Preparation and characterization of biodegradable hyperbranched polymers via $A_2 + B_3$ polycondensation

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Abstract

Hyperbranched polymers (HBPs) are macromolecules with a large number of branches and, hence, a large number of end groups. Due to their highly branched three-dimensional structure, multi-functionalities, high solubility, low viscosity, unique chemical and physical properties as well as potential applications in numerous areas, HBPs have become a hot subject in both the academic and industrial research.

In the present work, linear aliphatic polycarbonates with different structures were firstly synthesized via classic two-step polycondensation of diols and eco-friendly dimethyl carbonate (DMC) using organo-catalysts. Based on these investigation results, a novel one-pot method to obtain linear and hyperbranched polycarbonates under relatively mild polymerization conditions was developed in the second part. Different from other works using toxic phosgene based carbonates to obtain hyperbranched polycarbonates, eco-friendly DMC was used in this work.

The use of renewable feedstock, such as vegetable oils, instead of petroleum in material science has drawn great attention in recent years. Trifunctional monomers, triols, trialdehydes and tricarboxylic acids, were successfully obtained from soybean oil and castor oil via ozonolysis process with high purity. Using these monomers, a variety of vegetable oil based hyperbranched polymers, such as hyperbranched polycarbonate (HBPC), polyester (HBPE), polyacetal (HBPA) and polyurethane (HBPU), were successfully synthesized.

The resulting linear and hyperbranched aliphatic polycarbonates were characterized by NMR spectroscopy, size exclusion chromatography (SEC), differential scanning calorimetry (DSC) as well as ESI-ToF-mass spectrometry. Moreover, the hydrolytic and enzymatic degradation for linear and hyperbranched polycarbonates were evaluated under various conditions. All HBPs in this work have potential applications for preparation of biodegradable cross-linked materials.

Kurzzusammenfassung

Bei hochverzweigten Polymeren (HBPs) handelt es sich um Makromoleküle mit einer hohen Anzahl von Verzweigungen und damit einer Vielzahl von Endgruppen. Aufgrund ihrer hochverzweigten, dreidimensionalen Struktur, Multifunktionalitäten, hohen Löslichkeit, niedrigen Viskosität, einzigartig chemischen und physikalischen Eigenschaften und zahlreichen Anwendungsmöglichkeiten in unterschiedlichen Bereichen, rückten jüngst HBPs ins Zentrum der akademischen und industriellen Forschung.

In der vorliegenden Arbeit wurden lineare aliphatische Polycarbonate mit verschiedenen Strukturen zunächst via klassischer zweistufiger Polykondensation von Diolen und umweltfreundlichem Dimethylcarbonat (DMC) in Anwesenheit von Organo-Katalysatoren synthetisiert. Gemäß den Untersuchungsergebnissen wurde eine neue Eintopf-Methode für die Herstellung der linearen und hochverzweigten Polycarbonate unter milden Polymerisationsbedingungen entwickelt. Im Gegensatz zu anderen Arbeiten wurde DMC statt des toxischen Phosgens in dieser Arbeit verwendet.

Der Einsatz von nachwachsenden Rohstoffen, wie Pflanzenöle, anstelle von Erdöl in der Materialwissenschaft hat große Aufmerksamkeit in den letzten Jahren auf sich gezogen. Trifunktionelle Monomere, Triole, Trialdehyde und Tricarbonsäuren, mit hoher Reinheit sind via Ozonolyse von Pflanzenölen erhalten worden. Unter Verwendung dieser Monomere wurden eine Vielzahl von pflanzenölbasierten hochverzweigten Polymeren, z.B. hochverzweigte Polycarbonate (HBPC), Polyester (HBPE), Polyacetale (HBPA) und Polyurethane (HBPU) erfolgreich synthetisiert.

Die resultierenden linearen und hyperverzweigten aliphatischen Polycarbonate wurden durch NMR-Spektroskopie, Größenausschlusschromatographie (SEC), dynamische Differenzkalorimetrie (DSC) und ESI-ToF-Massenspektrometrie charakterisiert. Darüber hinaus wurden die hydrolytischen und enzymatischen Abbauprozesse für lineare und hochverzweigte Polycarbonate unter verschiedenen Bedingungen untersucht. Alle HBPs haben potenzielle Anwendungen für die Herstellung von biologisch abbaubaren, vernetzten Materialien.

„Challenges make life interesting, however, overcoming them is what makes life meaningful.” – Mark Twain, Writer

Contents

1 Introduction

1.1 Statement of problem

The use of renewable feedstock instead of petroleum in material science has been drawn great attention in recent years. Nowadays, approximately 7% of all oil and gas worldwide used is consumed by producing polymeric materials (from petroleum based non-renewable raw materials). From the points of sustainable development, there is urgent need to develop renewable raw materials for preparation of polymeric materials.[1-3] Recently, a variety of renewable feedstocks, such as vegetable oils, wood, proteins and polysaccharides was used to prepare polymers.[4,5] Among them, vegetable oils have begun to attract a lot of attention in polymeric material science due to their relatively low cost, low toxicity, worldwide availability, inherent biodegradability and versatile functionality.[6,7] In recent 10 years, the annual global vegetable oil production rose from 149 million tons (in 2005/2006) to 210 million tons (in 2015/2016) (an increase of 41%) based on the data released from Food and Agriculture Organization of the United Nations (FAO), and about 19% of vegetable oil production was consumed by industry.[8] Different types of biodegradable polymers such as polyesters, polyanhydrides, polyesteramides and poly(ester anhydrides) have been produced based on the vegetable oil platform. These polymers were mainly used for biomedical applications such as drug delivery system and tissue engineering. However, there are still few works concerning hyperbranched polymers synthesized from vegetable oil based monomers.[9-11]

Hyperbranched polymers (HBPs) are highly branched macromolecules with three-dimensional structure. HBPs have attracted significant attention in recent decades due to their unusual chemical and physical properties in comparison to linear polymers, such as good solubility in common solvents, low viscosity and good compatibility with other materials.[12-19] Employing the ozonolysis technology to cleave the carbon-carbon bonds in vegetable oils is an important and effective method to obtain trifunctional B_3 monomers with unique structures. These monomers can be used to synthesize hyperbranched polymers via $A_2 + B_3$ polycondensation.

According to this strategy, a variety of vegetable oil based HBPs with different biodegradability properties can be obtained by using various A_2 monomers.

1.2 Motivation and goal of the present work

Aim of the present work is the synthesis and characterization of hyperbranched polymers with different degradation properties from castor oil and soybean oil via ozonolysis pathway. In order to optimize the polymerization conditions and understand the mechanism of A_2 + B_3 polycondensation, this work was started with synthesis of linear and hyperbranched polycarbonates using different catalysts. Firstly, a series of organo-catalysts were synthesized for further applications. Using these catalysts, the synthesis of linear polycarbonates by a classic two-step polycondensation as model reaction was investigated to optimize the polymerization conditions. Based on the results of polycarbonates synthesis, hyperbranched polycarbonates were then prepared from commercially available triols and eco-friendly dimethyl carbonate using a novel one-pot polycondensation. In the third part, tiols, trialdehydes and tricarboxylic acids as B_3 monomers were synthesized from soybean and castor oils via ozonolysis. Using these B_3 monomers, a variety of HBPs, such as hyperbranched polycarbonate (HBPC), polyester (HBPE), polyurethane (HBPU) and polyacetal (HBPA), were obtained via A_2 + B_3 polycondensation.

Structures and properties of the resulting polymers were studied by nuclear magnetic resonance (NMR) spectroscopy, size exclusion chromatography (SEC) and differential scanning calorimetry (DSC). Electrospray ionization Time of Flight mass spectrometry (ESI-ToF-MS) was employed to investigate the structure and end group composition of linear poly(butylene carbonate) (PBC). Moreover, the hydrolytic and enzymatic degradation investigations for linear and hyperbranched polycarbonates were evaluated under various conditions as well.

2 Theoretical background

2.1 Hyperbranched polymers (HBPs)

Hyperbranched polymers (HBPs) are macromolecules with highly branched structures and a large number of end groups.[14] Due to their highly branched three-dimensional structure, multi-functionalities, high solubility, low viscosity, unique chemical and physical properties as well as potential applications in numerous areas, HBPs have become a hot subject in both the academic and industrial research.[13,14] The first hyperbranched macromolecule was obtained as a resin from tartaric acid and glycerol at the end of 19th century by Berzelius.[20] In the 1940s, the concepts of "degree of branching" and "highly branched species" were introduced by Flory et al.[21-25] In 1988, Kim and Webster prepared soluble hyperbranched polyphenylene and established the concept "hyperbranched polymer" for the first time.[26,27]

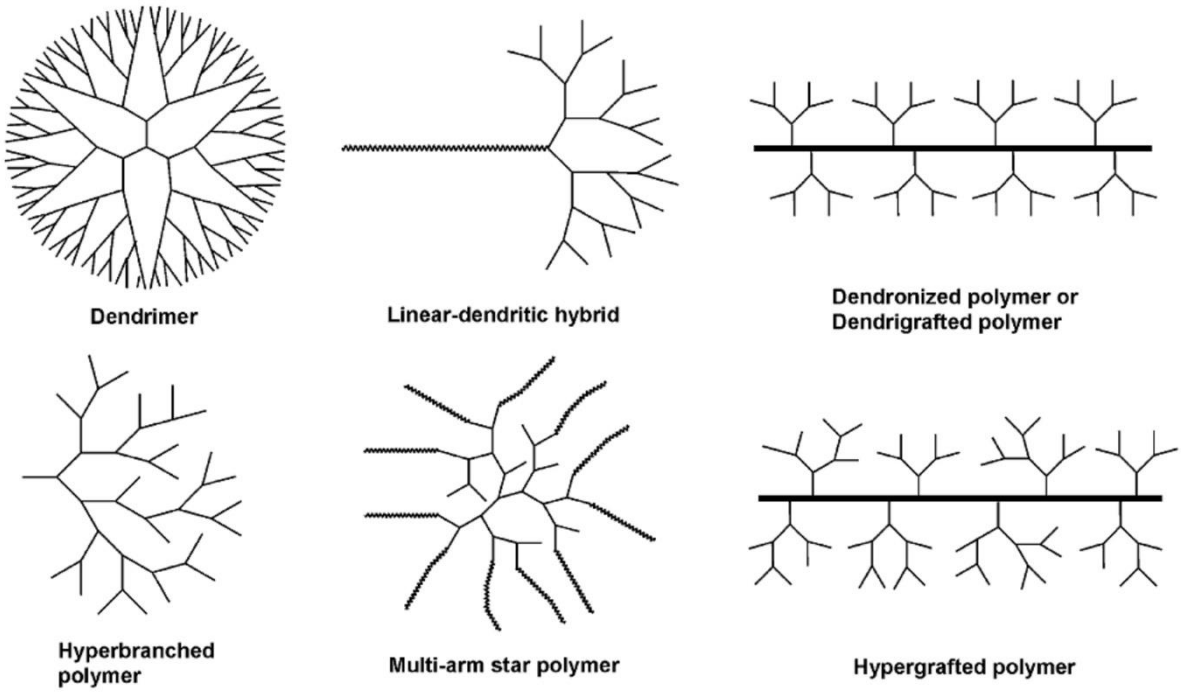


Figure 1. Schematic description of dendritic and hyperbranched polymers [Reprinted with permission from Reference 14, Copyright © 2004 Elsevier Ltd.]

According to the architecture features, dendritic and hyperbranched polymers are divided into six types (Figure 1): 1) dendrimers; 2) linear-dendritic hybrids; 3) dendridronized or dendrigrafted polymers; 4) hyperbranched polymers; 5) multi-arm star polymers and 6) hypergrafted polymers.[14] Unlike dendrimers, which have completely branched star-like topologies with degree of branching (DB) of 1.0, HBPs are composed of three types of structural units: dendritic units (D), linear units (L) and terminal units (T). The dendritic and linear units are randomly located in the polymer frameworks, while the terminal units are always placed at the terminals.[13,14]

HBPs are prepared mainly via the one-pot step-growth polymerization. Based on the different polymerization mechanisms, the synthetic techniques for preparation of HBPs can be classified into three categories: 1) the single-monomer methodology (SMM); 2) the double-monomer methodology (DMM) and 3) the couple-monomer methodology (CMM). The difference of these three methodologies are illustrated in Figure 2.[28]

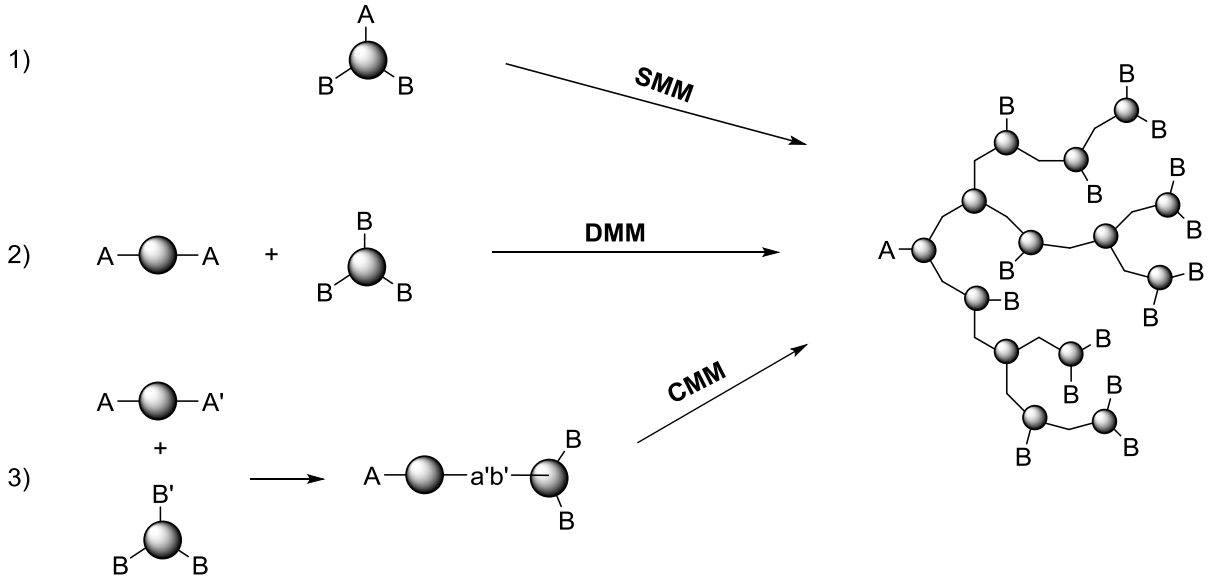


Figure 2. Illustration of three main methodologies for preparation of HBPs: 1) SMM, 2) DMM and 3) CMM. [Reproduced from Ref. 28 with permission from The Royal Society of Chemistry]

2.1.1 Synthesis of HBPs according to the single-monomer methodology (SMM)

The SMM involves the polymerization of an AB_n ($n \geq 2$) monomer via a one-step polycondensation. AB_n monomer contains one "A" functional group and two or more B functional groups. Reactions can be only taken place between A and B functional groups resulting in hyperbranched structures without gelation.[15] Many common types of polymerization techniques, e.g. the classic step-growth AB_n polycondensation and self-condensing ring-opening polymerization (SCROP) of latent AB_n monomers belong to the SMM family.[14,28]

The one-step polycondensation of AB_n has been widely applied for preparation of HBPs.[14,16,28,29] A series of HBPs, such as polyphenylenes[26,27,30-32], polyethers[33-41], polyesters[42-46], polycarbonates[47,48], polyamides[49-55] and polyurethanes[56-59], were prepared employing this methodology. The primary advantage of this strategy is that gelation caused by infinite network formation can be theoretically avoided as discussed by Flory.[60] However, gelation may take place when undesired side reactions (e.g. intermolecular or intramolecular transesterification) occur during the polymerization process or intermolecular hydrogen bonding is strong enough to form three-dimensional networks.[16,29]

The second strategy of SMM to prepare hyperbranched polyester or polycarbonate is the SCROP[14,28] or also called multibranching ring-opening polymerization (MBROP)[16]. The difference between SCROP and MBROP is that the MBROP is initiated by an additionally added compound and the branching points are formed during the propagation reaction (Figure 3a), while in the SCROP the polymerization can be initiated by a functional side group from monomer itself (Figure 3b). The first MBROP was reported by Suzuki in 1992 for producing hyperbranched polyamines from cyclic carbamate.[61]

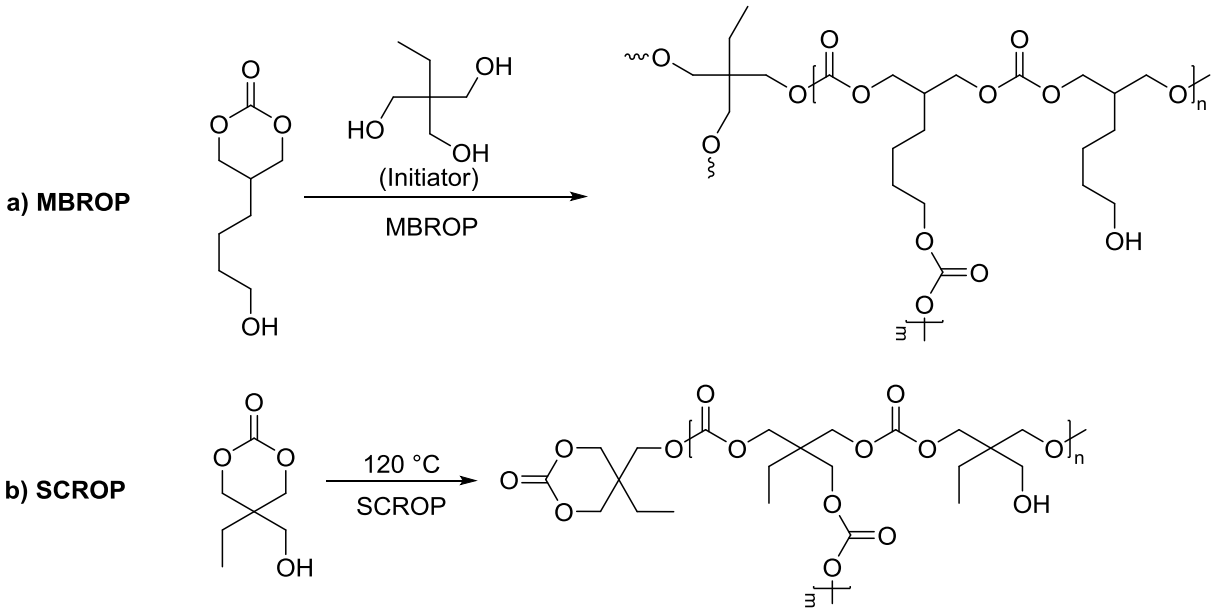


Figure 3. Schematic description of synthesis of HBPC via a) MBROP[18,64] and b) SCROP[62,63].

