of PEV (T_c= 149°C, ΔH_c= 35 J g^{-1}). The capability of crystalizing was strongly reduced when the amount of PRA was increased (P(EV-*co*-RA)-50/50, T_c= 99°C, ΔH_c= 18 J g^{-1}).

During the heating scan, T_m= 264°C and ΔH_m= 68 j g^{-1} were observed for PEV, T_m= 255°C and ΔH_m= 35 j g^{-1} for P(EV-*co*-RA)-80/20 and T_m= 135-172°C and ΔH_m= 20 j g^{-1} for P(EV-*co*-RA)-50/50. For P(EV-*co*-RA)-50/50 T_m was very lower, indicating that the influence of PRA was evident.

Only one glass transition is observed for the whole range of compositions and Figure 3.2.13. shows the variation of the T_g of the amorphous copolymers versus composition, which fits well the Fox equation.[30]

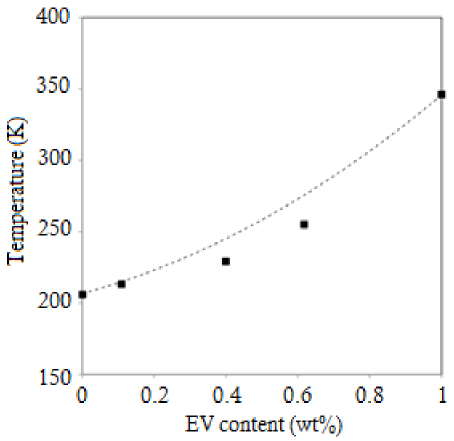

Figure 3.2.13.: Dependence of T_g of the amorphous samples on composition. The dotted line is calculated through the Fox equation.[30]

Therefore, it was reasonable to claim that the amorphous phase was homogeneous and this behaviour was surprising given the different structure of the two homopolymers. Probably, the random distribution of the comonomeric units in the chain did not allow the formation of separate domains.

3.2.3.4. Conclusions

VA was successfully copolymerized with ricinoleic acid, a highly abundant substance found in castor oil. The final properties of the random copolyesters thus obtained depended on the material compositions.

3.2.4. Experimental

Materials

Vanillic acid (VA), ethylene carbonate (EC), potassium carbonate K_2CO_3, ε-caprolactone (CL), dibutyltin oxide (DBTO), poly(ε-caprolactone) (PCL) and ricinoleic acid (RA) were purchased from Aldrich Chemical. All materials had high purity and were used as received.

Methyl vanillate was synthetized from the purchased VA.

Synthesis of a poly(ethylene vanillate) (PEV) homopolymer

Methyl vanillate (1.82 g, 10 mmol), EC (0.968 g, 11 mmol), K_2CO_3 (10 mg, 0.073 mmol) and DBTO (10 mg, 0.04 mmol) were introduced into a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer. The mixture was heated under a nitrogen atmosphere at 180°C for 1 hour until a solid bulk was formed.

The resulting solid mixture of low molecular weight oligomers was collected from the reactor, ground and sieved with a 0.4 mm sieve. The resulting thin powder was introduced into a 100 mL fluidized bed reactor under nitrogen flux for 48 hours at 200°C, for 48 hours at 210°C and for 48 hours at 220°C. Finally, the resulting material was collected from the reactor.

Synthesis of poly(ethylene vanillate-*co*-ε-caprolactone) copolymers (P(EV-*co*-CL))

Methyl vanillate (1.82 g, 10 mmol), EC (0.968 g, 11 mmol), K_2CO_3 (10 mg, 0.073 mmol), DBTO (5 mg, 0.02 mmol) and ε-caprolactone (different amounts of CL were used according to Table 3.2.2.) were introduced into a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer. The mixture was heated under a nitrogen atmosphere at 180°C for 3 hours. The pressure was then slowly reduced to 0.3 mbar while the temperature was gradually increased up to 260°C during 1 hour. Finally, the mixture was kept under this condition for up to 5 hours and the polymer was collected.

Synthesis of poly(ethylene vanillate-*co*-ricinoilec acid) copolymers (P(EV-*co*-RA))

Methyl vanillate (1.82 g, 10 mmol), EC (0.968 g, 11 mmol), K_2CO_3 (10 mg, 0.073 mmol), DBTO (5 mg, 0.02 mmol) and RA (different amount of RA were used according to Table 3.2.6.) were introduced in a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer. The mixture was heated under nitrogen atmosphere at 180°C for 3 hours. The pressure was then slowly reduced to 0.3 mBar while temperature was gradually increased up to 220°C during 1 hour. Finally the mixture was kept in this condition for up to 5 hours and the polymer was collected.

Characterization

The ^{1}H-NMR spectra were recorded at room temperature on samples dissolved in $CDCl_3/CF_3COOD$ (80/20 vol%) using a Varian Inova 600 spectrometer, the proton frequency being 600 MHz. The ^{13}C-NMR spectra were recorded at 150.8 MHz, with a Varian Inova 600 spectrometer, equipped with a direct broadband probe optimised for X detection, and obtained after accumulating 5000 scans (or more) with a digital resolution of 0.552 Hz/point, corresponding to a spectral width of 36199 Hz. The experiment used a pulse width of 3.95 μs, an acquisition time of 1.000 s and a relaxation delay of 3.000 s. The measurements were performed at 25°C.

Molecular weights (expressed in equivalent polystyrene) were determined by gel permeation chromatography (GPC), using a Hewlett Packard Series 1100 liquid chromatography instrument equipped with a TSKgel SuperMultiporeHZ-M column. A mixture of $CHCl_3$/1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (95/5 vol%) was used as eluent and a calibration plot was constructed with polystyrene standards.

The thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA4000 thermobalance under nitrogen atmosphere (gas flow 40 mL min^{-1}) at 10°C min^{-1} heating rate from 30°C to 800°C. The temperature of the maximum degradation rate (T_D), corresponding to the maximum of the differential thermogravimetric curve, was calculated.

The calorimetric analysis was carried out by means of a Perkin-Elmer DSC6, calibrated with high purity standards. The measurements were performed under nitrogen flow. In order to cancel the previous thermal history, the samples (ca. 10 mg) were initially heated at 20°C min^{-1} to different temperatures, varying from 150 to 300°C for PEV and for P(EV-*co*-CL) samples and ranging from 120°C to 300°C for (PEV-*co*-RA) samples, according to the sample characteristics. Samples were kept at high temperature for 1 minute and then cooled to -75°C at 20°C min^{-1}. After this thermal treatment, the samples were analyzed by heating them from -75°C to 150-290°C or 120-290°C at 20°C min^{-1} (2nd scan). During the cooling scan, the cold crystallization temperature (T_{cc}), the cold crystallization enthalpy (ΔH_{cc}), the crystallization temperature (T_c) and the enthalpy of crystallization (ΔH_c) were measured. During the 2nd scan, the melting temperature (T_m) and the enthalpy of fusion (ΔH_m) were determined. The glass transition temperature (T_g) was measured during a heating scan at 20°C min^{-1} after quenching in liquid nitrogen of the molten sample.

3.2.5. References

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3.3. A new approach to the synthesis of monomers, polymers and copolymers incorporating furan/maleimide Diels-Alder adducts

The Diels–Alder (DA) reaction between furan (F) and maleimide (M) moieties is a well-known and widely used strategy to build macromolecular structures with peculiar properties. These structures are partially bio-based, since furans can be readily obtained from a vast array of natural resources. The F-M adducts are thermally reversible because they can be broken above about 100°C and recombined at lower temperatures. At the moment, only the monomers exhibiting the F or the M moieties on their extremity are used in order to get linear or cross-linked polymeric structures. The innovative idea described here consists in using a monomer bearing two carboxylic acidic groups on its extremities and a F-M DA adduct *within* its structure. This monomer can give rise to classical polycondensation reactions leading to polymers incorporating a DA adduct into the main chain. These polymers (which are polyesters in the present case) can undergo depolymerization at high temperatures by means of a controlled reverse DA reaction and produce segments exhibiting F or M moieties at their extremities, which at lower temperature recombine leading to random or block copolymers. This technique can be exploited for the preparation of materials exhibiting self-healing and recyclable features.

3.3.1. Introduction

The DA reaction generally provides simple, efficient, and clean procedures to generate new bonds by inter- or intramolecular coupling and represents one of the most useful synthetic methods in organic chemistry. The application of DA chemistry to polymer synthesis, modification and (reversible) cross-linking has received much attention.[1]

The F ring is one of the most important heterocycles used as the diene in DA reactions.[2] Interest in exploiting the DA reaction in the context of F chemistry is clearly shown by (i) the renewable character of these heterocyclic compounds (furfural is an industrial commodity obtained from a wide variety of agricultural residues),[3, 4] (ii) the pronounced dienic nature of the furan ring which makes it particularly suitable in terms of kinetics and yields and (iii) the readiness of many adducts to undergo the reverse reaction when heated to an appropriate temperature, thus regenerating the original reactants.[5]

Among the large variety of dienophiles, M are among the most commonly used reagents because of their high reactivity, since the particular orbitals arrangement (due to their cyclic structure) makes these molecules particularly suitable for taking part in DA reactions.

The DA reaction performed with model compounds allowed a deeper understanding of the system.[3, 6] The quantitative kinetic results indicated that temperatures around 60°C are best suited for the growth reactions, whether the depolymerizations are best conducted just above 100°C.

It is precisely the experimental convenience associated with this range of temperatures, together with the fact that side reactions and possible thermal degradation mechanisms are negligible, that the F-M couple represents a highly suitable choice for building a large variety of thermally reversible macromolecular architectures.

The reversible coupling can be simply pictured as in Figure 3.3.1.

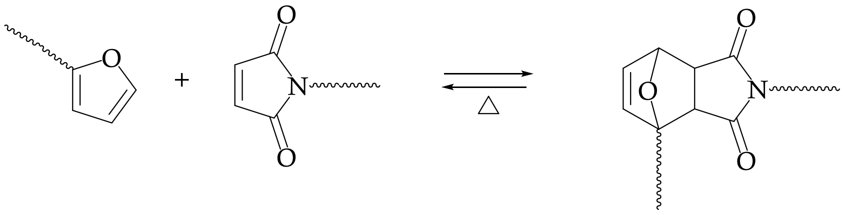

Figure 3.3.1: The DA equilibrium between F and M end groups in a stepwise macromolecular synthesis.

It is important to emphasize that the presence of specific groups in the vicinity of either heterocycle (i.e. on the polymer chain), such as carboxylate, amide and hydroxyl functions, can considerably affect the rates of these DA couplings, as pointed out in the case of reactions involving small molecules.[7, 8]

Several approaches to implement the general strategy depicted in Figure 3.3.1. have been adopted.[9, 10] Without going through those concerning very specific situations (e.g. the construction of dendritic macrostructures or the decoration of nanoparticles), one of them involves complementary monomers with an average functionality greater than 2 to prepare highly branched or cross-linked polymers or to synthesize hyperbranched macromolecules that cannot form a network.

However, the most diffused are the following systems:

1) Linear polymerizations

Linear polymerizations involve the reaction of AA and BB monomers (bisfuran and bismaleimides) or the use of a F-M AB monomer.

The first attempts to prepare a linear polymer from bisfuran and bismaleimide monomers date back to the ninety-eighties[11, 12] with systems involving different difuran compounds and bismaleimides bearing aliphatic, aromatic and dimethylsiloxane spacers. The purpose of these studies was to prepare heat-resistant polymers and therefore the authors converted the DA adducts along their chains into stable structures by aromatization, not studying the retro-DA behaviour of the polymers.

In 1990 a thorough investigation of the DA polycondensation of various difuran derivatives with classical bismaleimides was carried out,[13] and it is worth noting that a careful study of the polymer structure confirmed that the chain growth had indeed taken place through successive DA couplings.

A series of papers published in the early ninety-nineties[14, 15] dealt with similar systems, but they contributed only modestly to the advancement of the topic. Only Juramoto,[16] in 1994, focused the applied approach on the preparation of thermoreversible linear DA polymers. Difurfuryladipate and N,N'-bismaleimido-4,4'-diphenylmethane (BMDP) were submitted to DA polycondensations at temperatures of 30–70°C and the depolymerization was studied at 90°C.