Hyperbranched aliphatic polycarbonate was prepared by Feng et al. using the SCROP of 5-ethyl-5-hydroxymethyl-1,3-dioxan-2-one (EHDO).[62,63] The polymerization was carried out at 120 °C in vacuo without catalyst. EHDO carried one hydroxyl side group and could be recognized as a latent AB_2 multifunctionalized monomer. The number-averaged molar masses (M_n) measured by SEC were 18300, 29100 and 33400 g/mol after 24, 48 and 72 h polymerization time, respectively. Moreover, gelation was observed in the polymerization process. The 72 h product was relatively difficult to dissolve in tetrahydrofuran (THF).

Another example for preparation of aliphatic hyperbranched polycarbonate was presented by Parzuchowski et al.[18,64] A tin(II) 2-ethylhexanoate catalyzed MBROP of 5-(4-hydroxylbutyl)-1,3-dioxan-2-one using trimethylolpropane (TMP) as initiator and core molecule gave a HBPC whose M_n and dispersity ($Đ_M$) determined by SEC were 4350 g/mol and 1.70, respectively. The chemical structure of the polymer was evaluated intensively by means of ^{1}H and ^{13}C NMR spectroscopy as well as matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-ToF-MS). The hydroxyl end groups of the HBPC were modified by reacting with trifluoroacetic anhydride. The modified HBPC displayed a good solubility in supercritical carbon dioxide due to the presence of numerous fluorinated end groups.

2.1.2 Synthesis of HBPs according to the double-monomer methodology (DMM)

The polymerization of A_2 + B_3 monomers is a classic example of DMM. The most important problem of this approach is how to control the polymerization, to avoid gelation and to obtain high molar mass. Commonly, soluble HBPs can be obtained by adjusting polymerization parameters including the ratio of functionalities, solvent, catalysts, regent purity and polymerization time and temperature.[14,28,29] DMM in synthesis of HBPC was recently reported by Nishikubo et al. concerning the synthesis of aromatic HBPC from di-*tert*-butyl tricarbonate (DBTC) and 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) as A_2 and B_3 monomers (Figure 4).[65] The resulting HBPCs had M_n up to 7000 g/mol and DB in the range of 0.52 – 0.78. However, DBTC is not commercially available and has to be prepared from hazardous triphosgene.

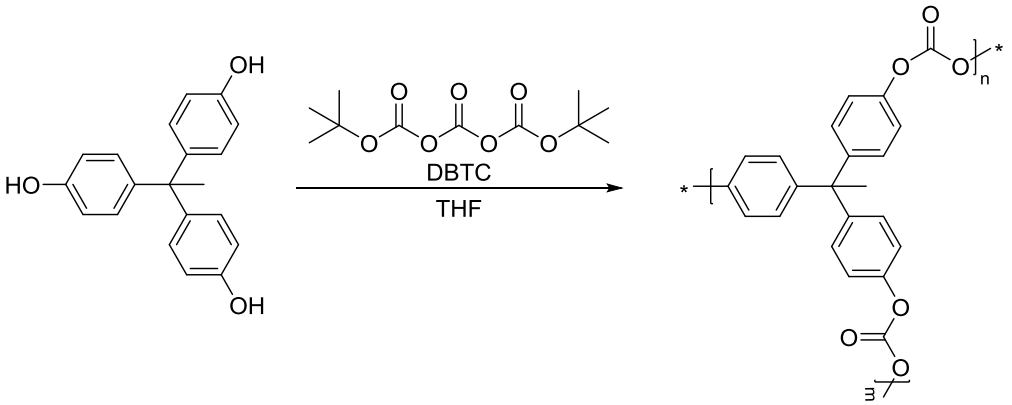


Figure 4. Synthesis of aromatic HBPC from DBTC and THBE using A_2 + B_3 polycondensation by Nishikubo et al.[65]

The CMM was invented by Gao and Yan[66,67], and DSM Research[68,69]. The basic principle of CMM is, that in the monomer couple A'A and B'B_2, A' has higher reactivity than A and B' is more active than B. In the initial state of polycondensation, fast coupling between A' and B' first take place and leads to an AB_2-like intermediate (A-a'b'-B_2) in situ, which can be subsequently polymerized in the manner of SMM. This approach combines the advantages of SMM and DMM and can produce HBPs with high molar mass without gelation.

2.2 Polycarbonates

Aromatic polycarbonates are widely used as engineering plastics because of their attractive mechanical properties, e.g. low moisture absorption, high impact strength, high elastic modulus, creep resistance and good thermal stability.[70-72] Aliphatic polycarbonate (APC) was firstly reported by Carother et al. around 1930.[73] Compared with traditional aromatic polycarbonates, APCs received little interest because of their poor thermal stability and high susceptibility to hydrolysis.[70,73-80] In recent years, however, aliphatic polycarbonates have attracted significantly increasing attention for biomedical applications, e.g., for the construction of biomedical implants and as drug delivery devices, due to their biodegradability, low toxicity and good biocompatibility.[81-90]

Currently, aliphatic polyester based materials are extensively applied in biomedical and pharmaceutical sciences.[91-94] These materials are known to degrade *in vivo* by bulk erosion process. However, the generated acidic degradation products would cause the local aseptic inflammation or living tissue injury and inactivate the loaded drugs.[95-100] In contrast, APCs undergo a surface erosion process with slower degradation rate and acidic degradation compounds are not present during the degradation process.

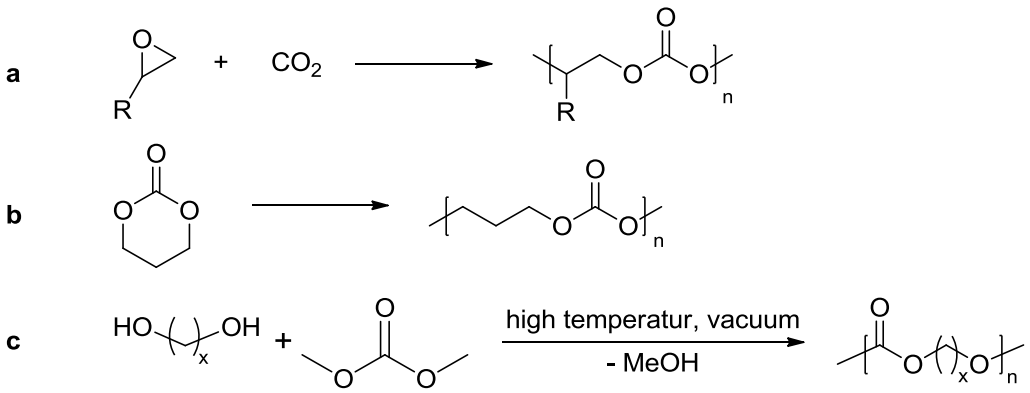


Figure 5. Three common methods for the preparation of aliphatic polycarbonates: a) copolymerization of carbon dioxide with epoxides; b) ring opening polymerization (ROP) of cyclic carbonate monomers; c) polycondensation between diols and dimethyl carbonate (DMC).[101]

APCs can be prepared through different methods, such as copolymerization of CO_2 with an epoxide (Figure 5a)[102-108], which is only suitable for the synthesis of aliphatic polycarbonates in which the carbonate linkages are connected by two carbon atoms, ring opening polymerization (ROP) of cyclic carbonate monomers (Figure 5b)[109-113] and polycondensation between dialkyl or diphenyl carbonate and aliphatic diols (Figure 5c).[114-121]

2.2.1 Copolymerization of carbon dioxide and epoxy

Due to the abundant resources, low-price and nontoxicity, carbon dioxide has become one of the most important sustainable raw materials for application in industrial process. The use of carbon dioxide for preparation of polycarbonate can be traced back to 1962.[118,122] Inoue et al. reported the enantioselective homopolymerization of racemic propylene oxide using a zinc-containing heterogeneous catalyst for the first time.[105,123,124] As the results of subsequent research, a number of homogeneous and heterogeneous catalyst systems have been reported, including aluminum-porphyrin complex[125], zinc-phenoxide derivatives[126], β-diiminate-zinc catalysts[127,128], chromium-salen catalysts[129-136], cobalt-salen catalysts[137-143] and aluminum salen catalysts.[144-149]

The mechanism of the copolymerization of carbon dioxide and epoxy using metal catalyst has been investigated deeply. A general mechanism is shown in Figure 6. The copolymerization is firstly started by the metal catalyzed ring opening of epoxy. Subsequently, the carbonate group is generated by CO_2 insertion into the metal-oxide bond. Two side reactions are often observed during the copolymerization. One side reaction is the generation of polyether chains by consecutive epoxide ring opening. These polyether chains are randomly located in polycarbonate backbone (Path A). The other side reaction is backbiting reactions resulting in the formation of cyclic carbonate by either dissociation of the central metal ion (Path B) or decopolymerization of the polycarbonate chain (Path C).[118,150]

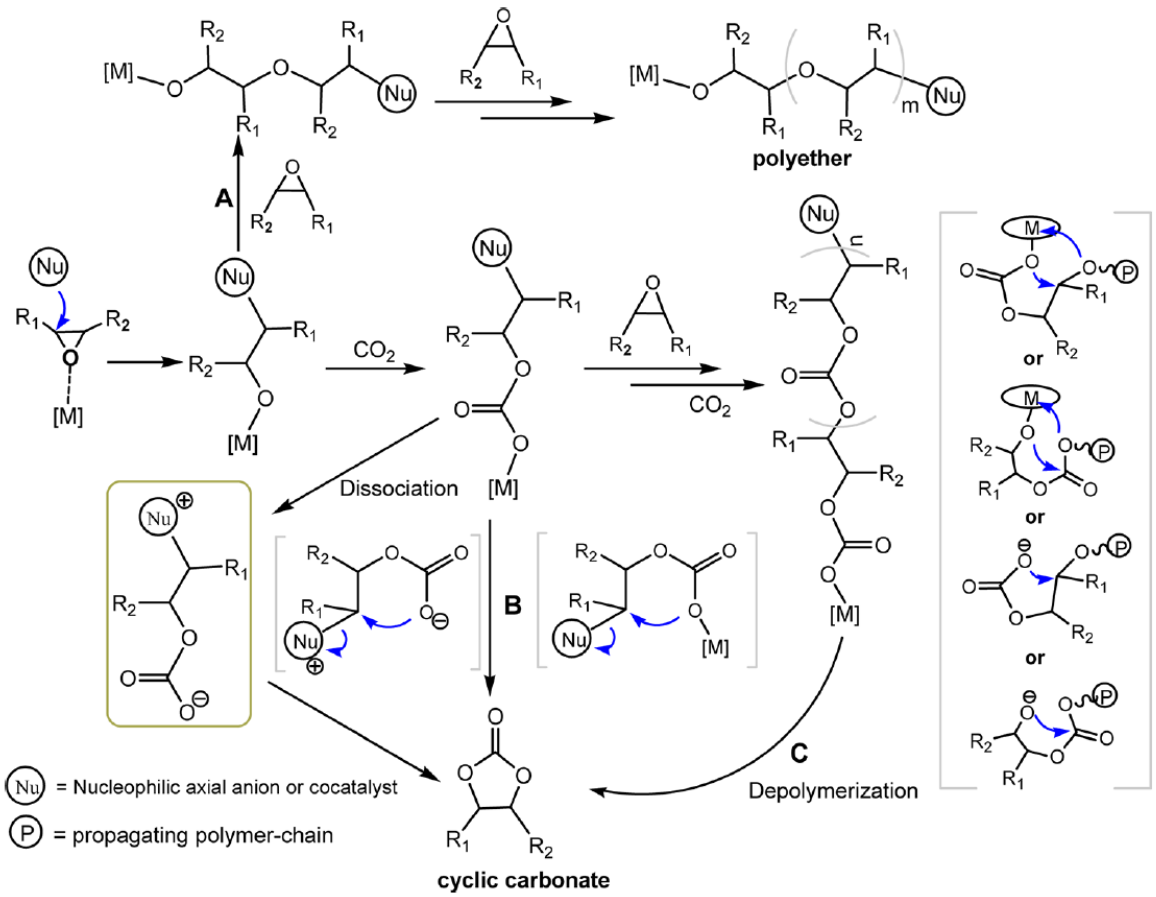


Figure 6. General mechanism of copolymerization of carbon dioxide and epoxy in the presence of metal catalysts.[150] [Reprinted with permission from Reference 150. Copyright 2012 American Chemical Society.]

Poly(cyclohexylene carbonate) was prepared in the initial studies and had a glass temperature (T_g) of 115 °C. However, this material has not found any practiced application due to its poor mechanical and physical properties in comparison to classic bis phenol A (BPA) based aromatic polycarbonate.[151] Another polycarbonate prepared based on this strategy is the biodegradable poly(propylene carbonate), which has a T_g of 40 °C and could be applied as a toughening agent for epoxy resins and sacrificial binder for ceramics.[152] Recently, a series of poly(propylene carbonate) based homopolymers or copolymers with built-in side chain functionalities, such as hydroxyl[153-155], epoxy[156] and aliphatic alkene[157] functional groups, were

successfully synthesized. These materials provide great possibilities in side group modifications for their potential applications (e.g. as biodegradable drug carrier).

2.2.2 ROP of cyclic carbonate monomers

The ring opening polymerization (ROP) of cyclic carbonates is one of the most effective methods to obtain polycarbonates with controlled molar mass, end groups, defined structure and low dispersity.[118,158] The Tin(II) bis(2-ethylhexanoate) ($Sn(Oct)_2$) has been widely used as effective catalyst for ROP.[159,160] However, the highly toxic tin compounds cannot be adequately removed from final polymer products.[161-163] Organo-catalyst could be used as an alternative to tin compounds. According to their chemical properties and catalytic mechanisms, organo-catalysts can be divided into three subclasses: 1) Lewis/Brönsted bases, 2) Brönsted acids and 3) bifunctional catalyst system combining a Lewis base and a hydrogen-bond donor.[164] Some basic organo-catalysts such as guanidines (1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0] dec-5-ene (MTBD))[165-168], amidines (DBU)[166], tertiary amines (dimethylaminoethanol (DMAE), 2-(dimethylamino)ethyl benzoate (DMAEB))[111] and N-heterocyclic carbenes (NHCs)[90] have been used in the ring opening polymerization of TMC and shown to yield poly(trimethylene carbonate) (PTMC) with a high molar mass, low dispersities and well-defined terminal groups. Among them, TBD and DMAP displayed the highest activities toward ROP of TMC with turnover frequency (TOF) of 49200 h^{-1} and 55800 h^{-1}, respectively.[111]

However, the strong nucleophilicity of TBD and DMAP enhances not only the polymerization rates but also the rates of competitive intermolecular or intramolecular transesterification side reactions, resulting in broader molar mass distributions and loss of end groups.[169] Hedrick[166,170] and Dixon[171] demonstrated that thiourea based bifunctional organo-catalysts effectively activated the ring opening polymerization of cyclic esters. Moreover, Hedrick reported that electrophilic thioureas and nucleophilic bases are not required to be linked in

the same molecule.[166] The mechanism of ROP of TMC using bifunctional catalyst system (DBU + thiourea (TU)) is shown in Figure 7.

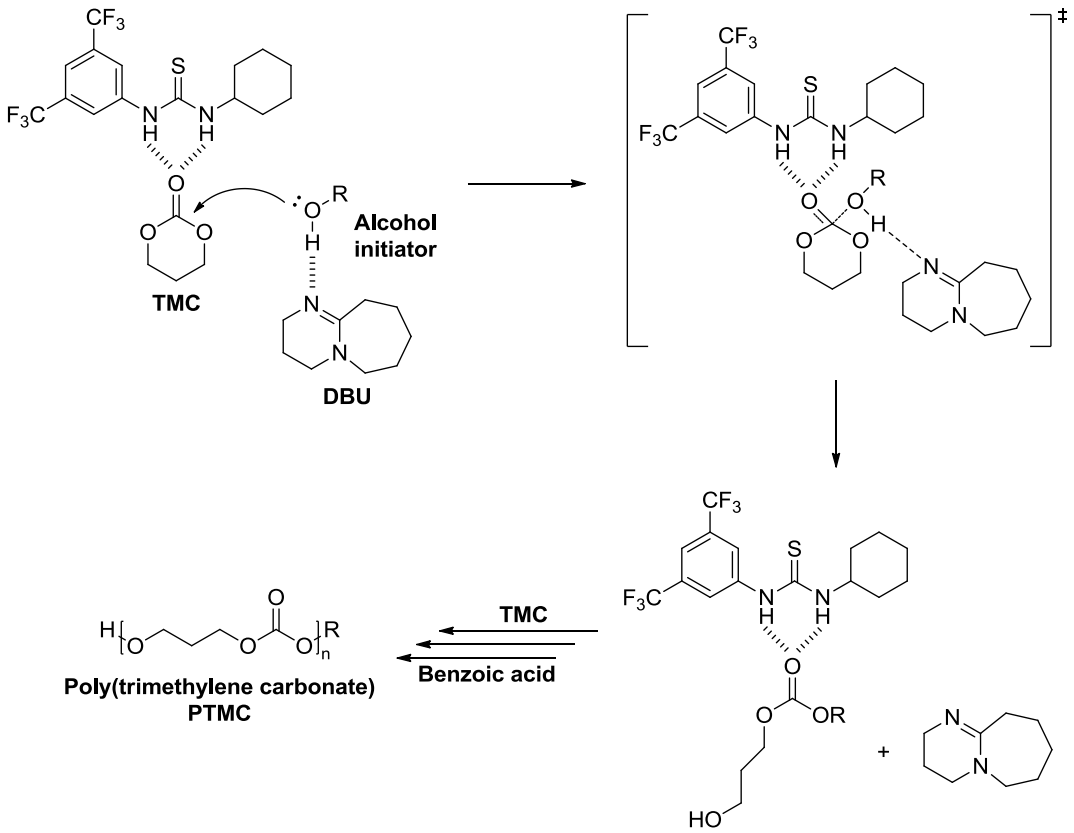


Figure 7. Base catalyzed ROP of 1,3-dioxan-2-one (TMC) using 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst and thiourea (TU) as cocatalyst.[158] [Adapted with permission from Reference 158. Copyright 2015 American Chemical Society.]