In more recent years, among the many published works, the following ones can be cited. In one of them the combination of a difuran monomer bearing acetal moieties and an aromatic (BMDP) or an aliphatic bismaleimide,[17] was studied (Figure 3.3.2,a). A similar investigation[18] was conducted using much more flexible monomer structures in order to enhance polymer solubility (Figure 3.3.2,b).

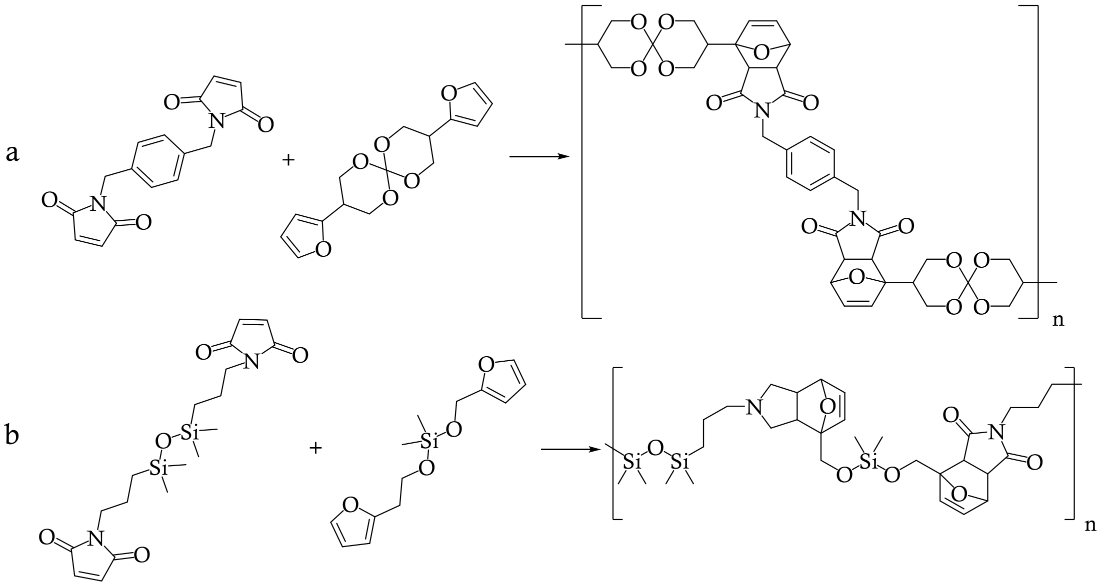

Figure 3.2.2.: DA linear polycondensation involving BMDP and a difuran cyclic diacetal (a) and one involving less rigid starting monomers (b).

The model DA reaction of furfuryl acetate with N-methylmaleimide and the linear polymerization of the corresponding difunctional monomers were carried out and followed by both UV and ^{1}H-NMR spectroscopy, allowing to obtain quantitative kinetic results.[3, 6] A more elaborate approach was then applied to F and M monomers prepared from two renewable resources (vegetable oils and furans) using two click chemistry mechanisms, i.e. the thiol–ene and the DA reactions,[19] as shown in Figure 3.3.3.

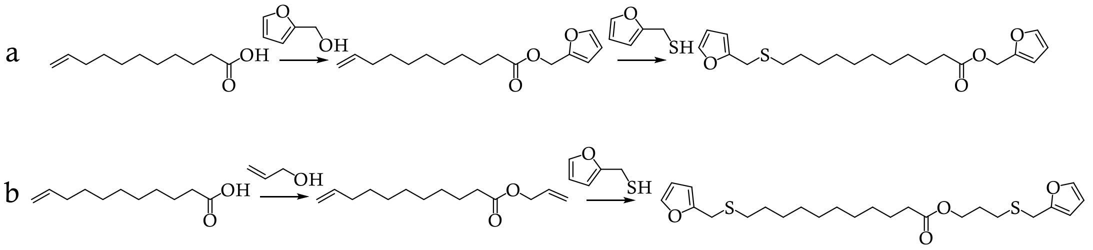

Figure 3.3.3.: Synthesis of two AA monomers from furans and vegetable oil derivatives using the thiol–ene click reaction.

The first attempts to prepare a molecular structure bearing both a F and a M moiety were reported in the early ninety-nineties,[20, 21] but they were not corroborated by a convincing structural analysis. The synthesis of the first structurally verified AB monomer, furfurylmaleimide, was carried out in 1998.[22] It is indeed the simplest F-M molecule, which was prepared in a classical fashion from furfurylamine and maleic anhydride. Because of the inadequate approach to the monomer synthesis, this compound did not polymerize through a simple DA polycondensation when its solutions were heated up to 70°C.[22] This issue was tackled almost ten years later by adopting a different approach:[23] the *in situ* synthesis of the polymer corresponding to furfurylmaleimide was performed and this polymer was subsequently depolymerized calling upon the retro-DA reaction (Figure 3.3.4.).

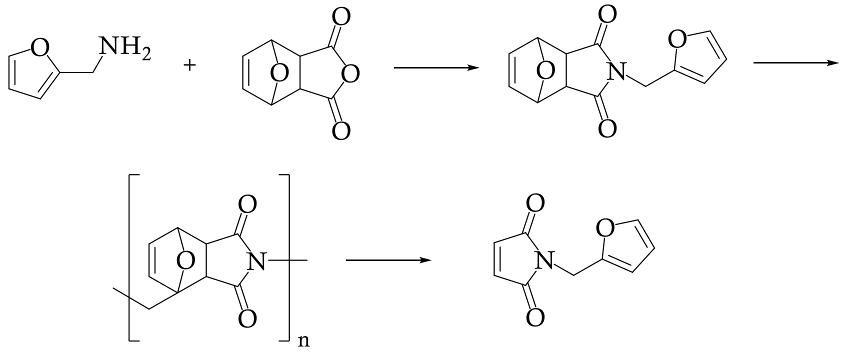

Figure 3.3.4.: Schematic route for the isolation of pure furfurylmaleimide through the depolymerization of its corresponding polymer.

F-M AB monomers were prepared and submitted to a high temperatures DA polycondensation, conditions that would not favor the forward DA reaction, i.e. the polymerization.[24]

The two protected novel AB monomers shown in Figure 3.3.5,a were prepared starting from a non-furan reagent, β-alanine, also from renewable resources.[25] The need for protecting one of the DA partners in these monomers was obviously essential to avoid their premature polymerization during isolation, characterization and storage. The two monomers were polycondensed: this investigation represents the first successful study of the behavior of a F-M AB monomer in the context of its thermally reversible linear polymerization. However, these new polyadducts displayed evidence of the presence of appreciable proportions of cyclic oligomers.[25]

A similar stategy was applied to the monomer depicted in Figure 3.3.5,b.[19]

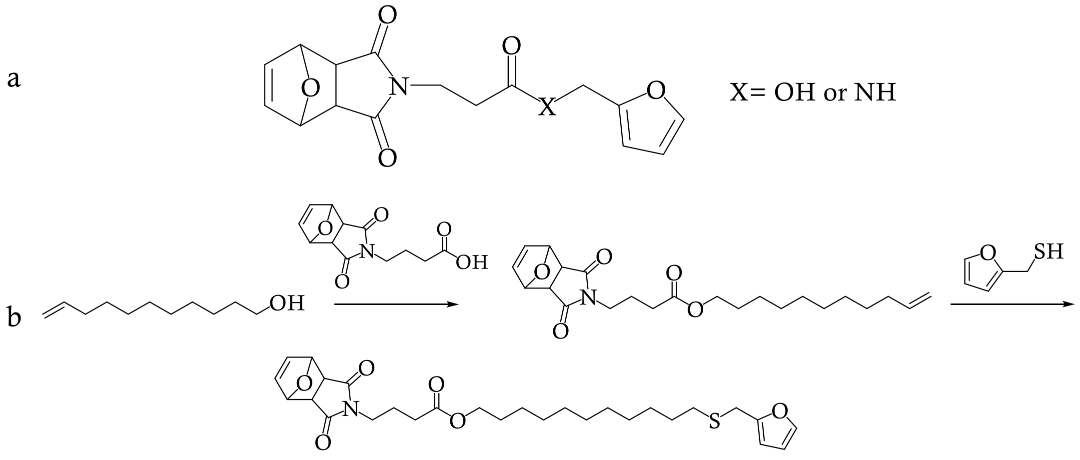

Figure 3.3.5.: Protected AB monomers.

2) Reactions involving polymers

These are cross-linking reactions of linear polymers incorporating pendant F heterocycles with a bismaleimide (or vice versa).

An early study dealing with the possibility of synthesizing thermally reversible networks from linear polymers bearing reactive DA functions describes the reaction of cross-linking of poly(styrene) with M side groups with a difuran compound.[26] It was however only starting from the ninety-nineties that this research topic gained momentum.[27]

The first systematic approach to a reversible DA/retro-DA cross-linking system[27] was carried out with styrene copolymers bearing different proportions of pendant 2-furfuryloxy moieties in conjunction with N,N'-methylenediphenylbismaleimide (MDPBM).[1]

Further studies in this context concerned a copolymer with elastomeric properties,[2] in which the starting copolymers were elastomers simulating conventional rubbers. Two different strategies were followed, i.e. (i) linear macromolecules bearing pendant furan moieties (low-T_g acrylic copolymers), to be cross-linked with an oligoether bismaleimide and (ii) linear macromolecules bearing pendant M moieties (low-T_g polysiloxane copolymers) to be cross-linked with a siloxane difuran reagent. Both types of combinations were optimized to give excellent reversibility without detectable side reactions.

Partially acetalized poly(vinylalcohol) (PVA) bearing pendant furan rings[28] was cross-linked with various bismaleimides[29] and the ensuing networks were shown to display the expected thermal reversibility through the retro-DA reaction.

Again, for example, the DA reversible crosslinking of styrene–furfuryl methacrylate copolymers in the presence of N,N'-bismaleimido-4,4'-diphenylmethane (BMDP) (Figure 3.3.6.) was carried out together with a characterization of the networks in terms of mechanical, swelling and thermal properties, which provided information about the cross-link density.[30]

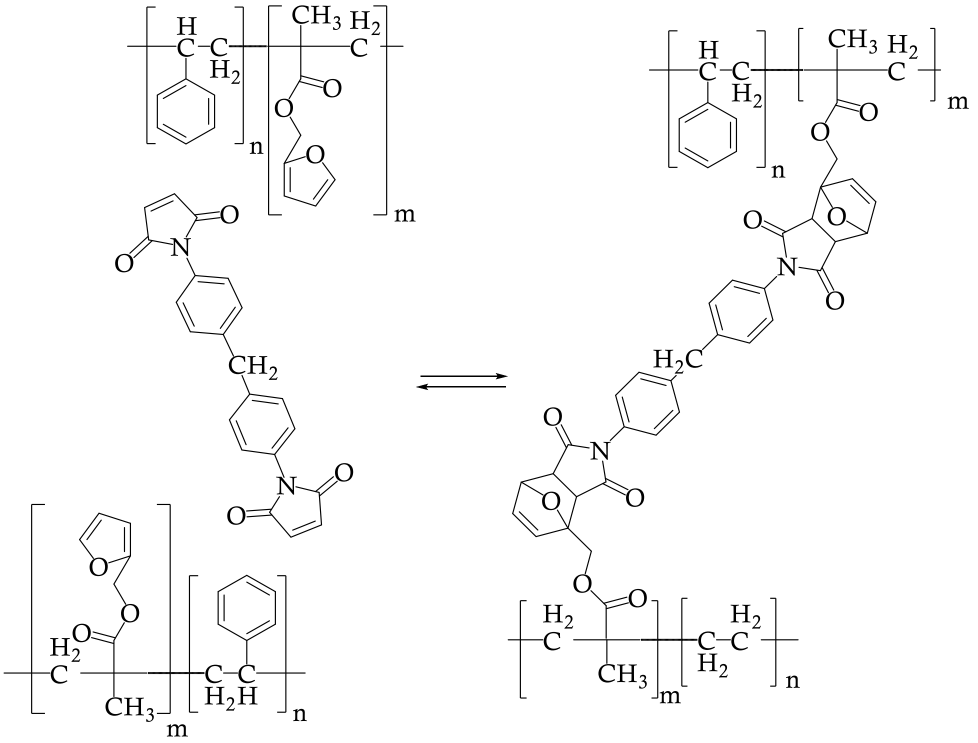

Figure 3.3.6.: DA reversible crosslinking of styrene–furfuryl methacrylate copolymers with BMDP.