Firstly, the electrophilic carbonyl group of TMC is activated by hydrogen bonds from TU, while the alcohol initiator is activated by DBU. Then a ring opening reaction of TMC takes place by nucleophilic attack of the alcohol to the carbonyl group via a hydrogen-bonded tetrahedral intermediate, resulting a linear carbonate with a hydroxyl terminal group. The terminal hydroxyl group can be considered as alcohol initiator, which can be activated by DBU and attacks the TMC in a nucleophilic acyl-substitution reaction, and leads to chain propagation until chain termination with an acid (e.g., benzoic acid) occures.[158] The major advantage of using a bifunctional catalyst system are guaranteeing the polymerization rates and at the same

time enhancing the selectivity of the catalyst towards monomer propagation over transesterification side reaction.[169]

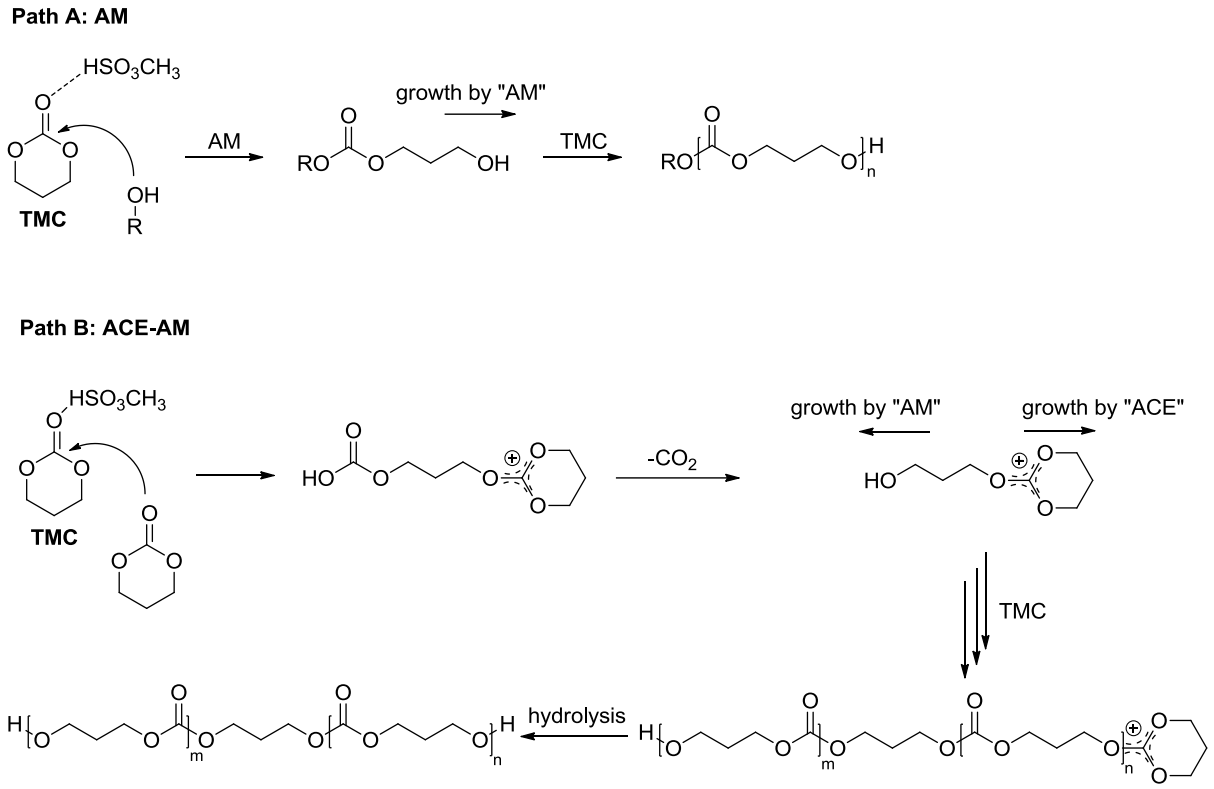


Figure 8. Mechanism of acid catalyzed ROP of TMC using methanesulfonic acid (MSA) as catalyst and alcohol as initiator. Path A: Activated Monomer (AM) mechanism (major) and Path B: Active Chain End (ACE) mechanism (minor)[164] [Adapted with permission from Reference 164. Copyright 2010 American Chemical Society.]

Moreover, the acidic organo-catalysts, diphenyl phosphate[109], triflic acid (TFA)[172], trifluoromethanesulfonic acid (HOTf)[164] and methanesulfonic acid (MSA)[164] showed also to promote ROP of TMC. As shown in Figure 8, the mechanism of acid catalyzed ROP of TMC has been discussed by Delcroix et al.[164] Two mechanisms were observed in the ROP process. The major mechanism was the activated monomer (AM) mechanism (Path A). Similar to the base catalyzed ROP, ring opening of TMC was firstly taken place by nucleophilic attack of alcohol to the carbonyl group activated by the acid catalyst and lead to formation of a hydroxyl terminated linear carbonate, which could act as initiator and repeat the same AM mechanism

resulting in chain propagation. Besides, a minor mechanism called active chain end (ACE) mechanism could be also envisaged (Path B). The ring opening of acid activated monomer was achieved by nucleophilic attack of another inactivated TMC monomer and give a bifunctional compound with one hydroxyl end group and an oxonium end group. The propagation process would then occur in both directions: hydroxyl terminal group initiated the AM mechanism and ACE mechanism proceeded from the oxonium chain end. The polymer obtained from the ACE-AM mechanism can be formally considered as result using 1,3-propanediol as initiator.
In addition, the ROP of TMC using lipases as eco-friendly enzyme catalysts have also been evaluated.[173-178] However, similar to acid catalysts, they showed less activity and poor control compared to basic organo-catalysts and bifunctional catalyst systems.

2.2.3 Polycondensation

ROP of cyclic carbonates is an effective strategy for preparation of polycarbonates. However, this strategy is only suitable for TMC based monomers and cyclic carbonate monomers are very expensive because of their low synthetic yields. Hence, polycarbonates from ROP have been mainly investigated for biomedical application.[119,179,180] The best strategy for large-scale preparation of aliphatic polycarbonates is the two-step polycondensation of carbonate compounds and aliphatic diols with more than three carbon atoms. Initially, toxic phosgene or its derivate were used as carbonate compounds. Later, considering the environmental pollution APCs were prepared using eco-friendly dialkyl carbonates (dimethyl carbonate and diethyl carbonate) instead of phosgene.[114]

The mechanism of polycondensation is shown in Figure 9. Oligomers with a molar mass lower than 1000 g mol^{-1} are obtained in the initial condensation step, due to the low equilibrium constant. In the second step, polymer chains propagated by transesterification between the hydroxyl and methyl carbonate or two methyl carbonate end groups in the presence of transesterification catalysts, while high temperature (about 200 °C) and high vacuum are required to remove unreacted monomers and freshly generated byproducts. The resulting

oligomers or polymers have three possible end group compositions, hydroxyl end groups, methyl carbonate end groups or a combination of both.[116-118]

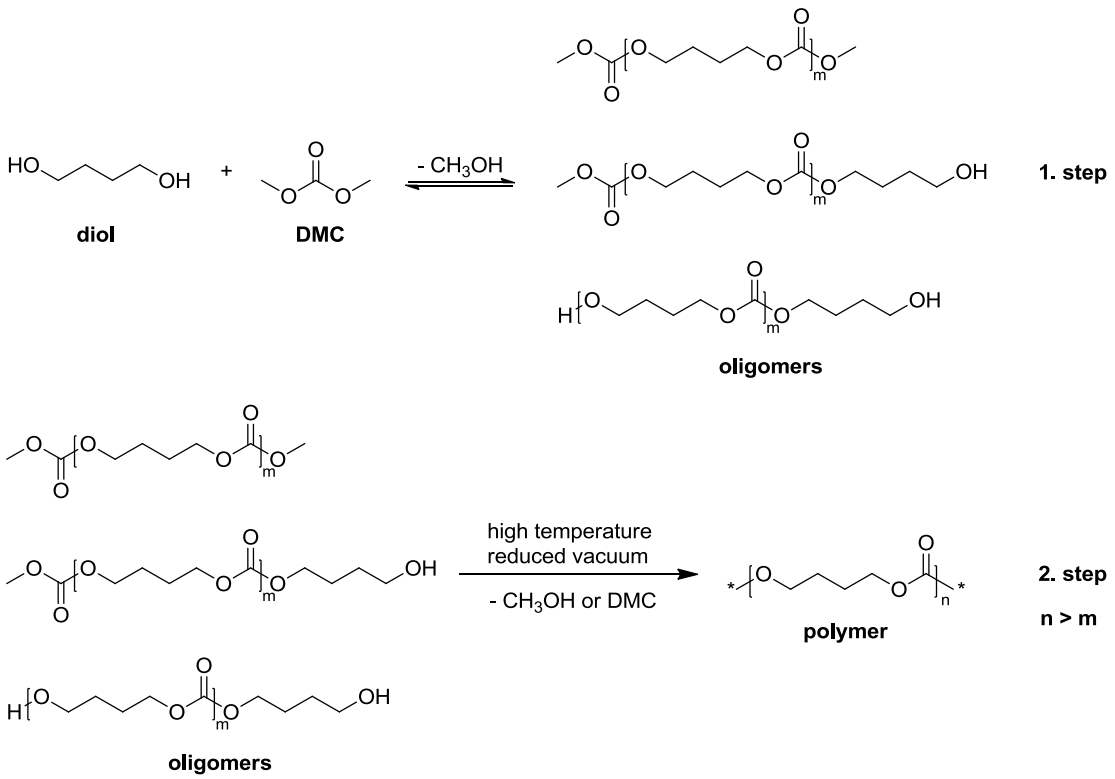


Figure 9. General method for the preparation of polycarbonates via a two-step polycondensation.

Metal based catalysts, organo-catalysts and enzymatic catalysts have been found to be effective in catalyzing the polycondensation of different diols and dialkyl carbonate. Recently, Li et al. have reported the preparation of polycarbonates with a high molar mass (M_n up to 94000 g mol^{-1}) using a novel TiO_2/SiO_2-poly(vinyl pyrrolidone)-based catalyst (TSP-44).[115] Lee et al. have used NaH as the catalyst to prepare aliphatic polycarbonates with a high molar mass (M_n up to 150000 g mol^{-1}) successfully with the prerequisite that the [–OH]/[–OCH_3] ratio of the oligomers generated in the transesterification step is about 1.0.[116] Picquet and Plasseraud described a route for the synthesis of aliphatic polycarbonates (M_n up to 7400 g mol^{-1}) using 1-*n*-butyl-3-methylimidazol-2- carboxylate (BMIM-2-CO_2) as a catalyst.[75] In contrast, the use of enzymatic catalysts can significantly reduce the operating temperature

and provide better control over branching. However, a high catalyst loading and a long reaction time are necessary and the resulting polymers have relatively low molar masses (< 10000 g/mol) and broad molar mass distribution.[115,181]

2.3 Biodegradable polymers from monomers based on vegetable oils

Vegetable oils are mainly triglycerides which are esters of glycerol with three saturated or/and unsaturated fatty acids (Figure 10). Fatty acids account for 95% of the total weight of triglycerides and their structures depend on the biological source and growing conditions.[3,4,7,8] A list of the most common fatty acids present in vegetable oils is summarized in Table 1.

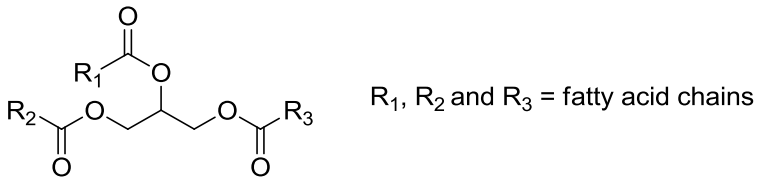


Figure 10. General structure of a triglyceride molecule

As can be seen from Table 1, fatty acids are long-chain molecules with chain length between C8 and C22. The double bonds are located at different position along the chain in most of unsaturated fatty acids with a *cis* configuration, for example oleic acid (C18:1), linoleic acid (C18:2) and linolenic acid (C18:3) are the most common unsaturated fatty acid with 1, 2 and 3 double bonds, respectively.[3,4,182,183]

Table 2 represents the fatty acid compositions of different vegetable oils. The chemical and physical properties of vegetable oils depend strongly on the number of double bonds, fatty acid chain length and functionalities. The chain length (or averaged molar mass) of all the fatty acids in the vegetable oil can be determinated by the saponification value. The long-chain fatty acids found in vegetable oil have a low saponification value due to their relatively low number of ester groups per unit mass of the oil, while the short-chain fatty acids have a higher value.[7] The degree of unsaturation is measured by the iodine value. The iodine value is the mass of iodine in milligram that is consumed by the reaction of the double bonds in 100 g of the

investigated vegetable oil. The higher the iodine values are, the higher the degree of unsaturation is. Depending on the iodine value, vegetable oils can be classified as drying oil (iodine value > 130, e.g. linseed oil), semi-drying (90 < iodine value < 130) and non-drying oil (iodine value < 90, e.g. olive oil).[3,7,183]

Triglycerides contain a variety of functional groups, such as double bonds, hydroxyl groups, epoxides and ester groups. By modifying these reactive sites, various easily polymerizable functional groups can be introduced in vegetable oil structure.[3-5] In this chapter, we will focus on the synthesis of monomers with functional groups from vegetable oils and the preparation of different kinds of biodegradable polymeric materials using these monomers. Properties, including chemical and physical properties, biocompatibility, application and biodegradability will be discussed in the flowing sections as well.

Table 1. Structures and formulas of the most common fatty acids[3,7,184]

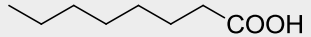
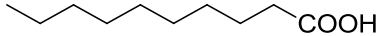
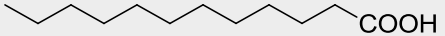
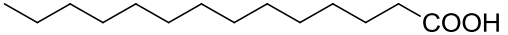
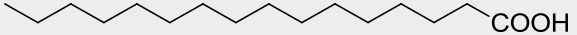
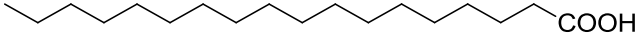
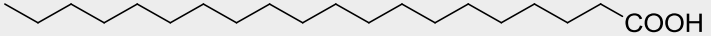
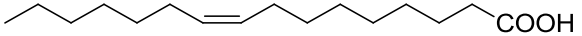
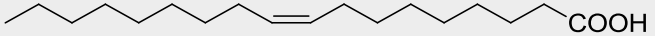
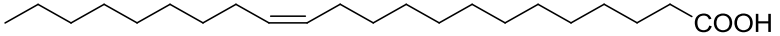
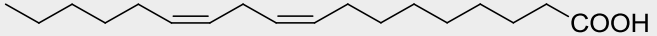
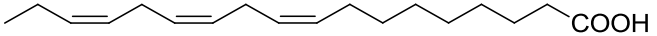
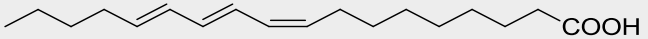
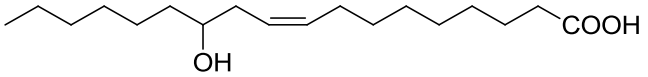
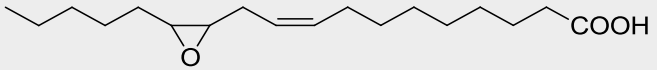
Fatty Acid	Scientific name	Formula	Structure
Caprylic	Octanoic acid	$C_8H_{16}O_2$	
Capric	Decanoic acid	$C_{10}H_{20}O_2$	
Lauric	Dodecanoic acid	$C_{12}H_{24}O_2$	
Myristic	Tetradecanoic acid	$C_{14}H_{28}O_2$	
Palmitic	Hexadecanoic acid	$C_{16}H_{32}O_2$	
Stearic	Octadecanoic acid	$C_{18}H_{36}O_2$	
Arachidic	Eicosanoic acid	$C_{20}H_{40}O_2$	
Palmitoleic	Hexadec-9-enoic acid	$C_{16}H_{30}O_2$	
Oleic	Octadec-9-enoic acid	$C_{18}H_{34}O_2$	
Erucic	Docos-13-enoic acid	$C_{22}H_{42}O_2$	
Linoleic	9,12-Octadecadienoic acid	$C_{18}H_{32}O_2$	
α-Linolenic	Octadeca-9,12,15-trienoic acid	$C_{18}H_{30}O_2$	
α-Eleostearic	Octadeca-9,11,13-trienoic acid	$C_{18}H_{30}O_2$	
Ricinoleic	(9Z,12R)-12-Hydroxyoctadec-9-enoic acid	$C_{18}H_{34}O_3$	
Vernolic	Cis-12,13-epoxy-cis-9-octadecenoic acid	$C_{18}H_{32}O_3$	

Table 2. Fatty acid composition of different vegetable oils and their properties[3,7,182,183]

Name	Number of double bonds	Iodine value (mg of I_2/100 g)	Palmitic (16:0)	Stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Ricinoleic (18:1+OH)
Canola	3.9	105-120	4.1	1.8	60.9	21.0	8.8	-
Corn	4.5	102-130	10.9	2.0	25.4	59.6	1.2	-
Cottonseed	3.9	90-119	21.6	2.6	18.6	54.4	0.7	-
Groundnut	3.4	80-106	11.4	2.4	48.3	31.9	-	-
Linseed	6.6	168-204	5.5	3.5	19.1	15.3	56.6	-
Olive	2.8	75-94	13.7	2.5	71.1	10.0	0.6	-
Palm	1.7	44-58	42.8	4.2	40.5	10.1	-	-
Rapeseed	3.8	94-120	4.0	2.0	56.0	26.0	10.0	-
Sesame	3.9	103-116	9.0	6.0	41.0	43.0	1.0	-
Soybean	4.6	117-143	11.0	4.0	23.4	53.3	7.8	-
Sunflower	4.7	110-143	5.2	2.7	37.2	53.8	1.0	-
Castor	3.0	82-90	1.5	0.5	5.0	4.0	0.5	87.5

2.3.1 Monomers from vegetable oils

2.3.1.1 Monomers from vegetable oils via monoglyceride/alcoholysis process

There are various techniques to obtain polyols from vegetable oils. The most commercially used method is the monoglyceride process. In this route, monoglycerides can be obtained by modification of the triglyceride ester groups through alcoholysis with glycerol in the presence of a base or acid catalyst. Figure 11 represents the chemical reaction for vegetable oil alcoholysis.[184]

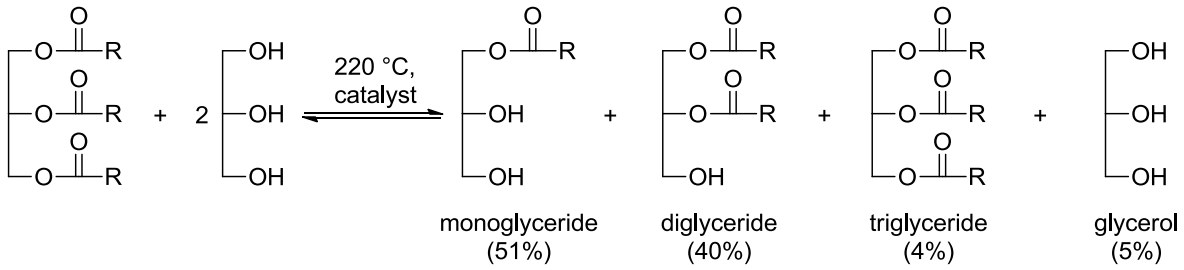


Figure 11. Alcoholysis of vegetable oils with glycerol[184]

The alcoholysis is a reversible ester interchange reaction when it is carried out homogeneously. According to the Le Chatelier's principle, use of an excess of glycerol over the 2 moles theoretically required will shift the equilibrium to the right, thus resulting higher total amount of monoglycerides.[185] The major challenge of this reaction is enhancing the solubility of the hydrophilic glycerol in initial hydrophobic vegetable oil or in subsequent fat-like phases. Only about 4% glycerol can dissolve in common vegetable oil at room temperature. To overcome this incompatibility, it will be necessary to conduct this reaction at elevated temperature (220 – 240 °C) in the presence of a catalyst.[185] Another reason for the high reaction temperature is to promote the formation of monoglycerides, while diglycerides are preferably formed at low temperatures. For this reason, to prevent the reversed reaction at the end of alcoholysis, the reaction mixture must be rapidly cooled to a low temperature (about 15 °C). The excess unreacted glycerol is then separated and removed as a lower layer. Can et al. found that rapid cooling of the reaction mixture with high speed stirring can improve the yield of

monoglycerides significantly.[186] The final composition after removing excess glycerol can be determined by different methods, such as thin layer chromatography (TLC), gas chromatography (GC) or high performance liquid chromatography (HPLC). Consequently, the resulting product mixture after alcoholysis with glycerol consists typically of 51% monoglyceride, 40% diglyceride, 4% triglyceride and 5% glycerol.[184]

Usually, the alcoholysis of vegetable oil is carried out by use of catalysts. In the absence of catalyst, a reaction temperature of 280 °C or higher is required and the products have dark color and high viscosity. Basic catalysts are used preferably in the alcoholysis reaction. A variety of basic catalysts has been studied, such as elemental metal (Na, K, Sn), metal oxides (CaO, SrO, PbO), metal hydroxides (LiOH, NaOH, KOH, $Ca(OH)_2$), metal salt of weak acids (calcium octate), metal alkoxides (NaOMe, NaOEt, NaO^tBu) and organotin compound (dibutyltin oxide (DBTO)). Among these catalysts, sodium alkoxides, LiOH, PbO and DBTO showed highest catalytic activities.[184] For industrial use NaOH and KOH are the preferred catalysts due to their relatively high efficiency and low prices. One disadvantage is that the used catalysts must be neutralized and removed from product mixture because the residual catalyst cause reversion. Moreover, the trace of catalyst can also lead to soapy taste, poor color stability and foaming problems for use of food emulsifiers. The removal of catalyst is usually conducted as follow: the basic catalysts are firstly neutralized with phosphoric acid and the neutralization products, metal phosphate, are absorbed with clays.[185] In addition, oxygen and traces of water have been reported to decrease the reaction rate. Carbon dioxide in the air can convert metal catalysts to carbonates. Thus the alcoholysis reaction should be carried out under nitrogen atmosphere to avoid oxidation and color problems.[184,185]

Similarly, besides using glycol alcoholysis of vegetable oils is often conducted with pentaerythrol.[187] Palm[188], soybean[186,187,189], tung[188], rapeseed[190], jatropha[190], castor[187], rubber seed[191], melon seed[191], mahua[192] and Nahar seed[193,194] oils have been used as raw materials to prepare monoglycerides *via* alcoholysis process. In most cases, the vegetable oil based monoglycerides are further modified with different anhydride (glutaric, phthalic, maleic and

succinic anhydrides), followed by polycondensation to form various alkyd resins.

2.3.1.2 Monomers from vegetable oils via ozonolysis process

Ozone molecule (O_3) includes three oxygen atoms with a delta positive and a delta negative electric charge. It is very unstable and has a short half-life. Therefore, ozone must be generated on-site by corona-discharge, UV-light, cold plasma or electrolysis method of oxygen containing feed gas in an ozone generator. The most common method for industrial and laboratorial use is corona discharge method. Ozone is produced in the corona as a direct result of electrical discharge. The electrical discharge causes the cleavage of the stable O_2 bonds to form two oxygen radicals. Ozone molecule can be consequence produced by combination of an oxygen radical with oxygen molecule.[195-197]

$$3\ O_2(g) \xrightarrow{\text{electricity}} 2\ O_3(g) \qquad \Delta H^\circ = 285\ \text{kJ}$$

To diffuse the spark into a corona and maintain the electrical discharge, a dielectric is present. The dielectric may be made from glass, ceramic, quartz or mica. Dried ambient air (21% oxygen) or dried pure oxygen can be used as feed gas. The generated ozone concentration is strongly dependent on the oxygen concentration in feed gas. The higher the oxygen content in feed gas is, the higher the ozone concentration generated is. Advantages of the corona discharge technique are cost-effective, sustainable and higher ozone production.[197]

The strong oxidizability of ozone is referred to its very high oxidation potential of 2.07 V in comparison to other oxidants (Table 3). Based on the high oxidizability, ozone has been widely used in industry including disinfection in pools and spas, wastewater treatment, producing chemicals via chemical reactions, food process and many more.[198]

As mentioned above, the unsaturated triglycerides contain a number of carbon-carbon double bonds. The presence of double bonds provides the possibility to introduce various functional groups by chemical reactions, such as hydrogenation, epoxidation, ozonolysis or olefin

metathesis.[199] However, the polymeric materials prepared from monomers based on olefin metathesis are usually non-biodegradable. Thus, this process will be not described in this chapter. This section is focused on the oxidation of double bonds in vegetable oils by ozonolysis process. Ozonolysis is an important and effective route to cleave carbon-carbon double bonds to give compounds with primary alcohols, aldehydes and carboxylic acids (Figure 12).

Table 3. Redox potential of oxidants[200]

Substance	Potential (V)
Fluorine (F)	2.87
Hydroxy radicals (OH)	2.86
Atomic oxygen (O)	2.42
Ozone (O_3)	2.07
Hydrogen peroxide (H_2O_2)	1.78
Chlorine (Cl)	1.36
Chlorine dioxide (ClO_2)	1.27
Oxygen molecule (O_2)	1.23

The best-established mechanism is given in Figure 13. The ozonolysis of double bonds begins with the formation of a five-member ring named molozonide (**b**) via a 1,3-dipolar cycloaddition of ozone with the double bond. Due to the high instability of the two O-O bonds the molozonide decomposes immediately to yield an aldehyde (**c**) and a carbonyl oxide (**d**). This decomposition reaction is referred to as a 1,3-dipolar cycloreversion. The carbonyl oxide will react further in one of two ways depending on the used solvent.

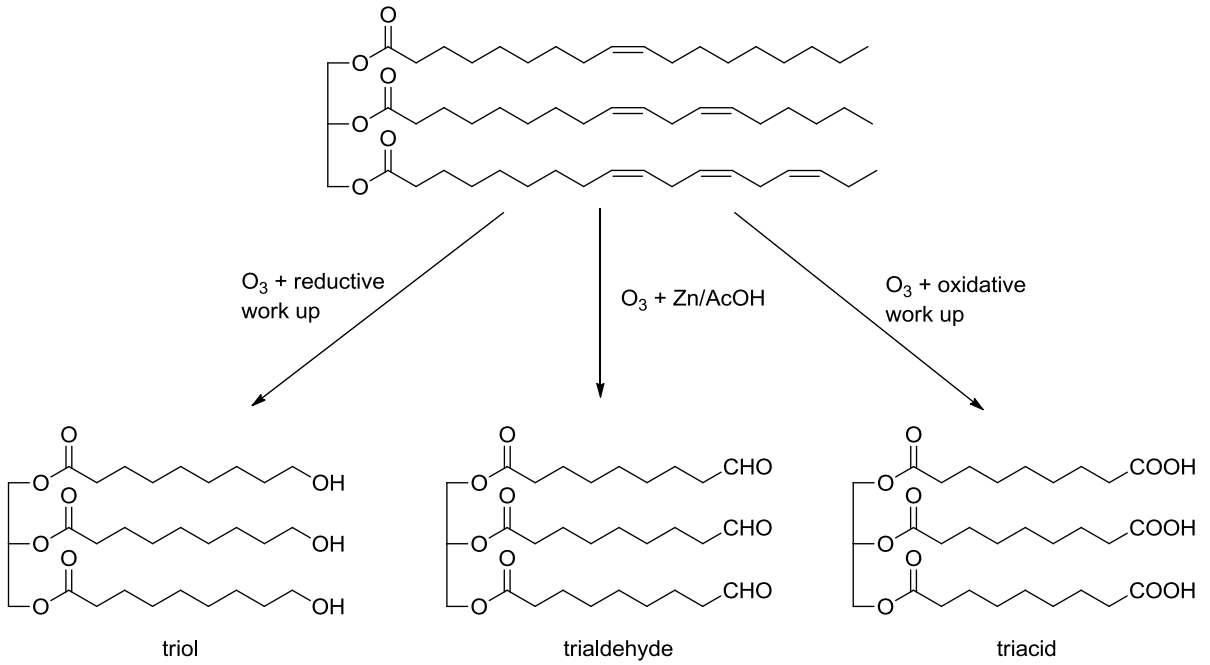


Figure 12. Ozonation of soybean oil to give triol, trialdehyde and triacid

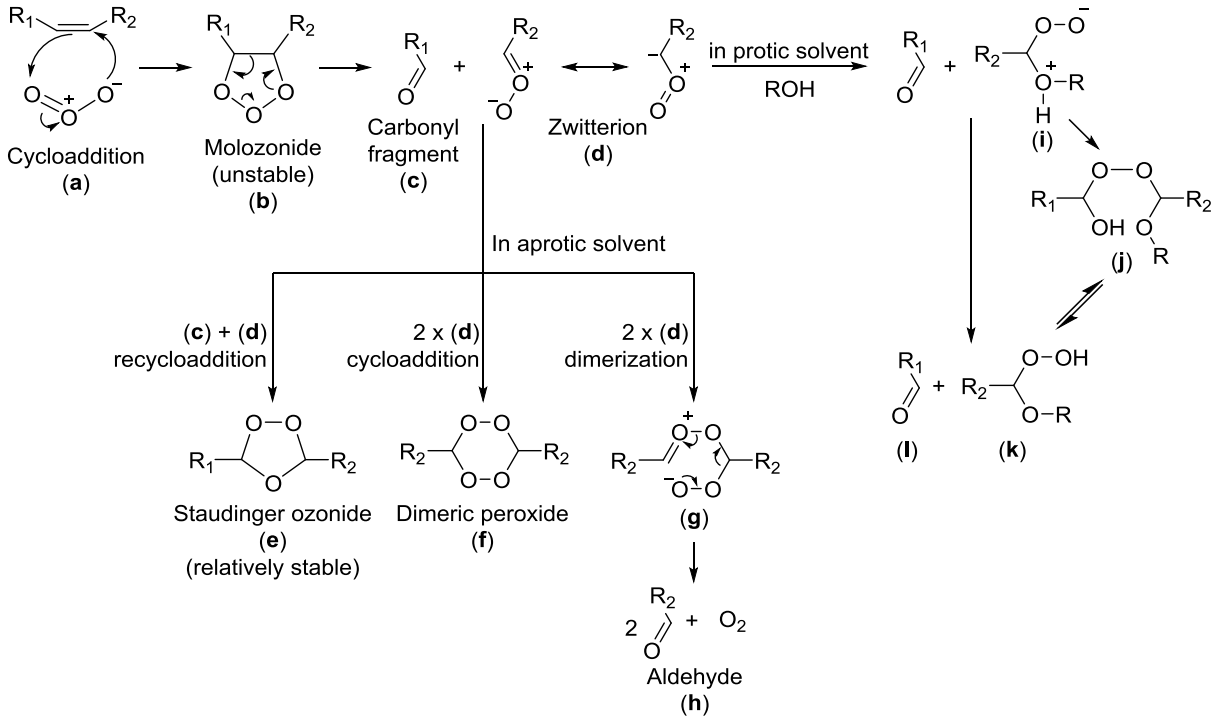


Figure 13. Proposed ozonation mechanisms of double bonds[201]

In protic solvent (e.g. MeOH or other alcohol solvents) the carbonyl oxide is captured by solvent molecule to form a hydroperoxide (**k**). Conversely, in the presence of aprotic solvent (e.g. dichloromethane) the carbonyl oxide (**d**) undergoes a cycloaddition to give the more stable secondary ozonide (**e**), which is named Staudinger ozonide. If the carbonyl oxide is formed along with a ketone instead of an aldehyde, a cycloaddition of two carbonyl oxide to an extremely explosive dimeric peroxide (1,2,4,5-tetroxane) (**f**) preferably happens. Moreover, the formation of the secondary aldehyde (**h**) via dimerization of two carbonyl oxide and followed decomposition has been also reported.[202-206]

Triols have been prepared by ozonation of different vegetable oils, such as castor, soybean, canola oils and trilinolein. Kong et al. has used a two-step ozonolysis- and hydrogenation-based technology to synthesize polyols from canola oil. In the first step, canola oil was ozonized in ethyl acetate at 10 °C resulting the Staudinger ozonide and followed reduced with zinc at room temperature to give a trialdehyde, which was then hydrogenated by Raney nickel as catalyst at 70 °C and 100 psi (Figure 14).[207]

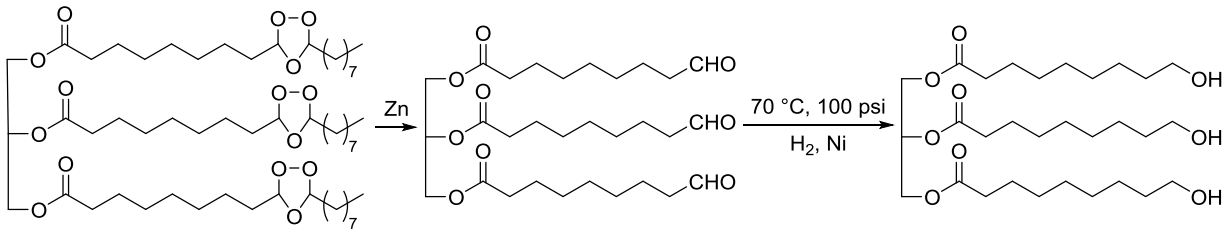


Figure 14. Two-step ozonolysis of canola oil[207]

Petrović et al.[208,209] has produced triols from castor, soybean, canola oils and trilinolein by a one-step ozonolysis in methanol/dichloromethane. Unsaturated triglycerides were firstly converted to mixture of aldehydes and hydroperoxides. They were reduced in the next step to hydroxyl groups by using $NaBH_4$ as reducing agent. Low molecular weight byproducts, such as mono- and diols were removed under vacuum. (Figure 15)

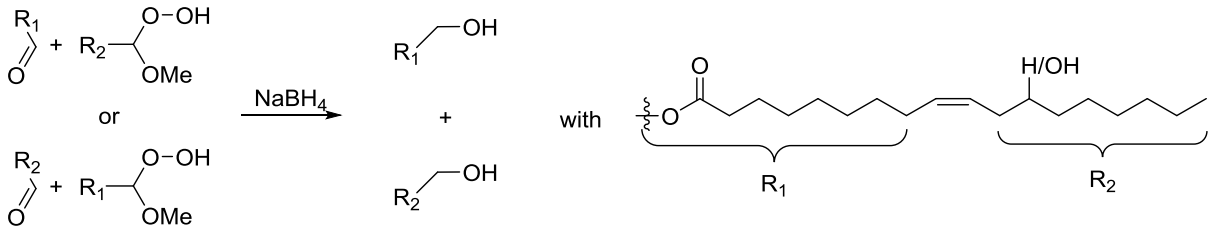


Figure 15. Ozonolysis of vegetable oil in methanol/dichloromethane[210]

Pryde et al.[210] described a relatively simple method of preparing trialdehydes from triolein under different conditions. The triglyceride was ozonized in methanol/dichloromethane (4:5 v/v) at -4 °C and reduced with zinc powder and acetic acid at room temperature (Figure 16). The trialdehyde oil was obtained by removal of zinc salt, unreacted acetic acid and volatile low molecular weight aldehydes to give a light yellow viscous liquid with yield of 85%.