Hydrogels generated by the DA reaction of various water-soluble copolymers with pendant F moieties were the subject of a series of publications.[31, 32] The network formation was insured in water by a bismaleimide bridged by an ethylene oxide oligomer (Figure 3.3.7.) and their retro-DA decoupling occurred at a growing rate between 80°C and 100°C in solvents such as DMF and DMSO, with no apparent return at 60°C and 70°C.

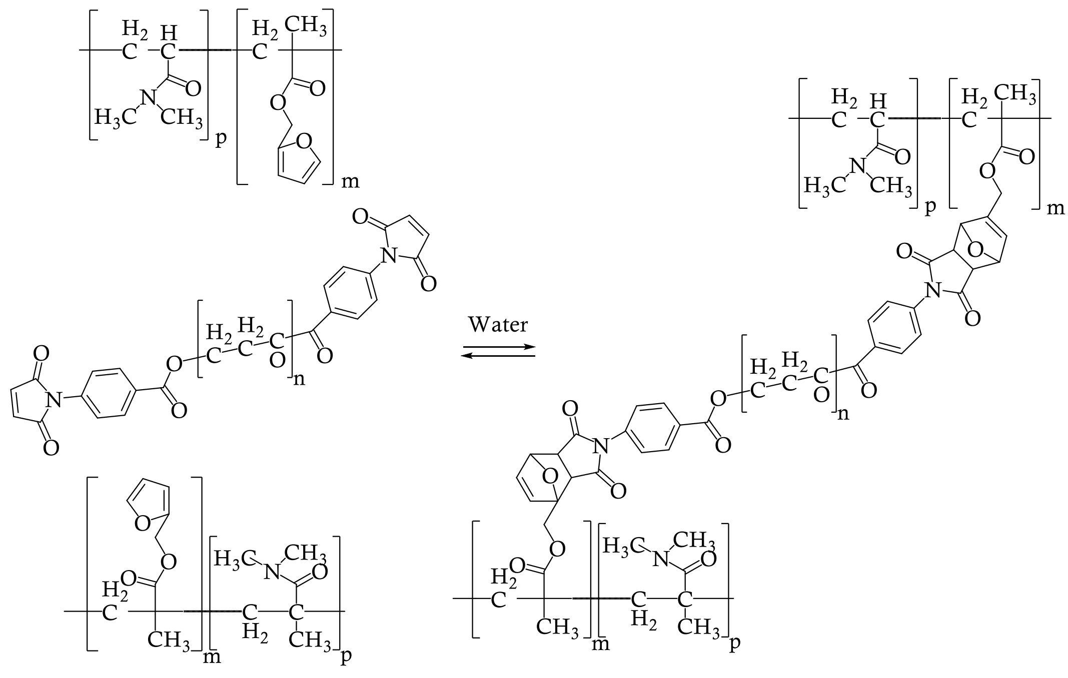

Figure 3.3.7.: Reversible aqueous cross-linking of various water-soluble copolymers with a bismaleimide bridged by an ethylene oxide oligomer.

An interesting and surprising feature of all these systems is their resistance to disassembling in hot water.[31, 32]

The application of these DA strategies has also been reported for molecules and macromolecules derived from biomass, more specifically it was applied to plant-oil monomers, starch, natural rubber, cellulose and nanocellulose fibers, chitosan, and gelatin.[33]
However, what must be underlined is that in each of the above reported cases the F and M moieties are present on the monomer extremities.

3.3.2. Aim of the work

The aim of this work consisted in preparing copolymeric structures not accessible through direct synthesis exhibiting self-mending features that can find a use as recyclable materials. Copolymer preparation was based on the exploitation of the well-known thermal reversibility of the F-M DA reactions, but the originality of this study stemmed from the fact that a monomer having a F-M DA adduct *within* its structure was employed. More specifically, the aim of this work consisted in setting up the synthesis of a diacidic monomer having a F-M DA adduct within its structure and in polymerizing it. Polymerizations occurred through classical polycondesation reactions with complementary diols (an aliphatic one, 1,6-hexanediol, and an aromatic one, 1,4-benzenedimethanol). The polyesters thus obtained were characterized and their kinetics involved in the breaking (retro-DA) and recombination (DA) of their DA adducts investigated. It was expected that, if the two different polymers obtained using this approach were heated together at the temperature at which the retro-DA occurs and then cooled, the recombination of the F and M moieties would occur randomly, leading to copolymers which could be random or block copolymers depending on the heating procedure. A similar strategy was already been discussed in a Brazilian patent[34] and in a paper.[35] Data collected thanks to the kinetic tests were applied to the preparation of a copolymer which was characterized and showed intermediate thermal properties with respect to those of the initial polyesters.

3.3.3. Results and discussion

Monomer synthesis and characterization

A new diacid monomer incorporating a F-M DA adduct was synthetized from 3-(2-furyl)propionic acid and 6-maleimidohexanoic acid (Figure 3.3.8.).

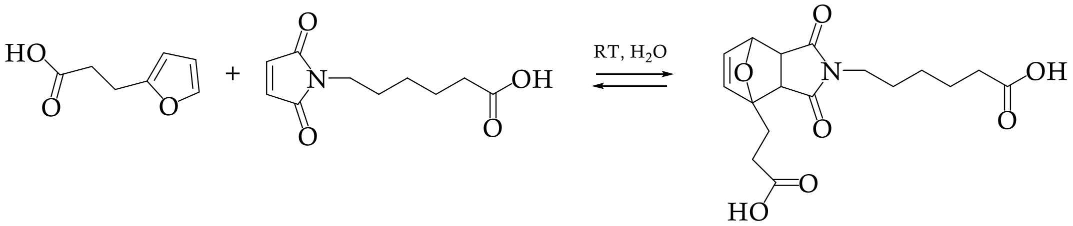

Figure 3.3.8.: Scheme of the synthesis of the diacid monomer.

The process used for the synthesis of the monomer was a sustainable procedure since water was used as the medium and it occurred at room temperature without any catalyst. This procedure was set up thanks to a publication in which similar reactions were reported.[36] The monomer, a slightly tan-colored solid, was collected by simple filtration from the aqueous reaction medium and no purification steps were required.

A complete characterization of the above-mentioned monomer was carried out.

First of all, in order to confirm its chemical structure, a ^{1}H-NMR spectrum was recorded, as reported in Figure 3.3.9.

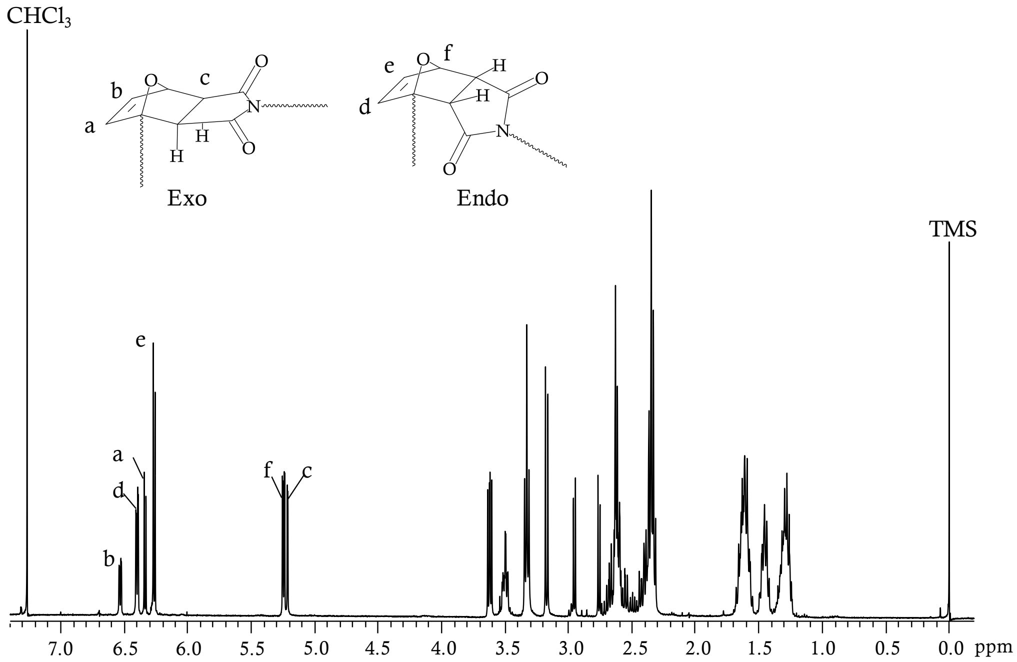

Figure 3.3.9.: ^{1}H-NMR spectrum of the diacidic DA monomer.

As it can be seen in Figure 3.3.9., no by-products were formed and the typical F-M adduct signals (between about 5 and 7 ppm) were present. Peaks H_a, H_b and H_c were attributed to the adduct belonging to the exo isomer, while H_d, H_e and H_f to the endo isomer. The endo:exo isomer ratio was around 2:1. It is well established that DA adducts are formed through two types of approaches that lead to endo or exo isomers, and that the endo isomer is usually kinetically favored over the exo isomer, although the letter is generally the thermodynamically preferred product. This can be attributed to the additional stability gained by secondary molecular orbital overlap during the cycloaddition.[37]

DSC analysis showed that the monomer had a complex thermal behavior (Figure 3.3.10.).

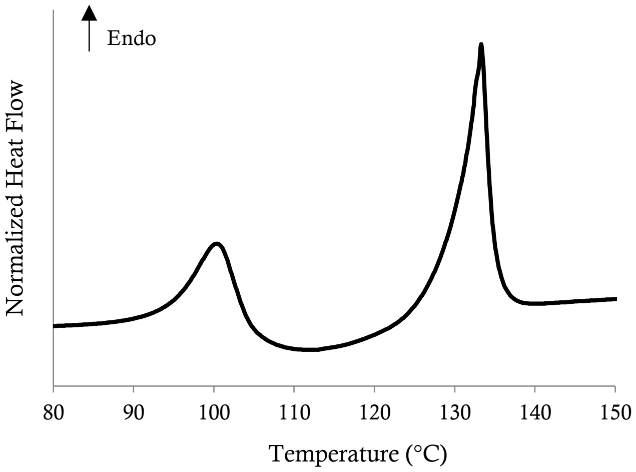

Figure 3.3.10.: DSC (first heating scan) of the diacidic DA monomer.

In the first heating scan two endothermic and one exothermic peaks corresponding to three thermal events could be observed. The understanding of this multiple behavior was possible thanks to an NMR analysis carried out on samples subjected to different heating scans, up to the end of each thermal event. In this way, the first endothermic peak (100°C) was attributed to the breaking of the endo isomer, the second exothermic process (115°C) to the recombination of the units obtained from the previous breaking and the third one (133°C) to the complete rupture of the DA adduct.

TGA analysis demonstrated that the degradation process occurred through a single step and that the monomer exhibited a good thermal stability: its T_0 (onset temperature, i.e. the initial decomposition temperature, the point where the material started disintegrating) was equal to 186°C, while its T_D (temperature of the maximum degradation rate, corresponding to the maximum of the differential thermogravimetric curve) was equal to 252°C.

Polymers synthesis and characterization

The monomer was polymerized with an aliphatic and with an aromatic diol in order to prepare two new polyesters using 1,6-hexanediol and 1,4-benzenedimethanol, respectively. In order to avoid the occurrence of the retro-DA reaction, polycondensations were carried out using N,N'-dicyclohexylcarbodiimide (DCC), a coupling agent which allows to work at temperatures below that at which the adduct retro-DA occurs. The polymerization procedure (Figure 3.3.11.) consisted in using acetonitrile as solvent, DCC, 4-

dimethylaminopyridine (DMAP) and in increasing the temperature from 0°C to room temperature.

The two polyesters were called P(DA-Al) and P(DA-Ar), where DA stands for the synthetized monomer with a DA adduct within its structure, Al for "aliphatic" (component coming from the aliphatic diol, 1,6-hexanediol) and Ar for "aromatic" (this part derived from 1,4-benzenedimethanol).