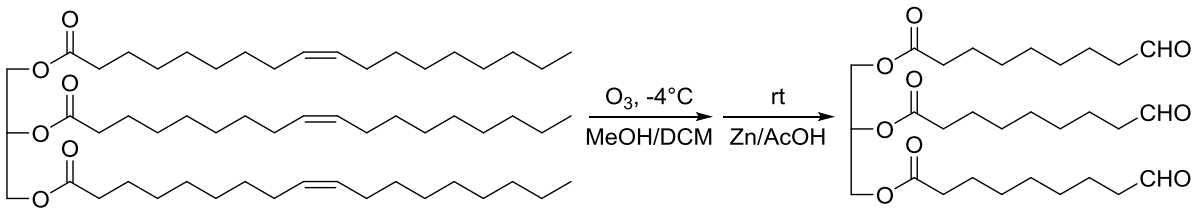


Figure 16. Preparation of trialdehyde from triolein[210]

2.3.1.3 Monomers based on epoxides from vegetable oils

Vernonia oil has attracted significant attention for preparation of polymeric materials. The vernonia oil is extracted from the seeds of *Vernonia galamensis* plants. The oil consists of 70 – 80% vernolic fatty acid, which contains an epoxy group in the 12th and 13th positions (Figure 17). Due to the presence of the three epoxy groups in the triglyceride structure, the *vernonia oil* can react as trifunctional monomer with other multi-functional regents, such as dibasic acids, diamines, to give crosslinked polymers. The resulting polymers are soft elastomers with low T_g and can be used to form interpenetrating polymer networks (IPNs) with other polymers.[211-213]

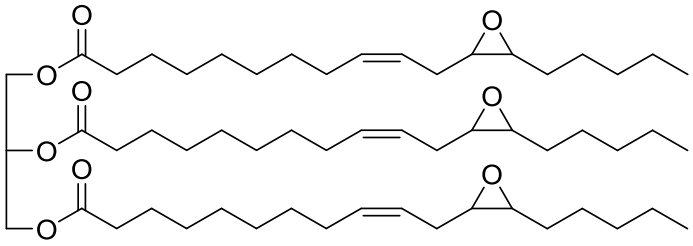


Figure 17. Structure of vernonia oil[212]

The unsaturated fatty acids in vegetable oils can undergo epoxidation to introduce epoxy groups, which can be utilized by ring-opening reaction to give a variety of polymerizable functional groups.[214,215] The synthetic route to epoxidized soybean oil (ESBO) is shown in Figure 18.[216] The carbon-carbon double bonds in glycerides are converted to epoxide groups by reaction with a peroxy acid. ESBO is nowadays commercially available.[217]

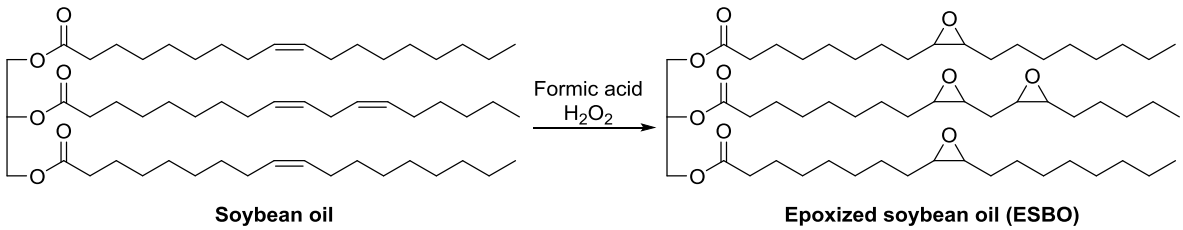


Figure 18. Synthetic route of epoxidized soybean oil (ESBO)[216]

A series of nucleophilic regents can be used to open the epoxy group to yield a new functional group and a hydroxyl group from epoxy oxygen atom. Figure 19 illustrates some examples for modification of epoxy groups. Acrylation of ESBO has been extensively studied. The acrylated epoxidized soybean oil (**AESO**) is obtained from the reaction of ESBO with acrylic acid (**a**).[216] As seen in route **b**, a multiaziridine-containing acrylated epoxidized soybean oil (**AESO-AZ**) was synthesized by grafting 2-methylaziridine onto ESBO through a Michael addition.[218] Lu et al. reported a further modification based on AESO to introduce carboxylic acid groups by the reaction of residual epoxy groups or hydroxyl groups with maleic anhydride (**c**).[216]

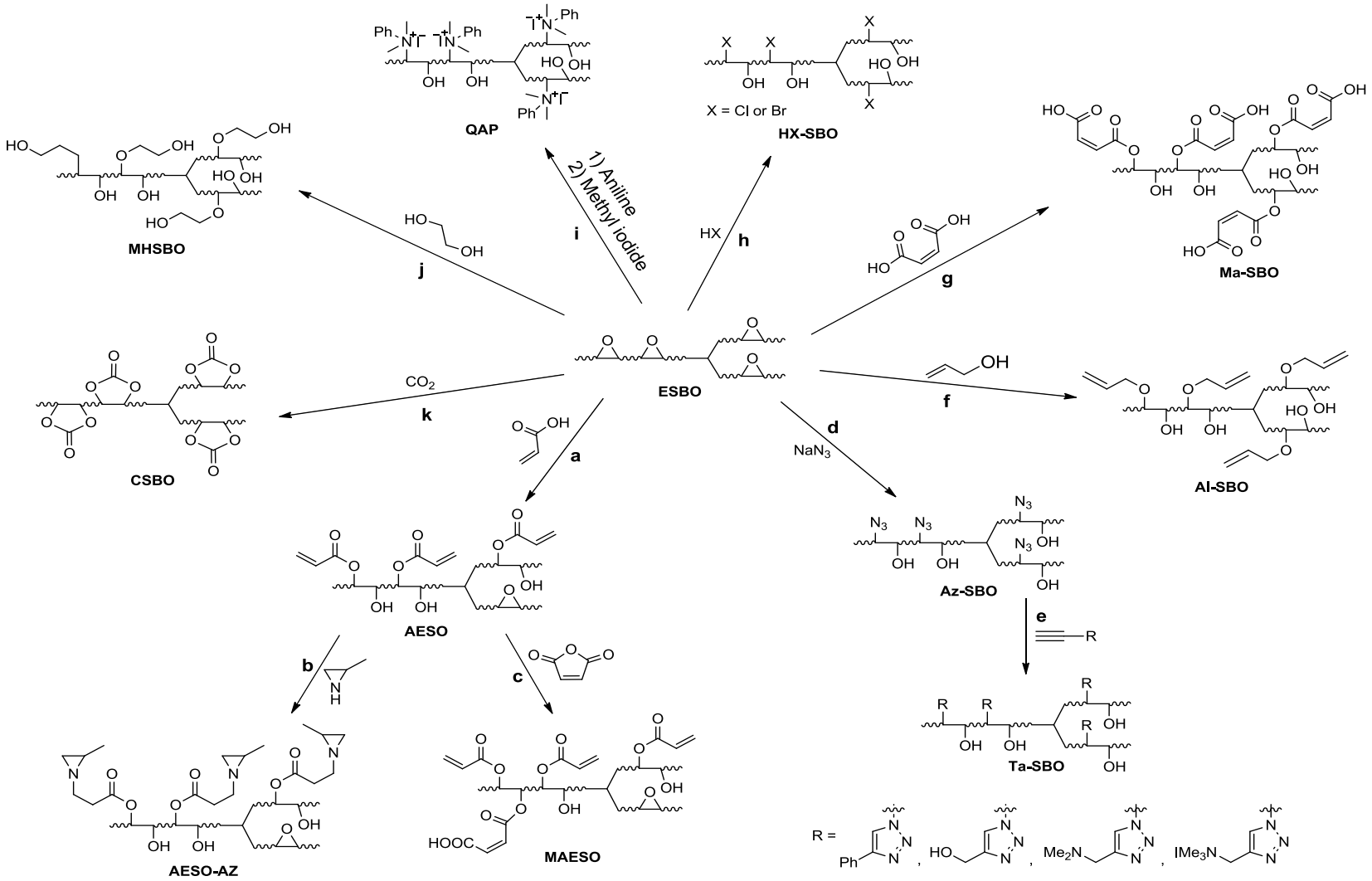


Figure 19. Synthesis of monomers with different functionalities by modification of ESBO

Recently, azide-containing polyols from soybean oil (**Az-SBO**) have been prepared from ESBO reacted with sodium azide (**d**).[217,219] The Az-SBO products can be further subjected to the cycloaddition with different alkynes through click chemistry (**e**). These polyols were used to produce polymeric coatings with biocidal activity.[217] Other functional groups such as alcohols, double bonds in side chains, carboxylic acid or halogen groups have been introduced into vegetable oil structures though the ring opening reaction with alcohols (e.g. allyl alcohol (**f**, **Al-SBO**)[220], ethylene glycol (**j**, **MHSBO**)[221]), maleic acid (**g**, **Ma-SBO**)[222] and hydrogen halides (e.g. HCl and HBr (**h**, **HX-SBO**)[223]), respectively, and utilized for further application. The treatment of ESBO with aniline, followed by methylation with methyl iodide allowed the synthesis of quaternary ammonium salts containing polyol (**i, QAP**) with antibacterial property.[224] Djalilian et al. described a novel method to convert ESBO to carbonated soybean oil (**CSBO**) using tetrabutylammonium bromide (TBAB)/calcium chloride as catalyst under ambient pressure of CO_2 gas (**k**).[225]

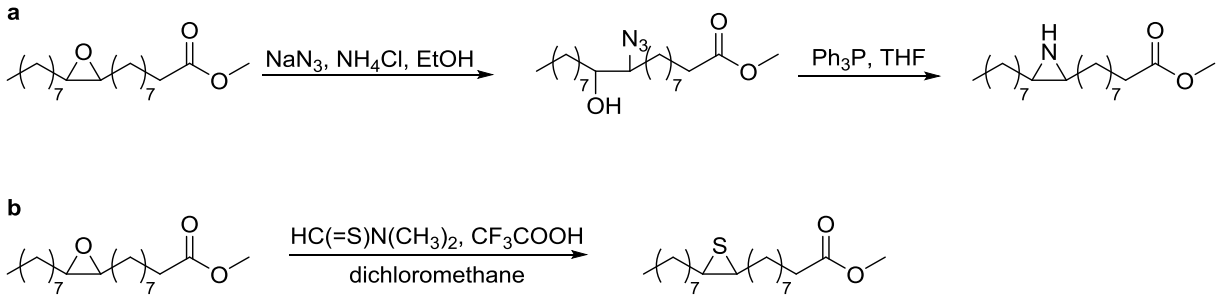


Figure 20. Synthesis of aziridine[226] and episulfide[227] from epoxidized methyl oleate

Besides ESBO, epoxidized methyl oleate has been transformed to aziridine[226] and episulfide[227] (Figure 20). These compounds are interesting intermediates in the synthesis of heterocyclic and highly functionalized substances.[214]

2.3.1.4 Cyclic monomers for ring opening polymerization from vegetable oils

ω-Hydroxy fatty acids are a class of straight long-chain aliphatic organic compounds with carboxylic acid and hydroxyl functionalities located at both ends of the fatty acid chain. The ω-

hydroxy fatty acids have been attracted much attention for preparation of mixed diesters, cosmetic formulations and phospholipids.[228] Ricinoleic acid (Table 1, row 14) is a common ω-hydroxy fatty acid obtained by hydrolysis of castor oil with a carboxylic acid group in the 1st position and a hydroxyl group in the 12th position. Domb and coworkers have reported the synthesis of macrolactone mixture (Figure 21, 1RM-6RM) from ricinoleic acid as raw material. According to the GPC analysis 1RM to 4RM could be separated by gel chromatography to the individual lactones. The compositions of macrolactones mixture were strongly dependent on reaction concentrations. Higher reaction concentrations led to preferably larger rings (4RM to 6RM). However, ring opening polymerization of these macrolactones was difficult and resulted only oligomers.[229]

Narine et al. demonstrated a synthetic route for the preparation of lactone from methyl oleate. The methyl oleate was ozonolysed, hydrogenated and saponified to be converted to 9-hydroxynonanoic acid. When di-2-thioyl carbonate was used as coupling regent and hafnium (IV) trifluoromethanesulfonate ($Hf(OTf)_4$) as catalyst, a monolactone product was obtained. The synthesis of dilactone with high yield (98%) was accomplished by using hafnium chloride ($HfCl_4$) as catalyst.[228,230]

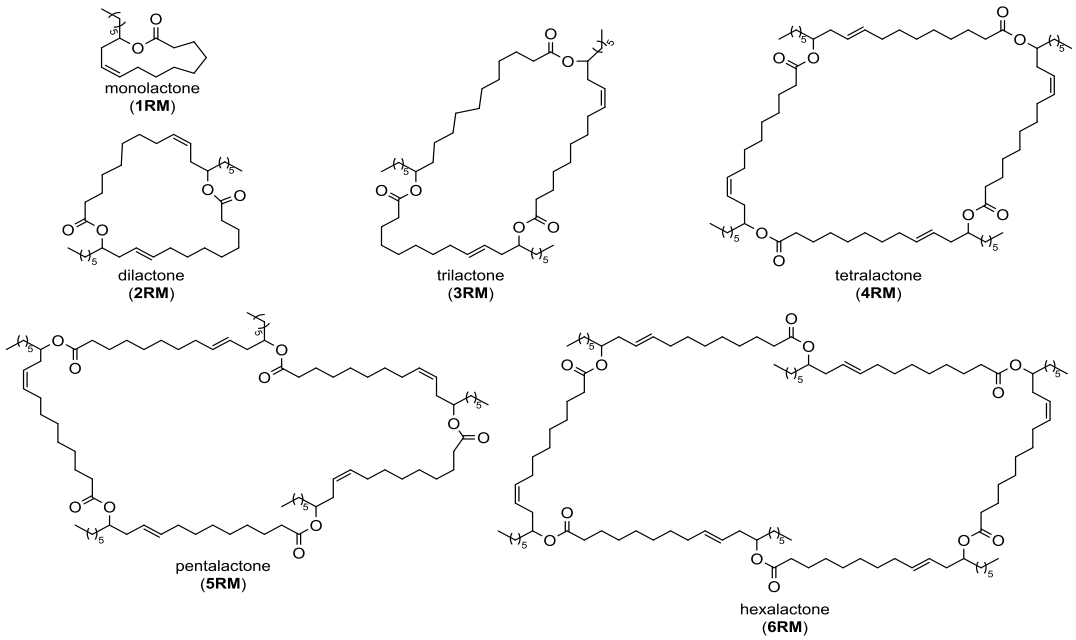


Figure 21. Synthesis of cyclic macrolactones from castor oil[229]

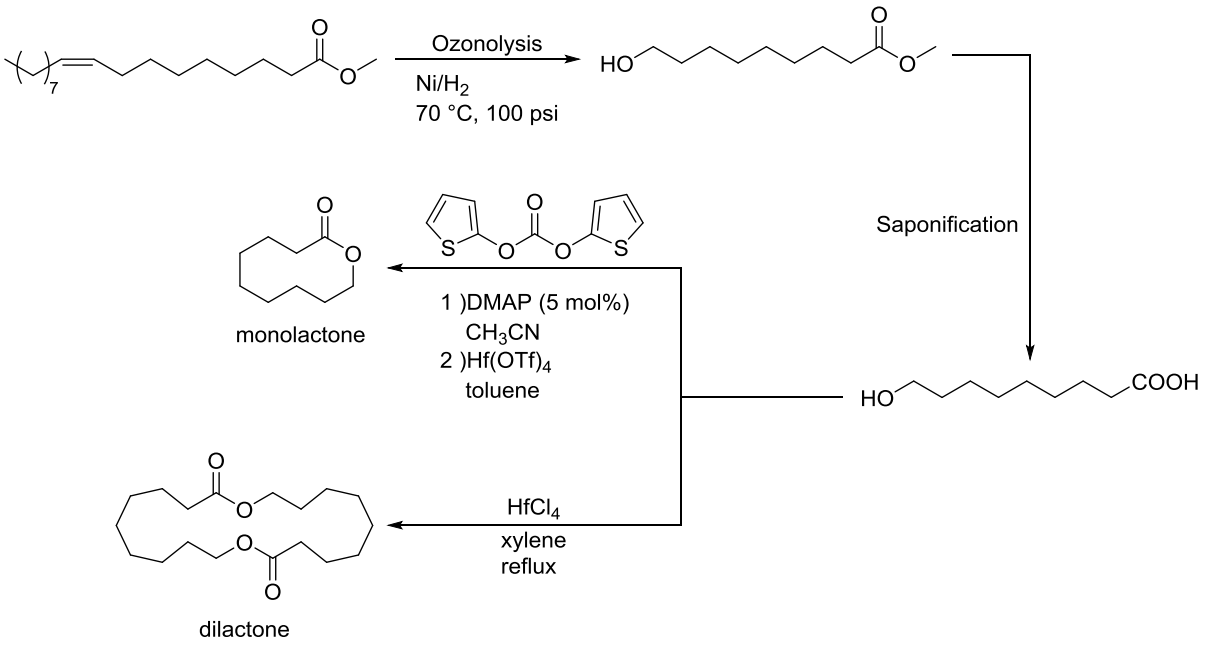


Figure 22. Synthetic route of monolactone and dilactone from methyl oleate[228,230]

2.3.2 Vegetable oil based biodegradable polymers

2.3.2.1 Vegetable oil based polyesters

Polyesters are the most widespread used biodegradable polymeric materials for drug carrier and tissue engineering. Polyesters can be synthesized either by ROP of cyclic ester monomers or polycondensation of two multifunctional monomers. Polycondensation is a polymerization process by which two molecules (monomer, oligomer or polymer molecules) are linked together by generating a new functional group with elimination of a small molecule resulting elongation of polymer chains. Polyester can be synthesized by polycondensation with the elimination of water molecules in each condensing step (Figure 23a). ROP of cyclic ester monomers is one of the most effective methods to obtain homo- or copolyesters with a high molar mass and low dispersity under milder reaction conditions in comparison to polycondensation (Figure 23b).[87,231] Metallic compounds[232], guanidine based catalysts[113,166,233], strong acids[113,166,234], phosphazene[171], N-heterocyclic carbine[75,235], bifunctional thiourea-amine[166,170,236] and enzyme[237-239] have been applied as catalysts to the controlled ROP of cyclic

esters.

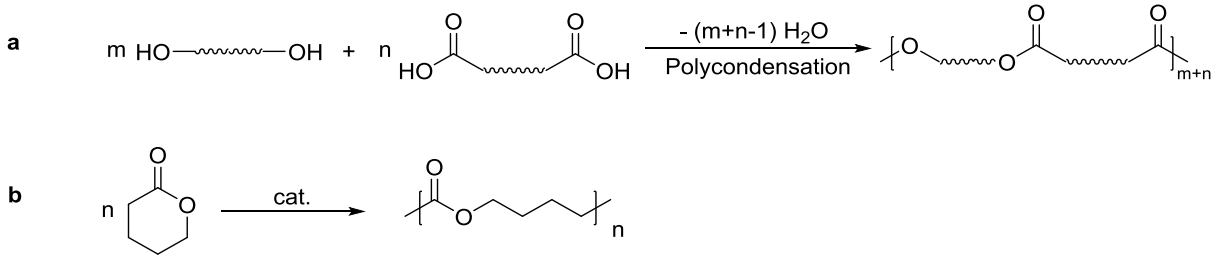


Figure 23. a) Typical polycondensation of synthesis of polyester; b) ring-opening polymerization of a lactone

Vegetable oil based polyester resins (alkyds) were mainly obtained by polycondensation from monoglyceride with dicarboxylic acid anhydride. The properties of the polyesters can be adjusted by using different type of dicarboxylic anhydride and monoglyceride/anhydride feed ratios. When dicarboxylic acid anhydrides with rigid structures are used, polyesters with higher glass transition temperatures and cross-linking densities will be obtained. The synthetic route is shown in Figure 24.

Monoglyceride from Nahar seed oil has been used for preparation of polyester resins by reaction with phthalic or maleic anhydride at high temperature. Investigation of the chemical resistance showed, that the resulting polyester films were highly resistant to dilute HCl acid, NaCl solution and distilled water, while they could be hydrolyzed under basic conditions.[193]

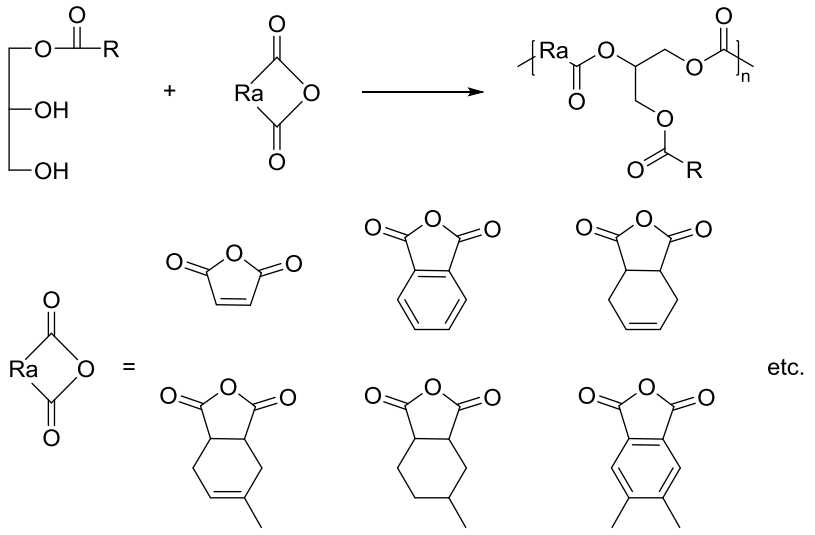


Figure 24. Synthesis of polyesters from monoglyceride and dicarboxylic acid anhydride

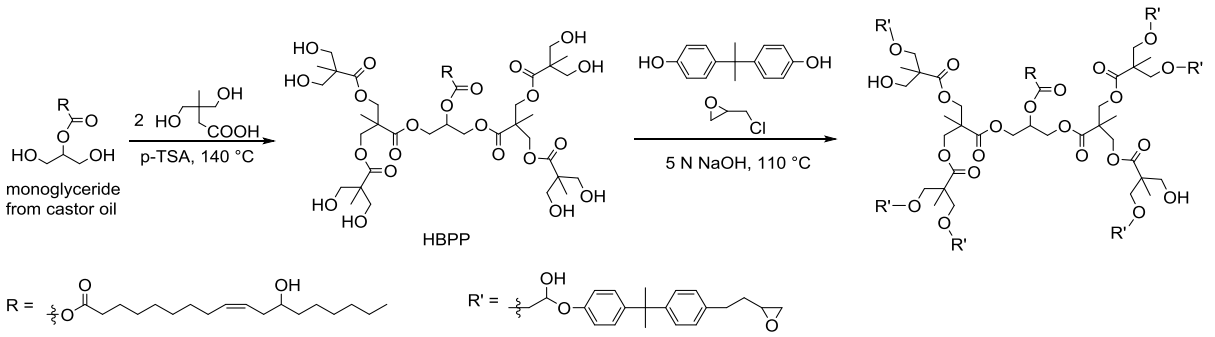


Figure 25. Synthesis of castor oil monoglyceride based hyperbranched epoxy thermoset[240]

Recently, a hyperbranched polyester polyol (HBPP) was synthesized by Karak and coworkers from castor oil based monoglyceride and bis(hydroxy methyl) propionic acid (Bis-MPA) (Figure 25). The HBPP was reacted with bisphenol A and glycidyl ether epoxy to form a hyperbranched epoxy with a polyester backbone. This castor oil monoglyceride based resins could be used as thermosets with excellent toughness, flexibility and elasticity, and they were relatively thermostable and biodegradable.[240]

Polynonanolactones were successfully prepared by employing the ROP of castor oil based monolactone and dilactone (Figure 22) with tin(II) 2-ethylhexanoate as catalyst. The number averaged molar mass of synthesized polynonanolactones were varied from 6000 to 13000 g/mol with dispersities below 1.40. The melting points (T_m) of these polylactones are about 50 °C and increased slightly with increasing molar mass.[230]

Castor oil is obtained from the seeds of castor oil plant (*Ricinus communis*) and has been widely used for preparation of various biodegradable polyesters. Compared to other vegetable oils, castor oil is a special monomer for polymerization, because it contains about 90% bifunctional ricinoleic acid with a double bond between the 9th and 10th position and an inherent hydroxyl group in the 12th position. The ricinoleic acid can be produced by hydrolysis of castor oil.[241] The structures of castor oil and ricinoleic acid are shown in Figure 26.

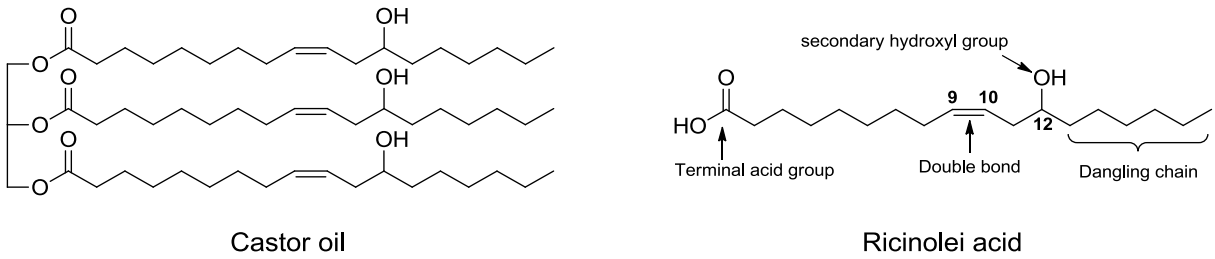


Figure 26. Structures of castor oil (left) and ricinoleic acid (right)

The presence of hydroxyl groups permits polymerization to prepare polyesters or polyester-anhydrides. The dangling chains as side chains in polymer structures improve hydrophobicity and they influence the mechanical and physical properties of the resulting polymers. These chains act as plasticizers by reducing the T_g and prevent crystallization even at very low temperatures.[242] The unique trifunctional castor oil can be considered as triol, which can copolymerize directly with dibasic acid, such as sebacic acid, to form hyperbranched or cross-linked polyesters. Castor oil based copolymerized, hyperbranched or cross-linked polymers have been widely used in biomedical applications, such as drug carrier and tissue engineering scaffold, due to their flexibility, hydrophobicity and injectability.[241]

Recently, Domb and Slivniak have reported the preparation of copolyesters based on ricinoleic (RA) and lactic (LA) acids using random polycondensation at 150 °C (Figure 27a) and transesterification of RA with high molar mass poly(lactic acid) (PLA) followed by thermal polycondensation (Figure 27b). In the first method, copolyesters P(LA-RA) with molar mass (M_w) between 2000-8000 g/mol were obtained. Copolyesters with RA content > 20% were in a liquid state at room temperature. Copolyesters synthesized by transesterification followed by polycondensation with LA/RA ratios of 9:1 to 5:5 w/w have increased molar mass (M_w) in the range of 6000-14000 g/mol. According to the DSC analysis, only polymers with LA/RA ratio of 9:1 w/w showed crystalline property. These liquid polyesters can be used as sealants and as injectable drug carriers.[243]

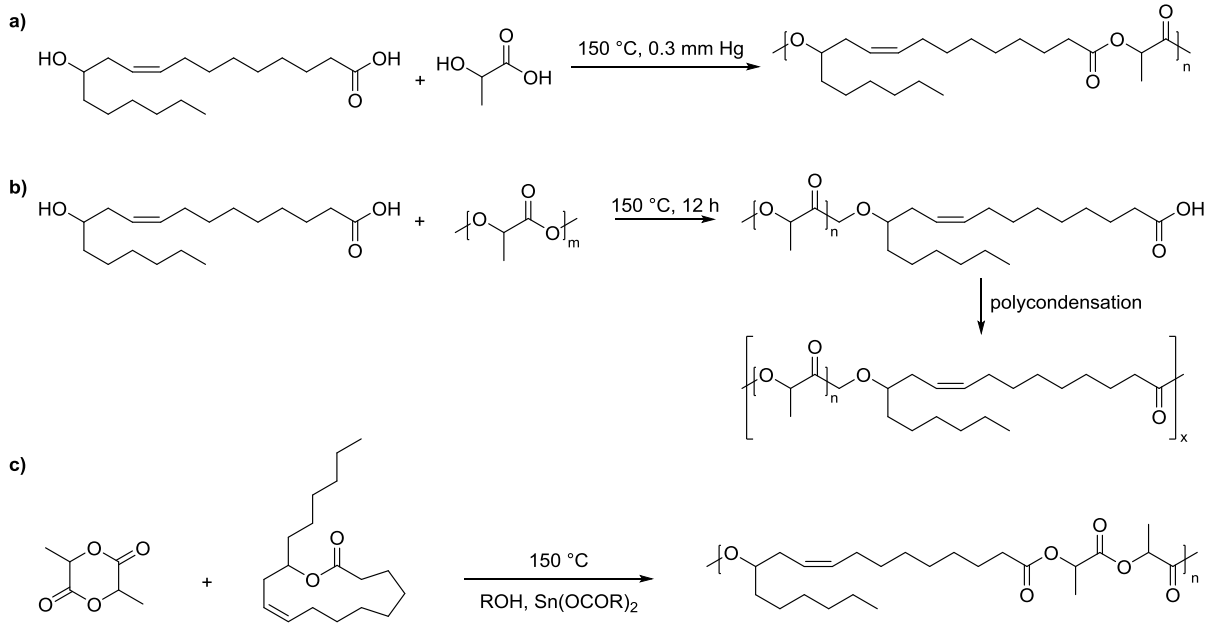


Figure 27. Synthesis of copolyesters based on RA and LA by a) random thermal polycondensation and b) transesterification of RA and PLA followed by thermal polycondensation[170,229,243] c) ROP of RA and LA-based lactones

In another study of Slivniak et al., copolyesters with molar mass (M_w) of 5000-16000 g/mol from L-lactide and cyclic RA-based monomer with ratios of 9:1 to 5:5 w/w were obtained via ROP (Figure 27c). The ROP was carried out at 150 °C using 10 wt% $Sn(OCOR)_2$ as catalyst. The synthesized polymers were off-white solid or semisolid materials.[170,229]

Guc et al. demonstrated a novel ricinoleic acid based hyperbranched resin (HBR) for use as drug carrier. In this study, a hyperbranched core with two generations was firstly synthesized from dipentaerythritol and dimethylol propionic acid. The reaction was carried out at 140 °C using 0.4 wt% p-toluenesulfonic acid (p-TSA) as catalyst (Figure 28). The core was then esterified with ricinoleic acid at 220 °C to form the HBR. A M_n of 11000 g/mol with dispersity of 2.11 was obtained for the hyperbranched resin (HBR) by SEC analysis. Drug molecules (idarubincin and tamoxifen) can be loaded by hydrogen bonding of unreacted hydroxyl groups in HBR providing controlled delivery.[9]

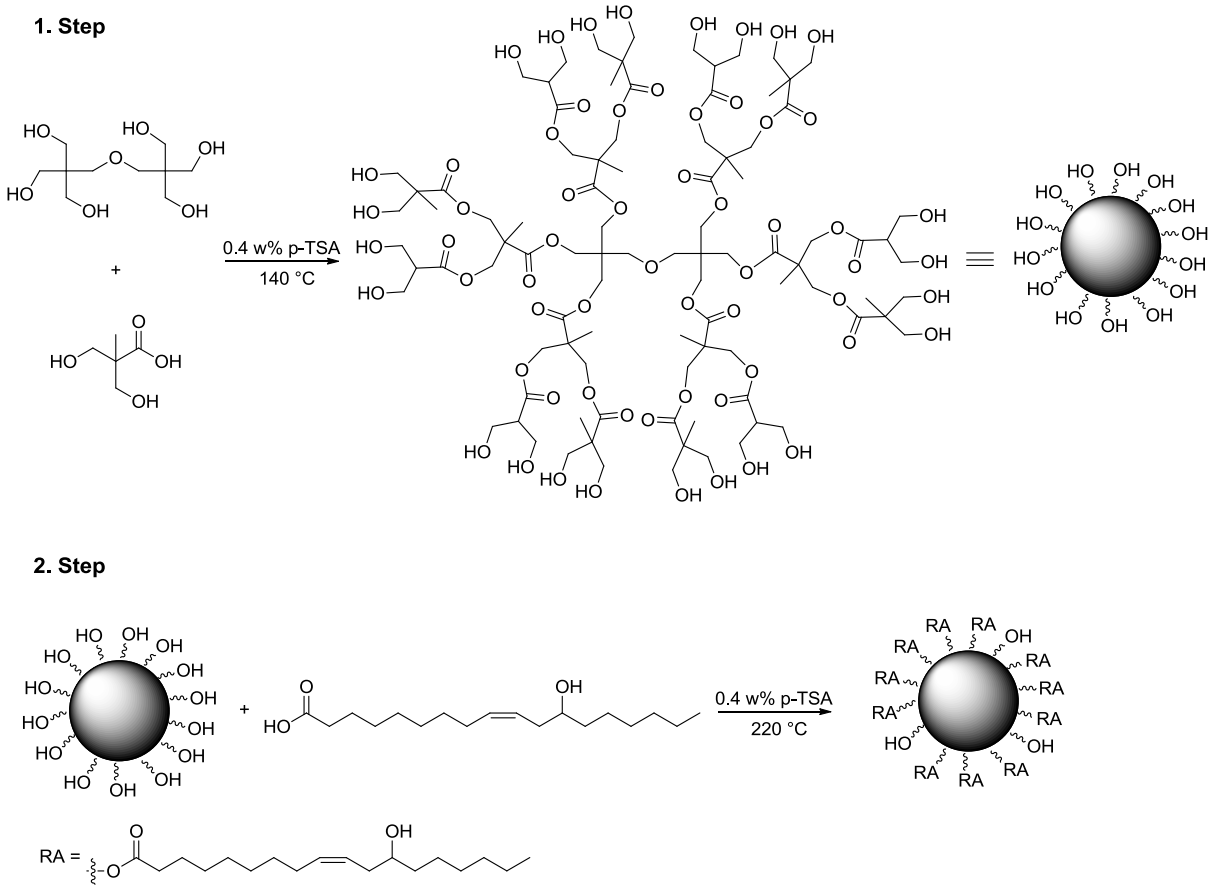


Figure 28. Synthetic route of ricinoleic acid hyperbranched resin (HBR)[9]

2.3.2.2 Vegetable oil based polyanhydrides

One other important class of biodegradable polymers are polyanhydrides. The anhydride linkages are hydrophobic and water-sensitive. Polyanhydrides based on vegetable oils or fatty acids undergo hydrolytic degradation to form water-soluble small molecules or naturally occurring body components.[10,244] Vegetable oils based polyanhydrides are widely used as implantable or injectable drug delivery systems because of their common physicochemical properties, such as biodegradability, biocompatibility, hydrophobicity, flexibility and low melting points.[245,246]

Polyanhydrides are usually produced by melt-polycondensation of dicarboxylic acid monomers

and acetic anhydride to give prepolymers, which can be converted to final polymers in the next step at elevated temperature and under vacuum removing the acetic anhydride byproduct.[244] Unfortunately, fatty acids are monofunctional and cannot be used for polymerization. To overcome this barrier, oleic acid and erucic acid were dimerized to polymerizable dicarboxylic acid monomers.[247] A series of copolyanhydrides based on sebacic acid prepolymer and oleic or erucic acid prepolymers with various composition were obtained (Figure 29a). The homopolymers of oleic acid and erucic acid dimers were viscos liquids, while copolymers with sebacic acid content >30% were solid. The melting points (30-70 °C) increased as a function of sebacic acid content.[245] However, according to the *in vivo* studies in dogs one significant disadvantage of these polyanhydrides was that the degradation products, fatty acid dimers, were not easily metabolized (6 months) *in vivo*, which was probably attributed to the carbon-carbon linkage between two fatty acids molecules.[248]

Domb et al. reported the synthesis of a second class of linear fatty acid based polyanhydrides from ricinoleic acid, sebacic acid and succinic and maleic anhydrides. Ricinoleic acid was firstly acidified with succinic or maleic anhydride to give ricinoleic acid succinate (RAS) and ricinoleic acid maleate (RAM), which was then hydrogenated to 12-hydroxystearic acid succinate (HSAS). After purification of these diacids by column chromatography removing unreacted ricinoleic acid and monofunctional fatty acids, copolymers were synthesized by melt-polycondensation of RAS, RAM and HSAS with sebacic acid and acetic anhydride (Figure 29b). These polymers have molar masses exceeding 50000 g/mol and melting points below 100 °C.[248-250]

Poly(anhydride-ester) including two biodegradable bonds in the polymer backbone is a modification of polyanhydrides. These polymers display two degradation stages: water-sensitive anhydride bonds are rapidly cleaved by hydrolysis to polyester prepolymers which have a much slower degradation rate.[244] The incorporation of ester bonds into polyanhydride backbones was achieved by the random reaction of a polyanhydride with the hydroxyl group of ricinoleic acid to form poly(anhydride-ester) oligomers with carboxylic acid end groups. High-molecular weight poly(anhydride-ester) was then prepared by repolymerization of these

oligomers at high temperature and under reduced pressure (Figure 29c).[251,252]

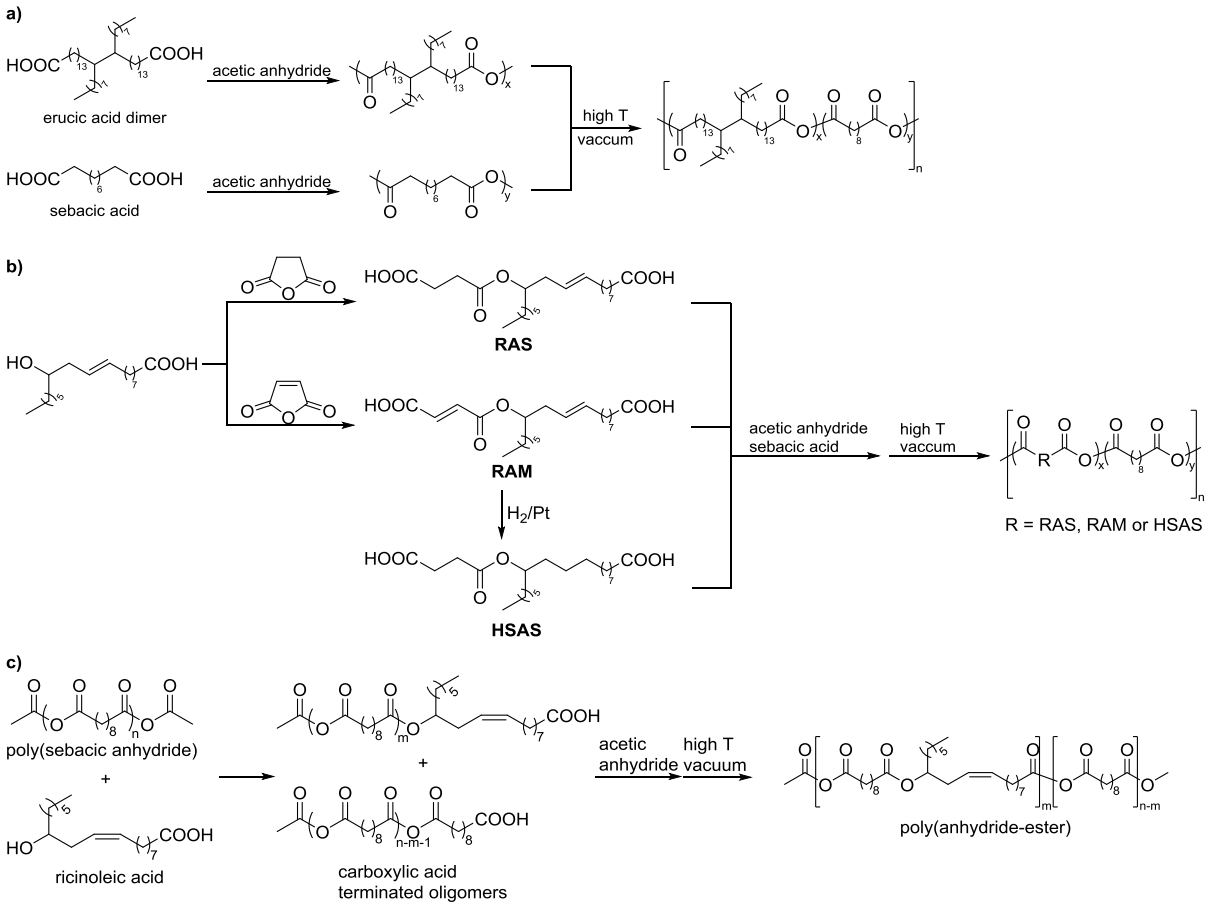


Figure 29. Synthesis of vegetable oil based polyanhydrides, a) branched polyanhydride from erucic acid dimer and sebacic acid; b) polyanhydrides based on with succinic or maleic anhydride modified ricinoleic acid; c) poly(anhydride-ester) from sebacic and ricinoleic acids.