These polyesters were characterized by ^{1}H-NMR spectroscopy, GPC and DSC. GPC and DSC data are summarized in Figure 3.3.11.

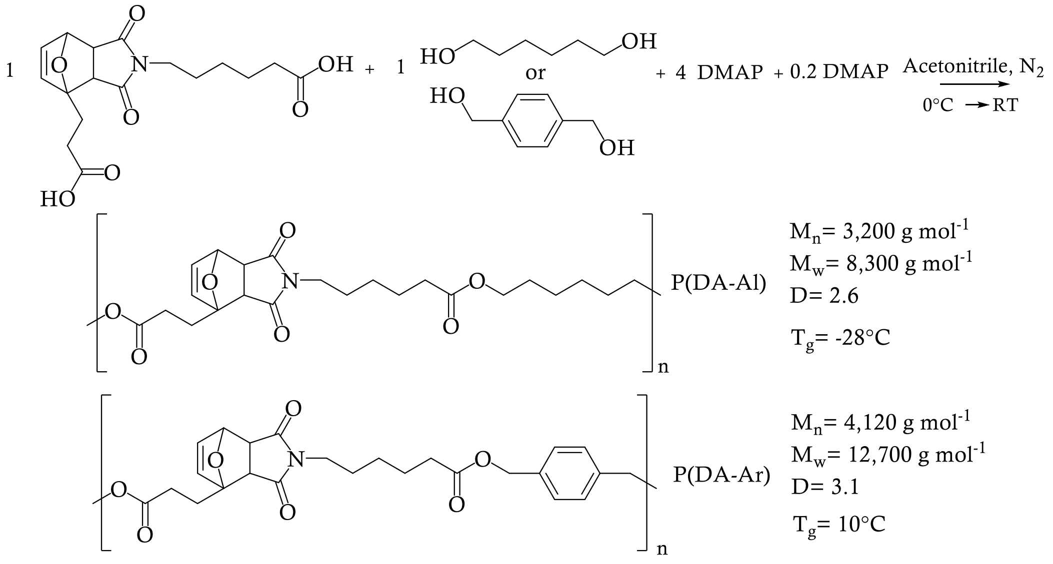

Figure 3.3.11.: Polymerization procedure, the corresponding polyesters and GPC and DSC data for P(DA-Al) and P(DA-Ar).

The ^{1}H-NMR spectra confirmed the expected polymer structure and that no unwanted side reactions had taken place.

GPC analysis showed that the achieved molecular weights were high enough to subject the two polyesters to depolymerization and recombination studies. More specifically, P(DA-Al) exhibited molecular weight (M_w) of 8,300 g mol^{-1} and P(DA-Ar) of 12,700 g mol^{-1}.

DSC thermograms were recorded by setting 90°C as maximum temperature, the temperature above which thermal events occurred, in order to avoid changes in the polymer structures, but also to guarantee an initial treatment to delete the eventual thermal history of the samples. Thermograms clearly showed the amorphous character of the polymers, probably due to the mixed structures imparted by the endo and exo isomers. Furthermore, DA adducts imparted a kinked shape to macromolecules, impeding the formation of a regular packing. No crystallization or melting peaks were observed, demonstrating that the polymers could not form crystals. For P(DA-Al), the registered T_g during the second heating scan at 5°C/min was equal to -28°C, while it was equal to 10°C for P(DA-Ar). Such a difference between the two polyesters was in agreement with their chemical structure.

Kinetic studies

A series of kinetic studies on P(DA-Al) and P(DA-Ar) was performed in order to check if their DA adducts were really able to perform retro-DA reaction and give rise to *monomeric* fragments, namely that derived from P(DA-Al) and from the breaking of two adjacent DA adducts was called **I**, while that from P(DA-Ar) **II**. Both of them are depicted in Figure 3.3.12.

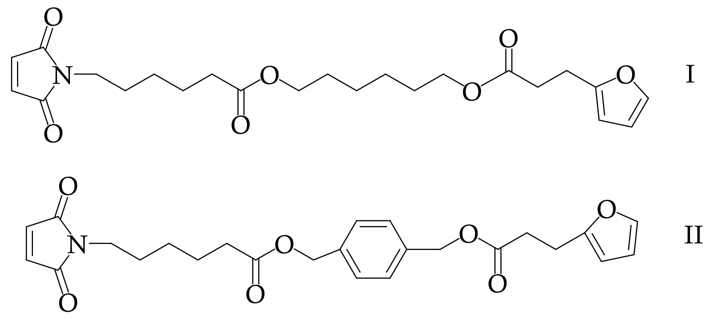

Figure 3.3.12.: *Monomeric* fragments resulting from P(DA-Al) (**I**) and P(DA-Ar) (**II**) after the breaking of two adjacent DA adducts.

Secondly, the aim was to verify if **I** and **II** were able to recombine to lead, again, macromolecular structures.

These experiments were fundamental also to find out the experimental conditions required in order to prepare a copolymer.

Experiments were carried out by putting separately the two synthetized polyesters in a solvent: these solutions were sampled at pre-set times and analyzed directly through NMR and GPC analysis. The solvent employed was deuterated tetrachloroethane (d-TCE), which was chosen because of its high boiling point (145-146°C at 737 mmHg), because it ensured high solubility of the prepared polymers and because it allowed to analyze directly the collected samples through ^{1}H-NMR spectroscopy.

First, P(DA-Al) was analyzed. It was placed in d-TCE and the solution warmed up to 110°C. Starting from the moment that that temperature was achieved, samples were collected after 15, 30, 45 and 60 minutes. Conversions of the polymer into fragments were calculated from the corresponding NMR spectra. As an example, Figure 3.3.13. shows the NMR spectrum after 15 minutes.

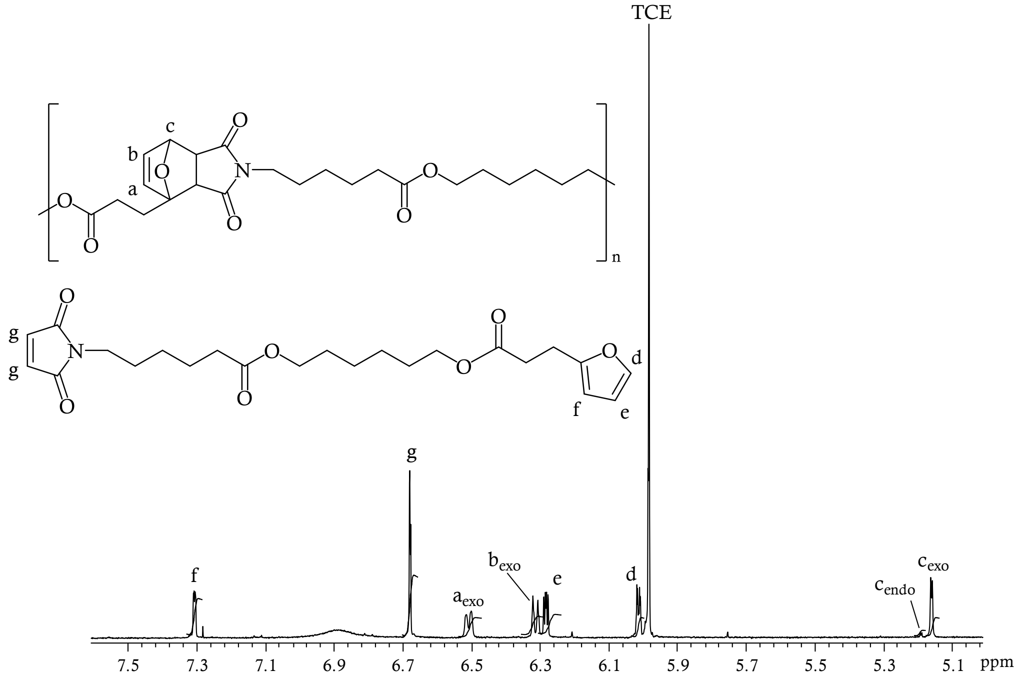

Figure 3.3.13.: NMR spectrum of P(DA-Al) placed in d-TCE for 15 minutes at 110°C.

In the mixture, both the remaining polymer DA adducts and the segments exhibiting F and M end-groups were present. These segments could be the result of the breaking of two adjacent DA adducts (compound **I**) or of not adjacent ones, but chemical shift of F and M signals was not affected by this fact. H_a, H_b and H_c were attributable to the signals of the DA adducts, H_g to that due to the double bond hydrogens of the M moiety and H_d, H_e and H_c to the peaks of the furanic ring present in the segments. F and M peak intensities indicated that the F:M ratio was equal to 1:1.

Conversion of the polymer into fragments with F and M moieties was calculated calling upon the following formula:

$$Conversion = \frac{I_f}{I_f + (I_{c_{endo}} + I_{c_{exo}})} \qquad (1)$$

where I stands for the intensity of the signals.
The data obtained are assembled in Table 3.3.1.

Time (minutes)	**Conversion (%)**
15	45
30	83
45	94
60	100

Table 3.3.1.: Conversion of P(DA-Al) into fragments exhibiting F and M moieties calculated through ^{1}H-NMR analysis.

Conversion equal to 94% was deemed a good yield value, especially considering the short reaction time (45 minutes). It was therefore decided to protract the following similar experiments for 45 minutes, also to prevent possible degradation phenomena, easily occurring at such high temperatures.
This sample collected after 45 minutes was analyzed by GPC, which confirmed that depolymerization had indeed occurred.
Once verified that an efficient breakdown percentage of DA adducts in the polymeric structure was obtainable, P(DA-Al) was subjected to recombination studies. P(DA-Al) was therefore placed in d-TCE and kept for 45 minutes at 110°C (in the light of the results collected from the depolymerization studies); after this lapse of time, the temperature was lowered to 55°C and the solution sampled after 24 hours from the moment that temperature had been reached. Elapsed 24 hours, the conversion of the fragment into the polymeric structure was calculated thanks to the recorded ^{1}H-NMR spectrum. Signals present were the same shown in Figure 3.3.13., i.e. the ones attributable to the F and M moieties and those of the DA adduct. Calling upon the same nomenclature used in Figure 3.3.13., the formula used for the calculation of the conversion into the polymer was (2):

$$Conversion = \frac{(I_{c_{endo}} + I_{c_{exo}})}{I_f + (I_{c_{endo}} + I_{c_{exo}})} \qquad (2)$$

where, again, I stands for the intensity of the signals.

After 24 hours, conversion was equal to 92%. Also corresponding molecular weights (M_n= 2,500 g mol^{-1} and M_w= 7,100 g mol^{-1}) demonstrated that the recombination had occurred (see Table 3.3.2.).

Depolymerization kinetics were studied also for P(DA-Ar). It was introduced in d-TCE and the solution sampled after it was kept for 45 minutes at 110°C. Conversion, calculated by means of NMR referring to the same peaks of Figure 3.3.13. and to equation (1), was equal to 100%, demonstrating that after this lapse of time all the DA adduct were completely depolymerized and that only compound **II** was present. GPC confirmed these results. The same solution was then taken to 55°C and sampled after 24 hours. Conversion of the fragments into the polymer, calculated by means of equation (2), was equal to 34%, demonstrating that also for P(DA-Ar) recombination reaction had taken place. To this corresponded M_n of 2,900 g mol^{-1} and M_w of 8,900 g mol^{-1}. For a better understanding, these data are reported in Table 3.2.2., together with those attributable to P(DA-Al).

Sample	**Conversion (24h, %)**	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**
P(DA-Al)	92	2.5	7.1
P(DA-Ar)	34	2.9	8.9

Table 3.3.2.: conversion of P(DA-Al) and P(DA-Ar) fragments in polymers calculated through ^{1}H-NMR analysis and corresponding molecular weights.

Conversion of the fragments into polymers was calculated through NMR and molecular weights through GPC.

Initially, as already pointed out, P(DA-Al) showed M_n of 3,200 and M_w of 8,300 g mol^{-1} and P(DA-Ar) M_n 4,100 of and M_w of 12,700 g mol^{-1}.