2.3.2.3 Vegetable oil based polyesteramides

Vegetable oil based polyesteramide resins have been applied in the paint and coating industries. These resins show good water and chemical resistance, low toxicity, adhesion, hardness and gloss properties. In addition, the incorporation of aliphatic and aromatic species in polymer backbones improved significantly the biodegradability and biocompatibility, which are important parameters in biomedical and environmental applications.[253-255] Linseed[253],

pongamia glabra[254], Nahar[255] and castor oils[256,257] have been used in the preparation of linear and hyperbranched polyesteramides. The synthesis of vegetable oil based polyesteramide is generally accomplished by polycondensation of N,N-bis(2-hydroxy ethyl) fatty amides, which were obtained by amidation of fatty acids with diethanolamine, with various dibasic acid or anhydrides (Figure 30).[256-258]

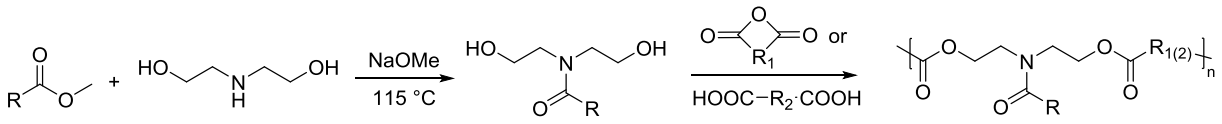


Figure 30. Synthetic route of vegetable oil based polyesteramides

In one study, biodegradable hyperbranched polyesteramides were prepared with maleic anhydride, phthalic anhydride and isophthalic acid from N,N-bis(2-hydroxyethyl) ricinoleic fatty amide. The weight average molecular weight of synthesized oligomers was found to be 2300 g/mol with dispersity of 1.40. It was observed that the oligomer was soluble in common organic polar solvents, such as dimethyl acetamide (DMAc), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), methanol and THF, whereas the oligomer had poor solubility in petroleum ether, diethyl ether and 4% NaOH solution. The higher solubility in comparison to linear fatty acid based polyesteramides was attributed to the hyperbranched structure. The properties of the cured polyesteramide thermoset was strongly affected by curing systems. The thermoset cured by epoxy-poly(amido amine) presented better scratch hardness, thermal properties and gloss and chemical resistance than cured by epoxy-cycloaliphatic amine sample. Because of the presence of numerous ester linkages in polymer backbones, the thermoset could be biodegraded using *P. aeruginosa* bacteria. The summarized the fatty acid based thermoset could be potentially used as biodegradable thin film material.[256,257]

2.3.3 Biodegradation

Polymer degradation can be considered as a number of processes, such as physical disintegration, chemical reaction resulting small molecules and degradation by biological mechanisms. Only polymers that can degrade in nontoxic byproducts without causing environmental pollutions can be called biodegradable polymers. The degradation of polymer means cleavage of polymer chains by chemical reaction, while erosion refers to the sum of degradation processes leading to depletion of polymer matrices. Polymer erosions follow mainly two processes: bulk erosion and surface erosion. In bulk erosion, material is lost throughout the polymer volume equally. The erosion rate is independent on the polymer size or shape, only dependent on the polymer volume and decreases during the erosion process. For ideal surface erosion, the degradation occurs from the exterior surface. The total erosion time can be altered by the material shape.[259-261]

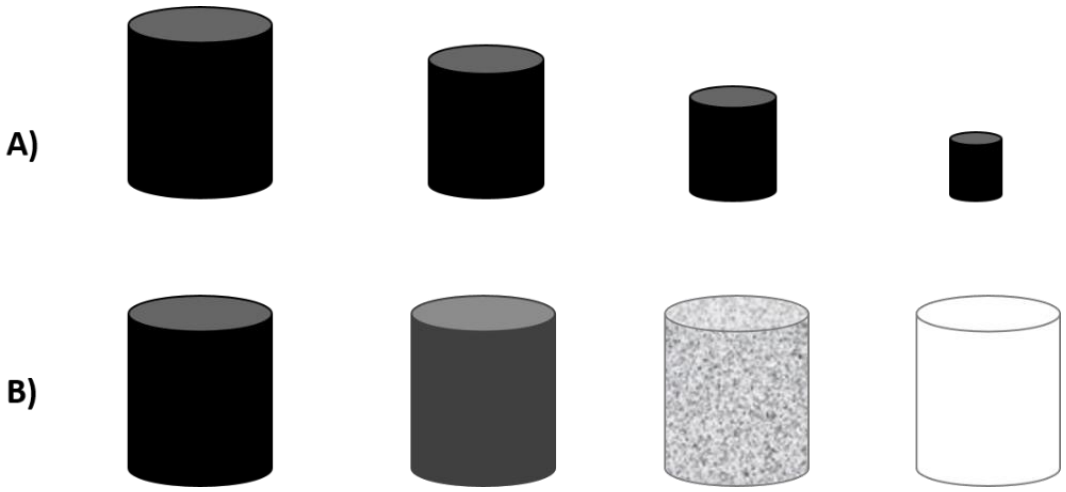


Figure 31. Schematic representation of A) surface erosion and B) bulk erosion

For many applications, for example drug delivery, surface eroding polymers are preferred since surface erosion is much easier to control and leads to zero-order drug release rate. Surface eroding polymers provides also better protection of the drugs from *in vivo* degradation than bulk eroding polymers, because water penetration will be retarded. The most common examples for surface eroding polymers are polyanhydrides and poly(ortho esters).[244] In

contrast, bulk erosion is satisfactorily used in other applications that do not require controlled release, such as degradable plastics for packaging. The material can remain intact during use and degrade completely after disposal. For example, the copolyesters poly(lactic/glycolic acid) [PLGA)], which is widely used in resorbable sutures and injectable drug delivery systems, displays bulk erosion characteristics.[259] Vegetable oil based biodegradable polymers are mainly referred to polyester and polyanhydride based polymers.

In the study of Narine et al., both enzymatic and hydrolytic degradation of polynonanolactones (PNLs) from castor oil based monolactone and dilactone were investigated and compared with polycaprolactone (PCL). The enzymatic degradation was performed in the presence of Proteinase K for PNL and *Pseudomonas cepacia* for PCL at 25 °C in 0.1 M phosphate buffer solution with pH = 7. The degradation results showed that PNLs obtained from monolactone had highest degradation rate and reached a weight loss of 80% in the enzymatic degradation, while PCL and PNLs from dilactone showed 77% and 45% weight loss, respectively. In the hydrolytic degradation, PNLs from monolactone showed higher degradation rate (0.6 %) than PNLs from dilactone (0.3%) after 8 days. The difference in degradation rates between PNLs from monolactone and dilactone in both degradation investigations can be correlated to their difference in polymer crystallinity.[230] In the study from Domb et al., the hydrolysis of copolyesters synthesized from lactide (LA) and ricinoleic acid (RA) lactone with w/w ratios from 9:1 to 5:5 was investigated by monitoring of weight loss and molecular weight loss. As shown in Figure 32, all polymers lost 20% - 40% weight with constant degradation rates after 60 days incubation. The M_n monitored by SEC decreased quickly to about 4000 g/mol during the first 20 days, followed by a slow degradation for another 40 days. The copolyesters maintained their integrity during the hydrolysis investigation and showed bulk erosion characteristics.[230] In another study of this group, copolyesters P(LA-RA) with 60:40 w/w was prepared by polycondensation, transesterification and ring opening polymerization. In comparison among the P(LA-RA) prepared by the three methods, all samples had about 20% weight loss after 60 days not depending on synthesis methods.[232]

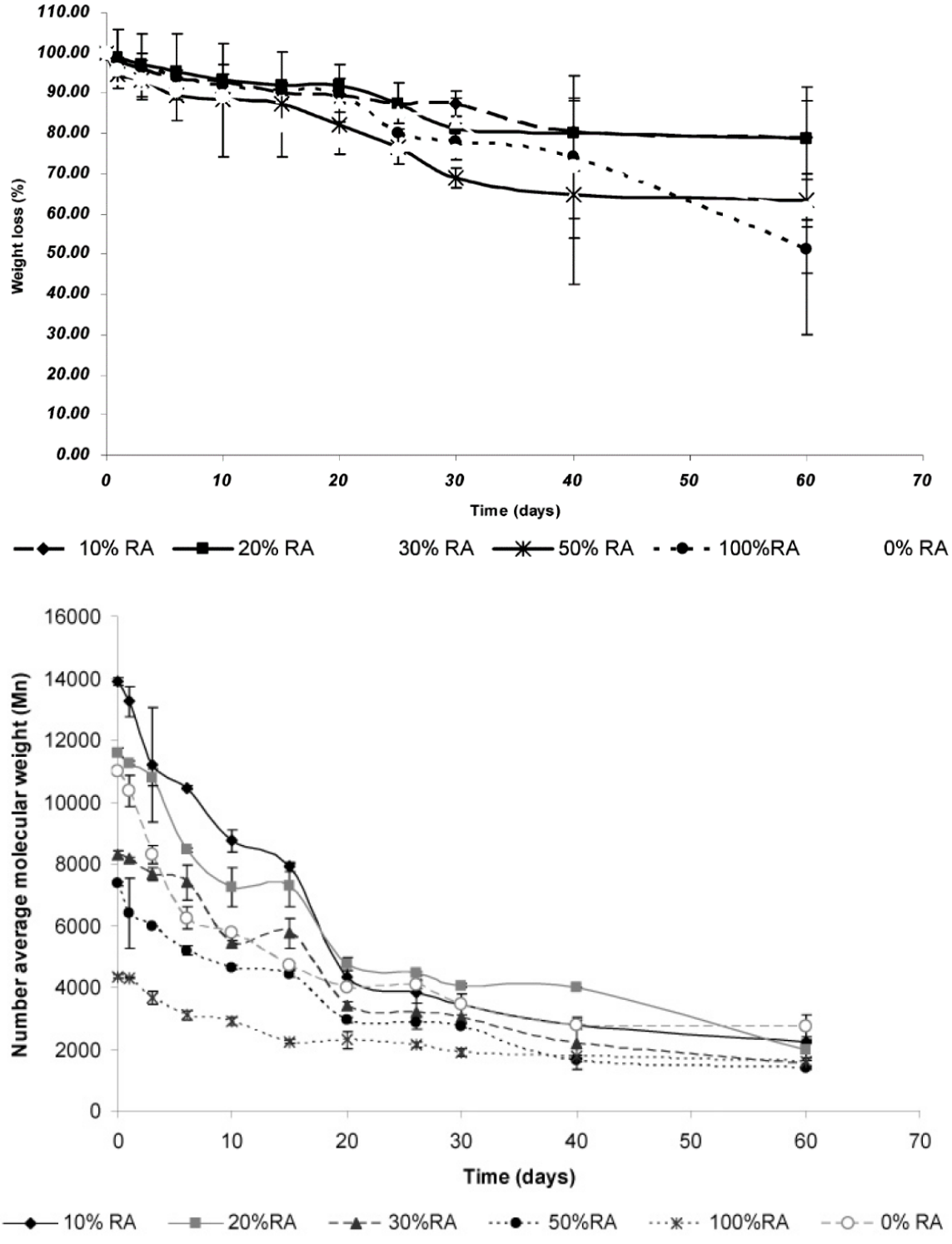


Figure 32. Investigation of Hydrolysis degradation of P(LA-RA) with different RA content by mention of weight loss (above) and molecular weight loss (below). (Reprinted with permission from Reference 229, Copyright 2005 American Chemical Society)

As mentioned above, polyanhydrides are known as a class of pure surface eroding biodegradable polymers. The anhydride bonds are highly hydrophobic and hence are believed to prevent water penetration into the polymer matrix. Only the labile anhydride bonds on the surface can be hydrolyzed and convert to two carboxylic acids in water medium. Hydrolytic degradation rate of polyanhydride depends on pH and solubility of the degradation byproducts.[262]

To identify the erosion type of fatty acid based polyanhydride, poly(fatty acid dimer:sebacic acid; FAD-SA, 50:50 w/w) was investigated by Shah et al. In this study, water uptake was investigated into cylinder and disk-shaped devices of P(FAD-SA) copolyanhydride in buffer solution with pH 1, 3, 5, 7.4 and 9. If P(FAD-SA) is hydrolyzed by pure surface erosion, water should not be found in the polymer bulk. At pH 1-5, there was no significant difference in the water uptake rate. Only about 5% (v/v) water was taken up into cylinder shaped devices under these pH conditions after 4 weeks incubation. In contrast, at pH 7.4 and 9, approx. two-fold water uptake to 8-9% (v/v) was obtained. The same investigation for disk-shaped devices showed similar water uptake of about 4% at pH 1-5. However, at pH 7.4 and 9, 15-20% (v/v) water uptake was observed in 2 weeks and was directly proportional to the surface area to volume ratio (SA/V) of disk-shaped device compared to that of the cylindrical device (3.27:1). Combining the observation by photomicrography and the large amount of water penetration found in devices, the hydrolysis investigation reveal that the P(FAD-SA) device was not undergoing pure surface erosion at pH 7.4 and 9.[263] As is well-known, polyanhydrides are mainly used as drug carrier. The correlation between drug release rate with erosion rate of polymer matrix was investigated in another study of Shah et al. As model compounds, highly water soluble mannitol (M = 182 g/mol), moderately water soluble inulin (M = 5000 g/mol) and lipophilic stearic acid (M = 284 g/mol) were incorporated into disk-shaped P(FAD-SA) copolyanhydride device. The results showed that the hydrolytic degradation of P(FAD-SA) is pH-dependent. At pH 9, the degradations of all the devices proceeded 8-10 times faster than that at pH 1-5 and 1.3-2 times faster than at pH 7.4. The pH-dependent property could be

explained by the base sensitive anhydride bond and higher solubility of degradation products resulting in rapid diffusion and dissolution out of the devices. In contrast, the degradation products, fatty acid dimer and sebacic acid, were unionized and insoluble in buffer solution at lower pH. Hence, water penetration into polymer matrix was blocked by forming a barrier from insoluble degradation products. Incorporation of water-soluble compounds into devices accelerated degradation rates at all pH, because the water-soluble compounds were rapidly released and created pores and channels in the devices resulting in water penetration into devices. In contrast, poorly water-soluble stearic acid retarded the degradation rate at all pH, except at pH 9 due to the enhanced water-solubility resulted from ionization of stearic acid at higher pH.[264] Another degradation study for P(RAM-SA) (Figure 29b) by Kumar et al. suggested similarly, that the fatty acid based polyanhydride degradation is not undergoing pure surface erosion.[265] In conclusion, the erosion of fatty acid based polyanhydride is a complex process depending on water uptake, bond cleavage, property of loading compounds and pH of the hydrolysis medium.

2.3.4 Applications

2.3.4.1 Controlled drug delivery system

Controlled drug delivery systems are one of the fastest growing areas of science and refers to transport a pharmaceutical compound in humans or animals to safely achieve a desired therapeutic effect. Developing novel drug delivery systems aim to reduce treatment toxicity and improve efficacy, such as increasing therapeutic activity and avoiding frequently repeated injections. As shown in Figure 33a, in temporal control, a drug is released over an extended duration, while in traditional injections drugs are rapidly metabolized and eliminated from the body. Figure 3b represents the benefit of distribution controlled drug release system. In distribution control, drugs are required to be delivered at the precise active site within the body to increase the drug concentration at site of action and maintain the systemic drug

concentration in a safe area to avoid causing side effects.[244]

The following key conditions must be met if any polymeric material is designed to use for drug delivery application[251]:

- Good biocompatibility of polymeric material and its degradation products;
- High hydrophobicity for controlled drug release;
- Degraded and metabolized completely from the body after implantation;
- Low melting point (normally <100 °C) and good solubility in common organic solvents for device fabrication;
- High flexibility, not broken during use and degradation;
- Low cost.