The data above reported were very promising, since they demonstrated the capability of P(DA-Al) and P(DA-Ar) to break and recombine when subjected to specific thermal treatments.

Copolymer - synthesis and characterization

Given the success of the developed procedure of depolymerization and repolymerization of the homopolymers, the process of copolymerization by means of DA recombination was studied.

Once the data for the depolymerization and recombination of P(DA-Al) and P(DA-Ar) were collected, the polyesters were introduced in d-TCE, and the same conditions for the preliminary studies were applied, so the mixture was kept for 45 minutes at 110°C (to which a total conversion into fragments and low molecular weights corresponded). The temperature was then lowered to 55°C and a sample was collected after 24 hours. Conversion into a polymeric structure was equal to 55%. Its M_n was of 2,100 g mol^{-1}, while its M_w was of 7,500 g mol^{-1}. Since conversion was not equal to 100%, oligormers and low molecular weight fragments were still present, the prepared macromolecular structure was subjected to a washing treatment. This cleaning procedure consisted in washing the copolymer with a saturated Na_2CO_3 aqueous solution. NMR spectra clearly showed the disappearance of the signals attributable to the F and M moieties. Figure 3.3.14,a reports the spectra of the macromolecular structure as it was, while Figure 3.3.14,b that of the one subjected to the washing procedure. Letters reported in these Figures refer to those of Figure 3.3.13.

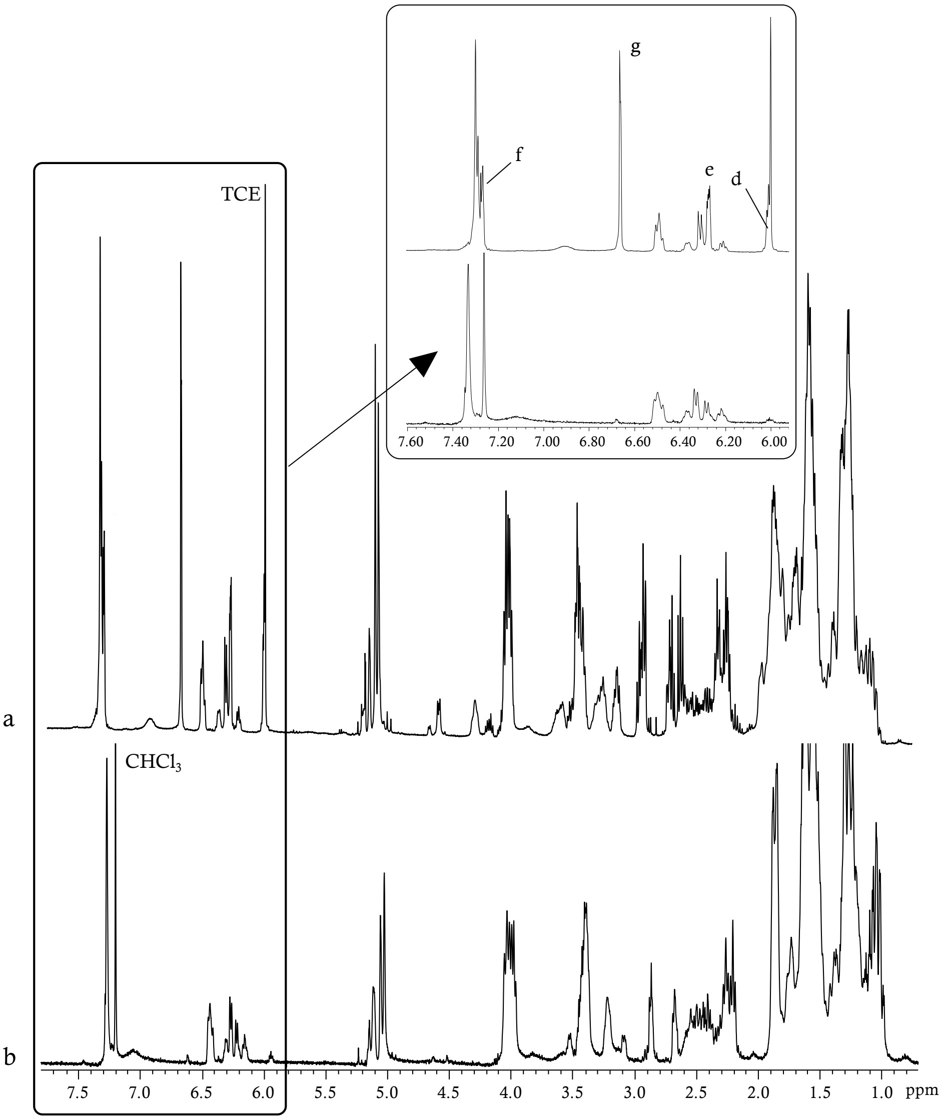

Figure 3.3.14.: NMR spectrum of the macromolecular structure resulting from the recombination experiments (a) and of the one subjected to the cleaning treatment with alkaline water (b).

The signals at 7.22, 6.61, 6.62 and 5.75 ppm in the first spectrum clearly refer to the F and M moieties. The second NMR spectrum reports the signals attributed to a completely pure polymeric structure. Its molecular weight was determined by GPC. M_n was equal to 2,400 g mol^{-1} and M_w to 8,000 g mol^{-1}, as reported in Table 3.3.3., together with the molecular weights of the starting polyesters. Again, these data clearly indicated that shorter fragments were successfully eliminated. The "washed" macromolecular structure was analyzed by DSC. As expected, the thermogram indicated its amorphous character. It was recorded by setting 90°C as maximum temperature, as for P(DA-Al) and P(DA-Ar). Only one T_g (1°C) was detectable, indicating a homogeneous amorphous phase. More interestingly, this value was between those of P(DA-Al) (-28°C) and P(DA-Ar) (10°C), clearly indicating the success of the copolymerization characterized by a single intermediate glass transition. The "washed" copolymer thermogram is reported in Figure 3.3.15. compared with those of the starting materials.

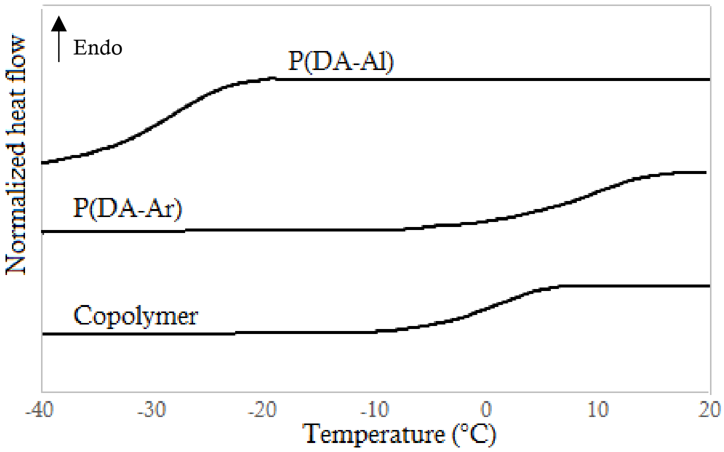

Figure 3.3.15.: DSC thermograms of P(DA-Al), P(DA-Ar) and of the copolymer subject to the cleaning treatment (second heating scan).

Table 3.3.3. summarizes the registered molecular weights and T_gs for P(DA-Al), P(DA-Ar) and the washed copolymer.

Sample	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**	**T_g (°C)**
P(DA-Al)	3.2	8.3	-28
P(DA-Ar)	4.1	12.7	10
Copolymer*	2.4	8.0	1

* Subjected to the cleaning treatment.

Table 3.3.3.: Molecular weights and DSC data of P(DA-Al), P(DA-Ar) and the copolymer subjected to the washing treatment.

M_n and M_w were determined by GPC analysis and T_g were measured by DSC during the second heating scan at 5°C min^{-1}.

3.3.4. Conclusions

A totally green synthesis of a new diacidic monomer containing a DA adduct within its structure was optimized starting from 3-(2-furyl)propionic acid and 6-maleimidohexanoic acid. A complete characterization of this monomer was performed. Two new polyesters were synthesized with 1,6-hexanediol and 1,4-benezenedimethanol thanks to a coupling agent (DCC) and ^{1}H-NMR, GPC and DSC analysis on these polymers were performed. A series of kinetic studies on the de-polymerization (retro-DA reaction) and on the re-polymerization (DA reaction) on the single polymers was carried out and they demonstrated their tendency to break and recombine through their DA adducts. A copolymer between the two synthesized polyesters was prepared calling upon the reaction conditions found for the two polyesters. This work can open the way to a new and innovative strategy for obtaining self-healing and recyclable materials consisting of tunable copolymer structures. The novel approach, based on the DA/retro-DA strategy, potentially applies to any combination of homopolymers, including, among others polyesters, polyamides, polyurethanes and epoxy moieties and hence to the synthesis of a wide variety of copolymer, some of which not accessible by direct copolymerization.

3.3.5. Experimental

Materials

3-(2-furyl)propionic acid, 6-maleimidohexanoic acid, 1,6-hexanediol, 1,4-benzenedimethanol, N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), acetonitrile and deuterated tetrachloroethane (d-TCE) were purchased from Aldrich Chemical. All materials had high purity and were used as received.

Monomer synthesis

2.80 g (0.0200 mol) of 3-(2-furyl)propionic acid and 4.22 g (0.0200 mol) of 6-maleimidohexanoic acid were placed in a 100 mL round bottom flask equipped with a magnetic stirrer together with 20 mL of water. The mixture was stirred at room temperature under nitrogen atmosphere for 24 hours. The tan-colored product was a non-dissolved solid that was filtered then vacuum dried. The product (yield = 100%) was analyzed through ^{1}H-NMR, GPC, TGA and DSC.

Polymerizations

1.00 g (0.00285 mol) of the DA diacidic adduct and 0.338 g (0.00285 mol) of the diol (1,6-hexanediol to get P(DA-Al) or 1,4-benzenedimethanol to obtain P(DA-Ar)) were placed into a 100 mL three-necked round bottom flask equipped with a magnetic stirrer together with 10 mL of anhydrous acetonitrile. The flask was placed in an ice bath. 2.35 (0.0114 mol) of DCC and 0.0696 g (0.000570 mol) of DMAP were dissolved in 10 mL of anhydrous acetonitrile and the solution was slowly dropped in the magnetically stirred flask contents under reflux and under nitrogen atmosphere. The temperature was allowed to increase spontaneously by letting the cooling bath reach room temperature. The reaction continued for 6 hours and 30 minutes. In both cases the polymers were separated from acetonitrile through filtration and the filtered products were dissolved in chloroform. The solutions were washed with an acidic aqueous solution, a basic solution and with water in order to remove impurities. $MgSO_4$ was used to get rid of water traces and chloroform removed under reduced pressure. P(DA-Al) and P(DA-Ar) were analyzed through ^{1}H-NMR, GPC and DSC.

Kinetic tests

- Depolymerization studies

100 mg of P(DA-Al) were placed in 8 mL of d-TCE in a 25 mL Schlenk tube equipped with a magnetic stirrer. The solution was heated under a nitrogen atmosphere at 110°C and sampled after 15, 30, 45 and 60 minutes. Samples were analyzed through ^{1}H-NMR and GPC.

50 mg of P(DA-Ar) were placed in 4 mL of d-TCE in a 25 mL Schlenk tube equipped with a magnetic stirrer, the solution warmed up to 110°C under nitrogen atmosphere and sampled after 45 minutes this temperature was achieved. Samples were analyzed through ^{1}H-NMR and GPC.

- Recombination studies

50 mg of the synthetized polyester (P(DA-Ar) or P(DA-Ar)) were placed a 25 mL Schlenk tube equipped with a magnetic stirrer with 4 mL of d-TCE. The solution was warmed up to 110°C under nitrogen atmosphere and sampled after 45 minutes. The temperature was then lowered to 55°C and after 24 hours solution was sampled and analyzed through ^{1}H-NMR and GPC.

Copolymerization

50 mg of P(DA-Ar) and the same amount of P(DA-Ar) were placed in 8 mL of d-TCE in a 25 mL Schlenk tube equipped with a magnetic stirrer. The solution heated at 110°C under nitrogen atmosphere and sampled after 45 minutes. After this lapse of time, temperature was lowered to 55°C and after 24 hours the solution was sampled and analyzed through ^{1}H-NMR and GPC.

Copolymer cleaning treatment

10 mg of the obtained copolymer were placed in a 100 mL round bottom flask equipped with a magnetic stirrer together with 50 mL of saturated Na_2CO_3 aqueous solution. The solution was subjected to a vigorous stirring and heated at 85°C for 3 minutes. The temperature was allowed to decrease spontaneously and, once that RT was achieved, the flask contents was filtered with filter paper and washed with pure water. The filtered product was dissolved in chloroform, the solution was washed with an acidic aqueous solution and with water (x2) in order to remove impurities. Water traces were then removed with $MgSO_4$ and chloroform removed under reduced pressure. The copolymer thus obtained was analyzed through ^{1}H-NMR and GPC.

Characterization

^{1}H-NMR spectra were recorded at 400 MHz with a Varian Mercury 400 spectrometer (chemical shifts are in part per million downfield from TMS); the solvents used were $CDCl_3$ for the monomer, for P(DA-Al) and P(DA-Ar) and for the copolymer and d-TCE for the samples coming from the kinetic studies.

Molecular weights (expressed in equivalent polystyrene) were determined by gel permeation chromatography (GPC), using a Hewlett Packard Series 1100 liquid chromatography instrument equipped with a TSKgel SuperMultiporeHZ-M column. $CHCl_3$ was used as eluent and a calibration plot was constructed with polystyrene standards. Samples coming from the kinetic studies were vacuum dried from d-TCE and subsequently re-dissolved in $CHCl_3$.

The thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA4000 thermobalance under nitrogen atmosphere (gas flow 40 mL min^{-1}) at 10°C min^{-1} heating rate from 30°C to 500°C. Onset temperature (T_0) and temperature of the maximum degradation rate (T_D) were calculated.

The calorimetric analysis was carried out by means of a Perkin-Elmer DSC6, calibrated with high purity standards. The measurements were performed under nitrogen flow.

Thermal behavior of the monomer was studied by submitting it (ca. 10 mg) to a first heating scan from 0°C to 180°C at 5°C min^{-1}, it was kept at high temperature for 1 min and then cooled to -0°C at 5°C min^{-1}. After this thermal treatment, the monomer was heated from 0°C to 160°C at 5°C min^{-1} (2nd scan). Thermal events were observed only during the first heating scans, in which the temperature corresponding to the maxima of two endotherms peaks and the minimum of an exothermic one were measured. In order to cancel the previous thermal history, P(DA-Al), P(DA-Ar) and the copolymer subjected to the cleaning treatment (ca. 10 mg) were initially heated at 5°C min^{-1} to 90°C, in order to prevent their DA adducts chemical rupture observed during DSC analysis performed on the monomer. Samples were kept at 90°C for 1 min and then cooled to -50°C at 20°C min^{-1}. After this thermal treatment, the samples were analyzed by heating them from -50°C to 90°C at 5°C min^{-1} (2nd scan). During the 2nd scan, glass transition temperature (T_g) was measured.

3.3.6. References

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3.4. New valorization routes of dihydroxyacetone, a glycerol derivative, to obtain bio-based polymers

This research project was developed during the abroad research period. It lasted six months and took place at the KIT (Karlsruher Institut für Tecnologie, Karlsruhe, Germany) in collaboration with Prof. Michael A. R. Meier, Full Professor in Applied Chemistry.

Specifically, the research project was divided into two phases, regarding:

- the development of an hydrogen transfer model reaction between a fatty acid with ketone functionalities in its carbon backbone and glycerol;
- the exploitation of dihydroxyacetone (DHA), the by-product of the above mentioned reaction, for obtaining totally innovative and bio-based polycarbonates and polyesters.

3.4.1. Introduction

In view of all problems connected to the exploitation of petroleum, current industrial and academic interest is increasingly oriented towards the preparation of chemicals and materials starting from renewable resources.

At present, fats and oils are the most widely used renewable raw materials in the chemical industry, since they offer widespread possibilities for different applications.[1-3]

Vegetable oils are triglycerides[4] constituted by fatty acids and glycerol, which constitute a large, easily available, low cost, non-toxic and non-depletable family yielding materials that are capable of competing with fossil fuel derived petro-based products.[1]

Fatty acids outstanding feature is given by their unique chemical structure with unsaturation sites, epoxies, hydroxyls, esters and other functional groups enabling them to undergo various chemical transformations; through these processes, a vast array of polymeric materials can therefore be produced.[2,3]

In the view of the bio-refinery concept (according to which in an industrial process the value derived from all the biomass components has to be maximized), each part of vegetable oils must be at most exploited, comprising glycerol. Glycerol can therefore be considered as an important building-block for the chemical and materials industry.[5]

DHA, the simplest of all ketoses, can be prepared from glycerol by several routes. One consists of a mild oxidation of glycerine, for example with hydrogen peroxide and a ferrous salt as catalyst.[6, 7] DHA can also be prepared in high yield and selectivity at room temperature from glycerol using cationic palladium-based catalysts with oxygen, air or benzoquinone acting as co-oxidants.[8-10] A third strategy is based on a fermentation process of glycerine.[11, 12]

The availability of DHA from renewable resources makes this triose an attractive potential building block for a range of new polymeric bio-materials such as polycarbonates and polyesters.

The chemistry of DHA is surprisingly versatile since it reacts intermolecularly to form the hemiacetal dimer[13] and conversion from the dimer into the monomer occurs in mild conditions (Figure 3.4.1,b).[14]

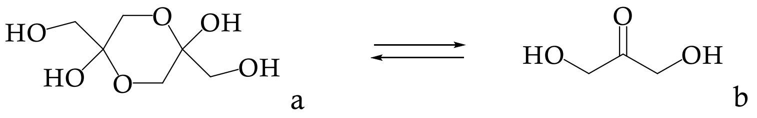
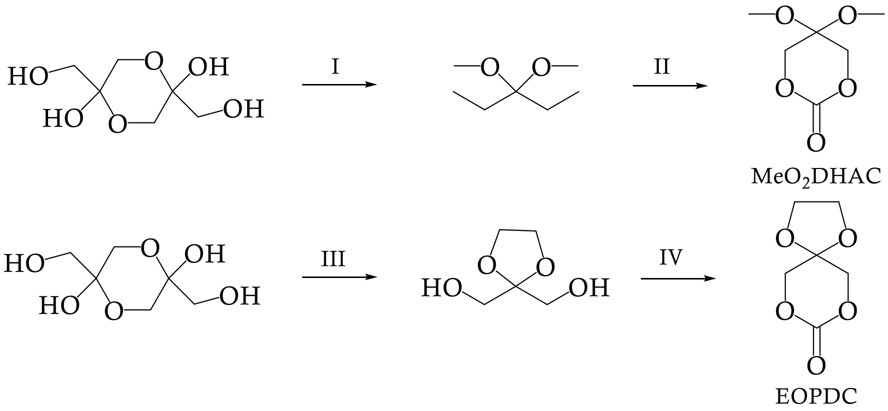


Figure 3.4.1.: Dihydroxyacetone (DHA) in the dimer (a) and monomer form (b).

Both of these forms possess OH groups which are available for polycondensation reactions leading to polymers bearing different structures.

Cyclic ketone-protected carbonate derivatives of DHA are used to synthesize homopolymers, random copolymers and diblock copolymers via ring-opening polymerization (ROP) with a variety of catalyst/initiator combinations.[15] ROP is a highly effective and widely used technique to generate polyesters, polycarbonates, polyamides, polyethers, and others.[16] Two cyclic ketone-protected DHA derivatives are used for ROP: 2,2-dimethoxypropylene carbonate (MeO_2DHAC, Figure 3.4.2,a)[17] and 2,2-ethylenedioxypropane-1,3-diol carbonate (EOPDC, Figure 3.4.2,b).[18, 19]



I. Trimethyl orthoformate, p-toluenesulfonic acid and methanol, followed by sodium carbonate.
II. Performed through three different methods involving trisphosgene,[17] ethyl chloroformate,[17] or oxidative carbonylation.[20]
III. p-toluenesulfonic acid, glycol, and benzene.
VI. triphosgene, pyridine, and dichloromethane.[18]

Figure 3.4.2.: Synthetic scheme to MeO$_2$DHAC (a) and to EOPDC (b).

The major drawback related to this approach resides in the keton protection step.[16] Ketone protection generally takes several days depending on the desired level of purity of the final product and generates low yields.[16] Furthermore, common protection strategies until now proposed employ toxic regents and solvents (trisphosgene, ethyl chloroformate, pyridine and benzene). For these reasons, the ability to directly esterify DHA without first protecting the ketone group is an attractive feature for the future of DHA-based macromolecules.

In 1969, Schreck et al. and Lasslo et al. showed that esters of DHA which retain the ketone functional group can be synthesized using acyl chloride compounds, such as undecanoyl chloride, in the presence of pyridine.[21-23] The goal of their studies was to develop sustained release mosquito repellent technologies in which DHA would anchor the compound to the skin, then degradation would lead to release of the active repellent molecule.[23] In 2010, Putnam and Yazdi showed that lipid diesters of DHA synthesized through these methods can be formulated into microparticles and are promising controlled release drug delivery vehicles.[24]

3.4.2. Aim of the work

The first of the objectives of this work consisted in developing an hydrogen transfer model reaction between a fatty acid with ketone functionalities in its carbon backbone and glycerol. This reaction by-product was DHA. It was decided to take into account this system because such approach could be a general strategy to be applied to natural oils; all of them are, in fact, naturally rich in double bonds that can be easily transformed into ketone groups to obtain polyalchols suitable for polyurethane synthesis. The second part of the research project consisted in exploiting the by-product DHA both in the monomer and in the dimer forms to get new totally bio-based polycarbonates and polyesters by reacting it respectively with carbonates and diesters from natural resources.

3.4.3. Results and discussion

1st part: Set up of the hydrogen transfer model reaction

Ketone methyl stearate was employed as model compound for the reaction reported in Figure 3.4.3.

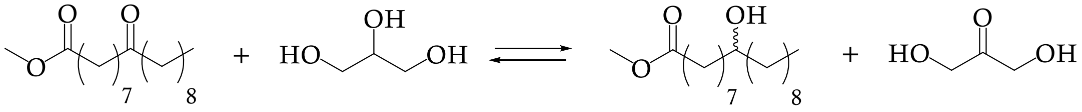


Figure 3.4.3.: Hydrogen transfer model reaction between a fatty acid with ketone functionalities in its carbon backbone (methyl stearate) and glycerol.

It derives from the Wacker oxidation of methyl oleate, obtainable through selective transesterification of triolein (representing 4-30% of olive oil)[4] with methanol.[25]

Many attempts were made and many operating parameters were varied:

- Ketone methyl stearate:glycerol ratio: 1:20, 1:43, 1:16 and 1:20;
- Solvents: no one, DMAC (dimethylacetamide), n-propanol, DMSO (dimethyl sulfoxide);
- Catalysts: Ru (Shvo) (Shvo ruthenium catalyst), Ru cymene
- Catalyst mol%: 10 and 5
- Co-catalysts: KOH, KOH and NaOH, no one
- Co-catalyst mol%: 15, 2, 10 or 5

- Temperature (°C): 70, 100, 80 and 60
- Time (h): 24, 3 and 30

All the parameters studied are summarized in Table 3.4.1.

Ketone methyl stearate	**Glycerol**	**Solvent**	**Catalyst**	**Cat (mol%)**	**Co-catalyst**	**Co-cat. (mol%)**	**T (°C)**	**Time (h)**
1	20	-	Ru (Shvo)	10	KOH	15	70	24
1	20	-	Ru (Shvo)	5	KOH, NaOH	2	70	3
1	20	-	Ru cymene	5	KOH, NaOH	2	70	3
1	43	-	Ru (Shvo)	5	KOH	10	100	24
1	43	-	Ru (Shvo)	5	KOH, NaOH	5	80	24
1	43	-	Ru cymene	5	KOH, NaOH	5	80	24
1	16	DMAC	Ru cymene	5	-	-	70	24
1	20	n-propanol	Ru cymene	5	-	-	60	30
1	20	DMAC	Ru cymene	5	-	-	60	30
1	20	DMSO	Ru cymene	5	-	-	60	30

Table 3.4.1.: All reaction conditions for the model reaction setting up.

Unfortunately, in all cases starting material conversion values were low (<5%) and reactions were directed towards the formation of an acetal resulting from the reaction between the fatty acid carbonyl group and glycerol. It meant that hydrogen transfer from glycerol did not occur easily, only in small percentages, even in the presence of catalysts.

In order to better understand the reaction mechanism, acetone was employed as simples system (Figure 3.4.4.).

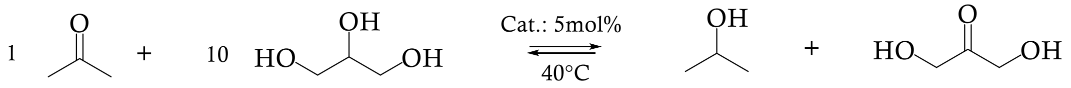


Figure 3.4.4.: Hydrogen transfer model reaction between acetone and glycerol.

Two reactions were performed by keeping unvaried all parameters except for the catalyst employed. More into detail, acetone:glycerol ratio was 1:10, temperature of 40°C and reaction time of 72 hours. Ru(cymene) and Ru(Shvo) were employed as catalysts with 5 mol%.

Also in this case no results were collected.

This fact pointed out that this specific system was more complex than initially expected, and, under the present conditions, it did not lead to relevant results for continuing working with the current approach.

In the light of these considerations, it was decided to abandon this topic and to focus on the preparation of novel bio-based polycarbonates and polyesters from DHA both in the monomer and in the dimer forms and carbonates and diesters from natural resources, respectively. Also this search pattern exhibits interesting features, given the possibility to obtain totally bio-based polymers.

2nd part: Synthesis of new bio-based polymers from DHA

DHA in the dimer form (DHA-D)

With the purpose of exploiting DHA as renewable monomer, the commercial dimer (DHA-D), was reacted with dimethyl carbonate (DMC), representing a bio-based building block for many chemical synthesis reactions (Figure 3.4.5.).[26-28]

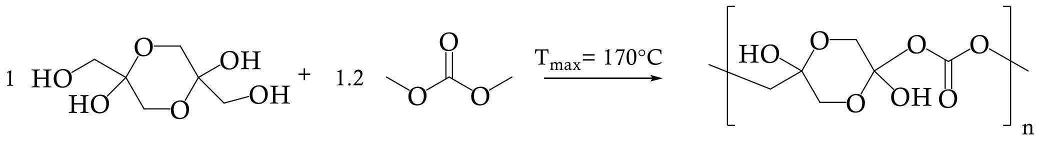


Figure 3.4.5.: Polymerization scheme between DHA-D and DMC.

Polymerization results are summarized in Table 3.4.2. M_n stands for number average molecular weight, while M_w for weight average molecular weight.

Entry	**Catalyst (5mol%)**	**$M_n \cdot 10^{-3}$ ($g\ mol^{-1}$)**	**$M_w \cdot 10^{-3}$ ($g\ mol^{-1}$)**
1	TBD	3.68	3.86
2	$Sn(Oct)_2$	/	/
3	TTIP	/	/

Table 3.4.2.: Polymerizations between DHA-D and DMC.

All polymerizations were carried out with a DHA-D:DMC ratio equal to 1:1.2 and by setting 170°C as maximum temperature, the varied parameter considered was the catalyst type. Two metal based catalysts were employed, i.e. titanium isopropoxide (TTIP) and stannous octoate ($Sn(Oct)_2$), and a coupling agent, triazabicyclodecene (TBD). All of them were inserted with a mol% equal to 5. TBD allowed to achieve M_w equal to 3,680 g mol^{-1}, corresponding to a D_p (degree of polymerization) of 17. This result demonstrated that, in this case, a coupling agent led to polycondensation.

DHA in the monomer form (DHA-M)

DHA in the monomer form (DHA-M) was polymerized with different chain length diesters to test the influence of the polar group coming from DHA in longer or shorter non-polar segments. These diesters were malonic acid dimethyl ester (M), glutaric acid dimethyl ester (G), suberic acid dimethyl ester (S) and a C_{22} dimethyl ester exhibiting a double bond on its C_9 and C_{10} positions (called C22 for simplicity). It came from the self-metathesis reaction of methyl 10-undecenoate, a castor oil derived platform chemical[29] (Figure 3.4.6.).

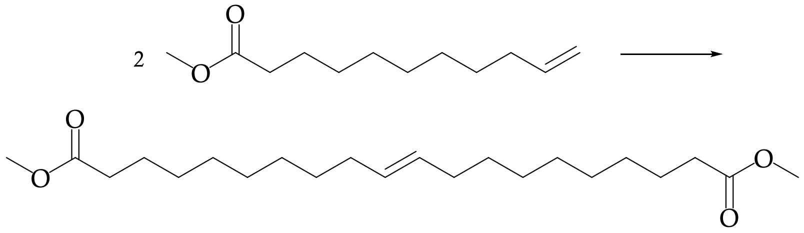


Figure 3.4.6.: Self-metathesis reaction to form C22.

Also the polymerization of DHA-M with DMC was carried out.

○ Polymerization of DHA-M + dimethyl carbonate (DMC)

Reaction between DHA-M and DMC is reported in Figure 3.4.7.

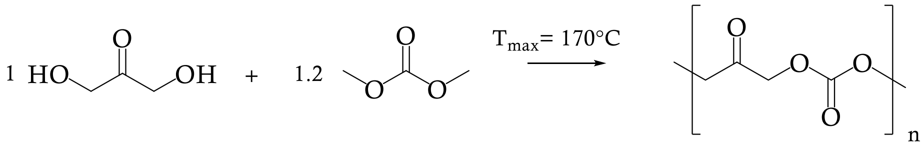


Figure 3.4.7.: Polymerization scheme between DHA-M and DMC.

As displayed in Figure 3.4.7., DHA-M:DMC ratio was 1:1.2 and maximum temperature of 170°C. The varied parameters also in this case was catalyst type. Results are listed in Table 3.4.3.

Entry	**Catalyst (5mol%)**	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**
1	TBD	4.81	6.30
2	$Sn(Oct)_2$	/	/
3	TTIP	/	/

Table 3.4.3.: Polymerizations between DHA-M and DMC.

Also in this case, TBD demonstrated to be the best catalyst, since it allowed to obtain reasonable molecular weights (corresponding to a D_p of 42) and $Sn(Oct)_2$, while TTIP did not ensure any polymerization result.

Coupling agents resulted as the most suitable catalysts for the preparation of polycarbonates. For the preparation of polyesters, both metal-based catalysts and coupling agents were investigated. For example for metal catalysts, TTIP was considered.

Other polymerizations aimed at obtaining polyesters, are summarized in Figure 3.4.8.

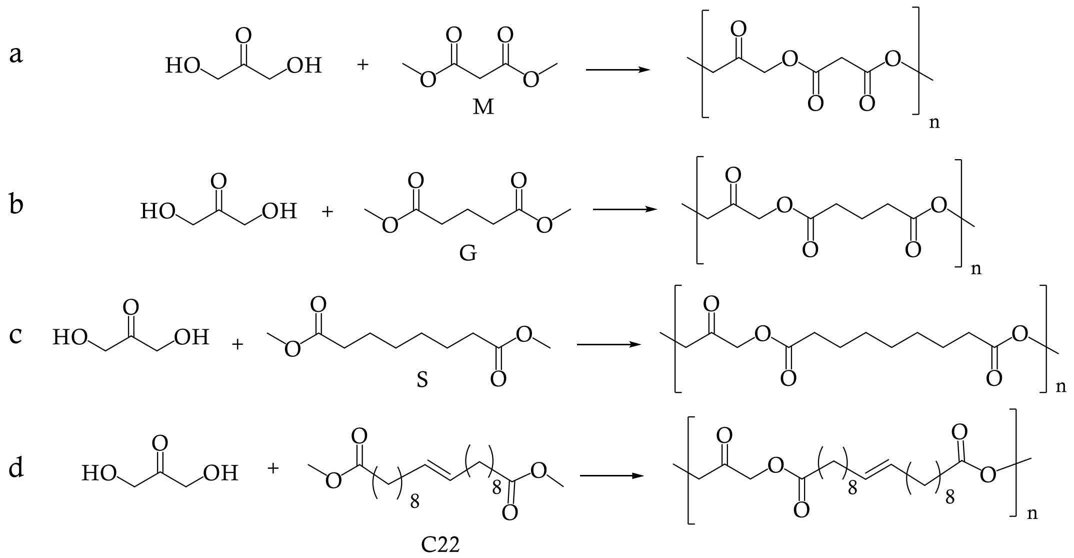


Figure 3.4.8.: Polymerization schemes between DHA-M and M (Figure 7, a), G (Figure 7,b), S (Figure 7, c) and C22 (Figure 7, d).

All these polymerizations were performed with a 1:1 ratio between the reactants.

- Polymerization of DHA-M + dimethyl malonate (M) (Figure 3.4.8,a)

First polymerization attempts were carried out with the shorter of the diesters considered, i.e. M. It derives from malonic acid, in turn obtainable from sugar.[30] The polymerizations parameters and subsequent results are reported in Table 3.4.4.

Entry	**Maximum temperature (°C)**	**Catalyst**	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**
1	180	TTIP (1 mol%)	/	/
2	120	TBD (5 mol%)	6.60	11.5

Table 3.4.4.: Polymerizations between DHA-M and M.

As for polycarbonates, differently from TTIP, TBD conducted to a polymerization.

- Polymerization of DHA-M + dimethyl glutarate (G) (Figure 3.4.8,b)

Glutaric acid, molecule from which G derives, can be prepared by the ring-opening of butyrolactone, a compound found in extracts of samples of unadulterated wines.[31]

Table 3.4.5. shows molecular weights achieved with different catalysts types and amounts.

Entry	**Maximum temperature (°C)**	**Catalyst**	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**
1	180	TTIP (1 mol%)	/	/
2	120	TBD (5 mol%)	6.19	11.4

Table 3.4.5.: Polymerizations between DHA-M and G.

Exactly as when M was employed, TBD allowed to obtain a polymer, while TTIP did not conduce to any result.

- Polymerization of DHA-M + dimethyl succinate (S) (Figure 3.4.8,c)

S is the dimethyl ester of suberic acid, which is formed from the action of nitric acid on cork.[32] Also for polymerization of DHA-M with G, TTIP and TBD were tested (Table 3.4.6.).

Entry	**Maximum temperature (°C)**	**Catalyst**	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**
1	180	TTIP (1 mol%)	/	/
2	120	TBD (5 mol%)	6.60	11.5

Table 3.4.6.: Polymerizations between DHA-M and S.

Also in this case, TBD was the only catalyst capable of guaranteeing a polymerization process.

- DHA-M + C_{22} dimethyl ester (C22) (Figure 3.4.8,d)

It was decided to employ C22, beside, of course, its natural origin, because its double bond was found interesting for eventual further chemical modifications. In this case, the use of a solvent was mandatory: without it, no miscibility could be guaranteed, given the great difference in polarity between the two reactants. For this reasons, all these polymerizations were performed in solvents. They were DMSO, dimethylformamide (DMF) and acetone (in this case, since high temperatures were achieved, reaction was conducted in a pressured reaction tube). All reaction conditions are summarized in Table 3.4.7.

Entry	**Solvent (2M)**	**Maximum temperature (°C)**	**Catalyst**	**$M_n \cdot 10^{-3}$ (g mol^{-1})**	**$M_w \cdot 10^{-3}$ (g mol^{-1})**
1	DMSO	150	TBD (5 mol%)	/	/
2	DMSO	150	TTIP (1 mol%)	/	/
3	DMF	150	TBD (5 mol%)	/	/
4	DMF	150	TTIP (1 mol%)	/	/
5	Acetone	120	TBD (5 mol%)	6.82	13.6
6	Acetone	120	TTIP (1 mol%)	10.3	32.7

Table 3.4.7.: Polymerizations between DHA-M and C22.

DMF and DMSO were chosen since they were able to dissolve both reagents and they were high boiling. Unfortunately, they did not lead to any polymer. Probably, they could not guarantee enough miscibility between the two reagents. For this reason, acetone was tested. With both catalyst, acetone led to a polymerization and, surprisingly, TTIP in this case conducted to higher molecular weights with respect of TBD.

The results for polyesters obtained from DHA-M and M, G, S and C22 demonstrated that a coupling agent, TBD, lead to good results when DMC and shorts diesters were used, while TTIP was required for the obtainment of polyesters from longer diesters.

3.4.4. Conclusions

The development of an hydrogen transfer model reaction between a fatty acid with ketone functionalities in its carbon backbone and glycerol was not possible since only small conversions in the wanted product were observed. However, polyesters and polycarbonates starting from DHA were obtained. TBD was an efficient catalyst, both for the preparation of polycarbonates and for polyesters starting from short diesters. TTIP was more suitable for longer diesters. It was also observed that homogenizing solvents promote polycondensations between monomers with different polarity. The platform of glycerol derivatives has been enlarged by developing new routes of valorization of DHA to produce new families of bio-based polymers. In the future, a deeper characterization on the produced polymers will be performed and correlations between structure and properties will be carried out.

3.4.5. Experimental

Materials

Dihydroxyacetone (DHA), dimethyl carbonate (DMC), triazabicyclodecene (TBD), tin(II)2-ethylhexanoate ($Sn(Oct)_2$), titanium isopropoxide (TTIP), boron trifluoride etherate, Ru (Shvo) (Shvo ruthenium catalyst), Ru cymenedimethylacetamide (DMAC), n-propanol, dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and acetone were purchased from Aldrich Chemical. All materials had high purity and were used as received.

Keton methyl stearate was synthetized from methyl oleate (purchased from Sigma Aldrich) through Wacker oxidation.

Malonic acid dimethyl ester (M), glutaric acid dimethyl ester (G) and suberic acid dimethyl ester (S) were synthetized starting from malonic acid, glutaric acid and suberic acid that were furnished by Aldrich Chemical.

C_{22} dimethyl ester exhibiting a double bond on its C_9 and C_{10} positions (C22) was prepared from methyl 10-undecenoate.

Hydrogen transfer model reaction between methyl stearate and glycerol

312 mg (1 mmol) of methyl stearate were placed in a 25 mL Schlenk tube equipped with a magnetic stirrer together with glycerol (20, 43 or 16 or 20 mmol), 6.66 mmol of the solvent (if present), 10 or 5 mol% of the catalyst (Ru(Shvo) or Ru cymene), 15, 2, 10 or 5 mol% of co-catalyst (KOH or KOH and NaOH, when present) and

the contents was heated to 70, 100, 80 or 60°C for 24, 3 or 30 hours under argon flux. All the reactions performed are summarized in Table 3.4.1.

Hydrogen transfer model reaction between acetone and glycerol

58.1 mg (1 mmol) of acetone were introduced in a 25 mL Schlenk tube equipped with a magnetic stirrer together with glycerol (921 mg, 10 mmol), Ru(Shvo) or Ru cymene (5 mol%). The flask contents was heated to 40°C for 72 hours under argon flux.

Conversion of DHA-dimer into DHA-monomer

10 mmol (0,9008 mg) of DHA in the dimer form was placed in 1 mL of acetone in a 10 mL Schlenk tube equipped with a magnetic stirrer with 0.1 mmol (14.2 mg) of boron trifluoride etherate. The solution was vigorously stirred at room temperature for 30 minutes.

Polymerizations

¤ *DHA-dimer with dimethyl carbonate (DMC)*

1 mmol (180.2 mg) of DHA in the dimer form were placed together with 1.2 mmol (108.1 mg) of DMC and 5 mol% of TBD, $Sn(Oct)_2$ or TTIP in a 10 mL Schlenk tube equipped with a magnetic stirrer. The flask contents was kept for 1 hour and 30 minutes at 70°C and then for 1 hour at 120°C under Argon flux. The temperature was then increased to 150°C, the mixture was kept at this temperature for 4 hours and at 170°C for 17 hours under high vacuum.

¤ *DHA-monomer with DMC*

1 mmol (90.1 mg) of DHA in the monomer form was placed together with 1.2 mmol (108.1 mg) of DMC and 5 mol% of TBD, $Sn(Oct)_2$ or TTIP in a 10 mL Schlenk tube equipped with a magnetic stirrer. The flask contents was kept for 1 hour and 30 minutes at 70°C and then for 1 hour at 120°C under Argon flux. The temperature was then increased to 150°C and the mixture was kept at this temperature for 4 hours and at 170°C for 17 hours under high vacuum.

¤ *DHA-monomer with dimethyl malonate (M)*

1 mmol (90.1 mg) of DHA in the monomer form was placed together with 1 mmol (132.1 mg) of M and 5 mol% of TBD or 1 mol% TTIP in a 10 mL Schlenk tube equipped with a magnetic stirrer. The flask contents was kept for 2 hours at 120°C. When TBD was employed, temperature was kept at 120°C and the mixture subjected to high vacuum for 4 hours. When TTIP was used, the temperature was

increased to 140°C for 1 hour and then for at 160°C 1 hour under Argon flux; the mixture was then kept at this temperature for 2 hours and at 180°C for 2 hours under high vacuum.

¤ *DHA-monomer with dimethyl glutarate (G)*

1 mmol (90.1 mg) of DHA in the monomer form was placed together with 1 mmol (160.2 mg) of G and 5 mol% of TBD or 1 mol% TTIP in a 10 mL Schlenk tube equipped with a magnetic stirrer. The flask contents was kept for 2 hours at 120°C. When TBD was employed, temperature was kept at 120°C and mixture subjected to high vacuum for 4 hours. When TTIP was used, the temperature was increased to 140°C for 1 hour and then at 160°C for 1 hour under Argon flux; the mixture was then kept at this temperature for 2 hours and at 180°C for 2 hours under high vacuum.

¤ *DHA-monomer with dimethyl suberate (S)*

1 mmol (90.1 mg) of DHA in the monomer form was placed together with 1 mmol (202.3 mg) of S and 5 mol% of TBD or 1 mol% TTIP in a 10 mL Schlenk tube equipped with a magnetic stirrer. The flask contents was kept for 2 hours at 120°C. When TBD was employed, temperature was kept at 120°C and mixture subjected to high vacuum for 4 hours. When TTIP was used, the temperature was increased to 140°C for 1 hour and then for at 160°C 1 hour under Argon flux; the mixture was then kept at this temperature for 2 hours and at 180°C for 2 hours under high vacuum.

¤ *DHA-monomer with a C_{22} dimethyl ester exhibiting a double bond on its C_9 and C_{10} positions (C22)*

1 mmol (180.2 mg) of DHA in the monomer form was placed in a 10 mL Schlenk tube together with 1 mmol (368.6 mg) of C22 with 1 mL of DMSO, DMF or acetone, 5 mol% of TBD or 1 mol% of TTIP. When DMSO or DMF were used, the flask contents were heated to 120°C for 1 hour and at 150°C for 5 hours under Argon Flux; later temperature was kept at 150°C for 17 hours under high vacuum. When acetone was used, temperature was gradually increased from room temperature to 120°C and kept at this value for 7 hours. Later high vacuum was applied for 26 hours.

Special cups were employed when acetone was tested because of the high temperatures achieved.

Characterization

GPC measurements were performed with a Tosoh EcoSEC HLC-8320 SEC system with HFIP containing 0.1 wt.-% potassium trifluoroacetate as the solvent. The solvent flow was 0.40 mL min^{-1} at 30°C. The analysis was performed on a three column system: PSS PFG Micro precolumn (3.0 × 0.46 cm, 10.000 Å), PSS PFG Micro (25.0 × 0.46 cm, 1000 Å) and PSS PFG Micro (25.0 × 0.46 cm, 100 Å). The system was calibrated with linear poly(methylmethacrylate) standards (Polymer Standard Service, Mp 102 – 981 000 Da).

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4. Conclusions

4. Conclusions

The research activity carried out during the PhD was focused on the preparation of new polymeric structures starting from green monomers or following new strategic synthetic pathways. It was mainly focused on aromatic polymers, since aromatics units give rise to good mechanical and thermal properties to the macromolecular chains. However, aromatic building blocks are, at the moment, obtained from petrol. For example, polyethylene terephthalate (PET), is constituted by aromatic units and it is one of the most exploited traditional polymers worldwide, especially for food packaging. PET derives from terephthalic acid (TPA) and ethylene carbonate (EC); only EC can be readily obtained from natural resources, TPA is actually oil-based.

Different research projects were carried out calling upon two strategies that can be employed to prepare polymers from natural resources:

1) Development of synthetic processes to get traditional polymers (currently obtained from petroleum) from biomass;
2) Exploitation of monomers from biomass to prepare new polymeric structures that can substitute the synthetic ones, derived from petroleum, or having advances functionalities.

The first research project was based on strategy 1) and aimed at exploiting a Diels-Alder (DA) reaction to get p-toluic acid, TPA and therefore PET precursor, from biomass. A tuned DA reaction led to an aliphatic ring starting from bio-sorbic acid and bio-acrylic acid and, thanks to an aromatization process, p-toluic acid was obtained in high yield and purity. The DA reaction and the aromatization procedures were totally green. This route allowed milder conditions as compared to approaches previously reported in the literature, and therefore contributed to a sustainable production of 100% bio-PET.

The second research field referred to strategy 2) and it was focused to polyesters and copolyesters derived from vanillic acid (VA), an aromatic molecule extracted from lignin. These macromolecular structures exhibited a repeating unit similar to that of PET. VA phenolic group poor reactivity was overcome by an etherification reaction with bio-based ethylene carbonate, leading to polyethylene vanillate (PEV). PEV showed melting and glass transition temperatures (T_g) very similar to those of PET. However, it was brittle, and to overcome this problem copolyesters were prepared between PEV and PRA (polyricinoleic acid) and PEV and ε-PCL (ε-polycaprolactone) to both increase the poor mechanical properties of aliphatic structures and to reduce PEV brittleness. The new materials properties could be tuned by varying their composition and, in copolymers obtained from PRA, possible antibacterial properties were introduced.

The third research project consisted in exploiting the DA reaction between furans (F) (molecules readily and economically obtainable from a vast array of natural resources) and maleimides (M) to prepare copolymers through an innovative manner according to strategy 2). A copolymer was obtained in high yields starting from two polyesters synthetized from a diacidic monomer exhibiting a F-M DA adduct within its structure. The copolymer was prepared by exploiting the tendency of DA adducts to break at temperatures above 100°C and to recombine at lower temperatures. The success of the copolymerization was demonstrated through DSC analysis indicating that the T_g of the copolymer was between the T_gs of the initial polymers. In this case, the possibility to obtain materials exhibiting groups able to associate and dissociate in a reversible manner depending on the temperature was demonstrated: this property can be exploited for the production of self-mending and recyclable materials.

A fourth research project, carried out during the abroad period, was dedicated to the valorization of certain compounds in accordance with biorefinery principles. It was divided into two phases:

- In tuning an hydrogen transfer process between a fatty acid exhibiting a ketone functional group in its carbon chain and glycerol. This reaction, once developed, could let us obtain polyols for the preparation of polyurethanes directly from natural oils, naturally reach in double bonds. Furthermore, the reaction by-product, dihydroxyacetone (DHA), is an interesting ketone with alcoholic functionalities. DHA is available in the dimer form but it is converted into the monomer in mild conditions;
- In exploiting the byproduct DHA to obtain polycarbonates and polyesters completely innovative and bio-based. DHA both in dimer and in the monomer form was reacted with dimethyl carbonate, a bio-based carbonate, and different chain-lengths diesters from natural resources. A new strategy for exploiting DHA

for the production of polyesters and polycarbonates was found also by testing the effect of different parameters, such as temperature, solvent, type and quantity of the catalyst and so on.

Generally, it can be concluded that new synthetic routes to monomers, polymers and copolymers from biomass were studied to get completely renewable polymers (bio-PET), new bio-polymers that can replace PET even with advances functionalities (e.g. antibacterial properties), innovative bio-copolymers for self-mending materials and new polyesters and polycarbonates to make the most of byproducts of other reactions, according to biorefinery principles.

5. Acknowledgments

5. Acknowledgments

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