The vegetable oil based polymers satisfy all above properties and thus can be used as drug carrier. Moreover, it is observed that the incorporation of vegetable oil moieties in polymers can enhance the biodegradation and provides a better control over drug release.[182,251] A series of vegetable based polyanhydrides, polyesters and their copolymers were developed and applied as drug carrier for anticancer drugs, local anesthetics, antibiotics and large molecule biological drugs (e.g. proteins, peptides, hormones etc.).[230,232,243,245,247-252,265-268] Poly(ester anhydride) based on sebacic acid and ricinoleic acid P(SA:RA) demonstrated injectable properties. The polymers with SA: RA ratios of 3: 7, 2.5: 7.5 and 2: 8 (w/w) were pasty and suitable for injection at 37 °C. After injection, the polymer was solidified by a mechanism of *in situ* gelling organogels. According to the *in vivo* toxicity test, the polymer was nontoxic. Hence, this polymer could be used as injectable drug carrier for anticancer drug paclitaxel. *In vitro* drug release investigation showed, that drug was released for months.[252,266-268] Furthermore, hyperbranched polymers based on vegetable oils were as well evaluated for their degradation and drug release properties.[9,10]

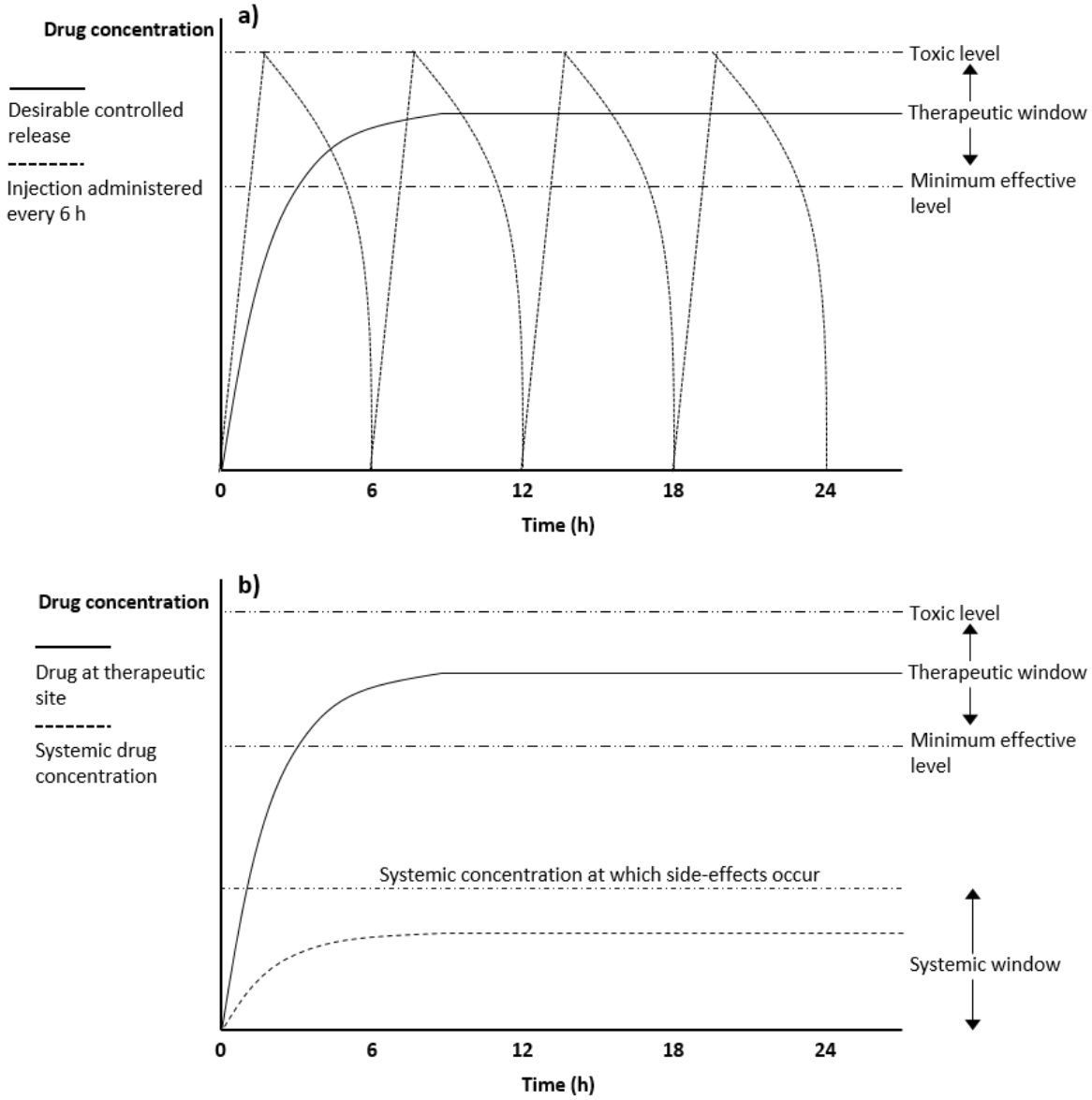


Figure 33. Schematic representation of controlled drug release: a) temporal control and b) distribution control. (Adapted with permission from Reference 244, Copyright 1999 American Chemical Society)

2.3.4.2 Tissue Engineering

Tissue engineering is an interdisciplinary field of engineering, life science and material sciences, and aims to regenerate or replace biological damaged tissues or generate replacement organs. Due to the biodegradable, biocompatible and versatile properties, vegetable oil based polymeric materials can be viewed as good candidate for tissue engineering. For example, poly(glycerol sebacate)ester based on sebacic acid and glycerol, which both are endogenous compounds in human metabolism, has been used in soft tissue engineering applications for repair of retina, nerve, vessel and myocardium. To study the *in vitro* fibroblast response and degradation, these polymers demonstrated satisfactory biocompatibility and biodegradation. Hard materials based on soybean oil and sunflower oil were as well investigated and showed cell adhesion and proliferation natures. However, most of these materials are based on non-degradable urethane cross-linked polymers.[8] Hence, an ideal cross-linked elastomer should be prepared from low toxic and *in vivo* metabolizable raw materials and additives (such as initiator, catalyst and solvent). Moreover, the used cross-linked polymeric materials should be biodegradable. Phosphoester cross-linked vegetable oil elastomers were prepared recently by Zhu et al. and meet all above principles. Investigations *in vivo* and *in vitro* confirm that the materials have good elasticity, biocompatibility and biodegradability, indicating potential applications in bone tissue engineering.[269]

2.3.4.3 Coating

Vegetable oils have been used as binder or additives in paints and coatings for a long time, even as constituent in coatings during the days of cave painting. In the last decades, vegetable oil based polyesters (alkyds), polyesteramides, polyetheramides and polyurethanes have been extensively investigated in coating applications. These coatings are available for specific uses due to their biocompatible, biodegradable and highly hydrophobic properties. However, the long aliphatic hydrophobic chains in the oil structure often lead to low mechanical strength,

lack toughness and water insolubility.[8,258] An example of biodegradable castor oil based polyesteramide for coating application was reported by Karak et al. They found that the coorperation of the ester and amide moieties in polymer backbone enhances the mechanical and thermal properties. The ester bonds could be degraded in the presence of lipase. The obtained adhesion strength, abrasion resistance, scratch hardness, gloss, impact strength and mechanical properties suggest applications in polymeric surface coatings.[256,257]

3 Experimental section

The used solvents and chemicals for preparation of low molecular weight compounds and polymers are summarized in the following Tables 4 and 5, in which the producer, purities and purification methods are presented.

3.1 Solvents

Table 4. Summary of used solvents

Solvent	Producer	Purity	Note
Acetonenitrile-d_3	Deutero	99 D%	-
Chloroform-d	Deutero	99.8 D%	-
Dichloromethane	-	-	distilled over calcium hydride
Diethyl ether	-	-	distilled
Dimethylformamide (DMF)	Acros Organics	99.8%	-
Dimethyl sulfoxide (DMSO)	Acros Organics	99.7%	-
Dimethyl sulfoxide-d_6	Deutero	99.5 D%	-
1,4-Dioxane	Grüssing	99.5%	dried over 4 Å molecular sieves
Ethyl acetate	-	-	-
n-Hexane	-	-	-
Methanol	-	-	distilled
n-Pentane	-	-	-

Pyridine	Alfa Aesar	99+%	-
Tetrahydrofuran (THF)	-	-	distilled over calcium hydride
Toluene	-	-	distilled over sodium
Water	-	-	bidistilled

3.2 Regents

Table 5. Summary of used regents

Regent	Producer	Purity	Note
Acetic acid	Sigma Aldrich	99.7+%	anhydrous
Acetic acid anhydride	Riedel-de Haën AG	-	shaken with phosphorus pentoxide, separated, then shaken with dry potassium carbonate, separated and fractionally distilled
Adipic acid (AA)	Acros Organics	99%	-
1,4-Butanediol (1,4-BD)	Acros Organics	99+%	vacuum distillation
3,5-Bis(triflurомethyl)aniline	Sigma Aldrich	97%	-
3,5-Bis(triflurомethyl)-phenyl isothiocyanate	Sigma Aldrich	98%	-
Bromoethylamine hydrobromide	Sigma Aldrich	99%	-
Castor oil	Carl Roth	-	-
Cyclohexaneamine	Acros Organics	99%	-
Cyclohexanedimethanol (CHDM)	Alfa Aesar	99%	cis+trans
Dibutyltin dilaurate (DBTD)	TCI	> 95%	-
Dibutyltin oxide (DBTO)	Acros Organics	98%	-

4-Dimethylaminopyridine (DMAP)	Fluka	> 99%	recrystallized from toluene
Dimethyl carbonate (DMC)	Acros Organics	99+%	-
Diphenyl carbonate (DPC)	Sigma Aldrich	99%	-
Formic acid	Merck	98%	-
1,6-Hexanediol (1,6-HD)	Sigma-Aldrich	99%	dried in vacuum overnight
Hexamethylene diisocyanate (HDI)	Fluka	> 98%	-
Hydrogen peroxide solution	Stockmeier	-	35% H_2O_2
Lipase solution from *Thermocyces languginosus*	Sigma Aldrich	-	≥100,000 U/g, pH 6.2
Lithium acetylacetonate (LiAcac)	Alfa Aesar	99.5%	-
Magnesium sulfate	-	-	anhydrous
7-Methyl-1,5,7-triazabicyclo-[4.4.0]dec-5-ene (MTBD)	Sigma Aldrich	98%	-
4 Å Molecular sieves	Merck	-	activated at 230 °C in vacuum overnight
1,5-Pentanediol (1,5-PD)	Fluka	96%	vacuum distillation
N-Phenyldiethanolamine	TCI	97%	-
Potassium carbonate	-	-	-
Potassium hydroxide	-	-	-
0.5 N potassium hydroxide solution	Alfa Aesar,	-	standardized
1,3-Propanediol	Alfa Aesar	99%	vacuum distillation
Pyridinium *p*-toluene sulphonate (PPTS)	Fluka	≥ 99%	-
4-Pyrrolidinopyridine (PPY)	Fluka	98%	-
Sodium azide	Sigma Aldrich	≥ 99%	-
Sodium borohydride	Acros Organics	98+%	-

Sodium chloride	-	-	-
Sodium hydrogencarbonate	-	-	-
Sodium hydroxide	-	-	-
Soybean oil	Alfa Aesar	-	-
1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD)	Sigma Aldrich	98%	-
Tri(ethylene glycol) diviniyl ether (TEDE)	Sigma Aldrich	98%	-
Tris(hydroxymethyl)ethane (THE)	Alfa Aesar	97%	dissolved in THF, purified by precipitation in *n*-hexane
Tris(hydroxymethyl)propane (THP)	TCI	> 98%	-
Tris(4-methoxy)phenyl phosphine	Sigma Aldrich	95%	-
Zinc powder	Sigma Aldrich	≥ 98%	< 10 µm

3.3 Measurements

3.3.1 NMR spectroscopy

^{1}H and ^{13}C NMR spectra were recorded by using a Bruker AV 500 spectrometer at 500 MHz and 125 MHz, respectively. All measurements were carried out at 25 °C. The chemical shift (δ) and coupling constant (J) are given in ppm and Hz, respectively. Chloroform-*d* ($CDCl_3$, 99.8 D%), dimethylsulfoxide-d_6 (DMSO-d_6, 99.5 D%) or acetonenitrile-d_3 (MeCN-d_3, 99 D%) were used as solvent for NMR measurements. Data were obtained and processed using MestReNova Software (Version: 6.0.2-5475, Mestrelab Research Chemistry Software Solutions).

3.3.2 Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR spectra were recorded on Vertex 70 spectrometer (Bruker Optik, Ettlingen, Germany) with a RT_DLaTGS Detector. All samples were measured in the wavelength region of 4000 cm^{-1} to 400 cm^{-1}. An air cooled tungsten halogen lamp was employed as light source for the visible (VIS), Near infrared (NIR), mid infrared (MIR) and far infrared (FIR) region.

3.3.3 Differential Scanning Calorimetry (DSC)

DSC was performed with Netzsch DSC 204 F1 Phönix® at a heating rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperature (T_g) and the melting point (T_m) values were recorded during the second run.

3.3.4 Size exclusion chromatography (SEC)

The molar masses and dispersities ($Đ_M$) of the linear polycarbonates were analyzed employing a size exclusion chromatography (SEC) system equipped with four consecutive columns (PSS-SDV columns filled with 5 µm gel particles with a defined porosity of 10^6 Å, 10^4 Å, 10^3 Å and 10^2 Å, respectively) and a Shodex RI-detector (RI-101) at 30 °C. The system was operated at a flow rate of 0.75 mL/min with chloroform as solvent. Polystyrene (PS) standards were used for calibration.

The molar masses and $Đ_M$ of HBPCs were analyzed on a SEC equipped with three consecutive columns (PSS-GRAM columns filled with 10 µm gel particles with a defined porosity of 10^4 Å, 10^3 Å and 10^2 Å, respectively), a Waters RI-detector (RI 2410) and a differential viscometer (PSS ETA2010) at 50 °C. As eluent, dimethylacetamide (DMAc) was used with a flow rate of 0.5 mL/min. Molar masses were obtained by using universal calibration.

The molar masses and $Đ_M$ of the vegetable oil based hyperbranched polymers were analyzed

employing a SEC system equipped with two consecutive columns (PSS-SDV columns filled with particles with a defined porosity of 10^5 Å and 10^3 Å, respectively) and a Knauer RI-detector (RI 2300) at room temperature. The system was operated at a flow rate of 1.0 mL/min with tetrahydrofuran (THF) as solvent. PS standards were used for calibration.

3.3.5 Electrospray Ionisation Time of Flight Mass Spectrosmetry (ESI-ToF-MS)

ESI-ToF-mass spectra were measured on a SYNAPT G2 HDMS ™ from Waters. The mass spectrometric parameters were the following: Capillary voltage: 2.5 kV; sampling cone voltage: 50 V; extraction cone voltage: 1 V; cone gas flow: 30 L/h; source temperature: 120 °C; desolvation gas flow: 650 L/h; desolvation temperature: 350 °C; helium cell gas flow: 180 mL/min; IMS gas flow: 90 mL/min; IMS wave velocity: 460 m/s; IMS wave height: 40 V. The PBC sample was dissolved in acetonitrile (2 g/L) and then mixed with NaI 0.1 g/L in methanol and methanol in the ratio of 5: 5: 990. Data were obtained and processed using Polymerix Software.

3.3.6 Thin-layer chromatography (TLC)

Silica gel 60 F_{254} aluminum plates (20 x 20 cm, from Merck KGaA) were used for TLC analysis. The compounds on TLC were analyzed under UV-lamp (from Merck KGaA, Germany) with a wavelength of 254 nm. Retardation factors (R_f) are given as results of TLC in synthesis procedures.

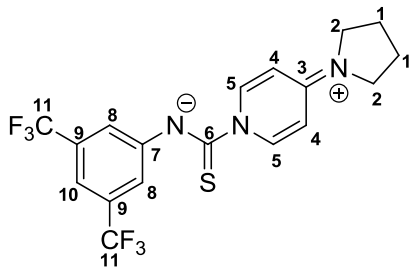
3.3.7 Column chromatography

In column chromatography, silica gel 60 (0.063 – 0.040 mm) was used as stationary phase. All solvents as eluents were freshly distilled before use. The mixing ratios (volume ratios) of used solvents were given in synthesis procedures.

3.4 Synthesis of low molecular weight compounds and polymers

3.4.1 Synthesis of (3,5-bis(trifluoromethyl)phenyl)(4-(pyrrolidin-1-ium-1-ylidene)-1,4-dihydropyridine-1-carbonothioyl)amide[270]

4-pyrrolidinopyridine (0.74 g, 5.00 mmol) was added to a solution of 3,5-bis(trifluromethyl)phenyl isothiocyanate (0.92 mL, 5.00 mmol) in toluene (10 mL) in a 25 mL round-bottom flask. The mixture was then stirred at ambient temperature for 2 h. The precipitated solid was filtered and recrystallized from toluene. The product was filtrated and dried under vacuum to give a yellow solid (1.47 g, 0.35 mmol, yield: 70 %, mp. = 132 - 133 °C).



^{1}H and ^{13}C NMR spectra: Figure SI-1

^{1}H-NMR (500 MHz, CD_3CN)

δ (ppm) = 2.00-2.14 (m, 4 H, $^{1}CH_2$), 3.13-3.69 (m, 4 H, $^{2}CH_2$), 6.45-6.72 (2H, ^{4}CH), 7.61-7.96 (m, 3 H, $^{8,10}CH$), 8,10-8.12 and 9.59-9.61 (m, 2 H, ^{5}CH).

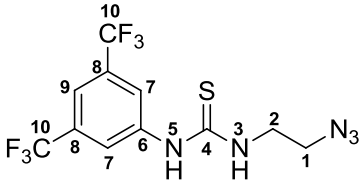
^{13}C-NMR (125 MHz, CD_3CN)

δ (ppm) = 24.77 and 24.94 (2 C, $^{1}CH_2$), 46.76 and 48.73 (2 C, $^{2}CH_2$), 105.91 and 106.91 (2 C, ^{4}CH), 120.85 (1 C, ^{10}CH), 123.31 (2 C, $^{11}CF_3$), 126.69 (2 C, ^{8}CH), 137.99 (2 C, $^{9}C_q$), 148.97 (2 C, ^{5}CH), 151.93 (1 C, $^{7}C_q$), 153.88 and 155.15 (1 C, $^{3}C_q$)

3.4.2 Synthesis of 1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(((4-methoxyphenyl)-phosphinylidene)amino)ethyl)thiourea[171]

Step 1:

Sodium azide (0.96 g, 14.6 mmol) was added to a solution of bromoethylamine hydrobromide (1.00 g, 4.88 mmol) in bidistilled water (5 mL) at room temperature. The mixture was then stirred at 80 °C overnight and a red solution was formed. After cooling to room temperature, the mixture was neutralized with potassium hydroxide (1.60 g, 28.5 mmol) and extracted with diethyl ether (3 x 50 mL). The organic extracts were dried over anhydrous magnesium sulfate. The diethyl ether was removed under a flow of nitrogen. Then anhydrous THF (25 mL) and 3,5-bis(trifluromethyl)phenyl isothiocyanate were added to the flask. The mixture was stirred under argon atmosphere at room temperature for 3 h. THF was removed *in vacuo* and a further purification followed by flash chromatography over silica gel using ethyl acetate/*n*-hexane (3:7, R_f = 0.40) to afford a colorless solid (1.00 g, 2.81 mmol, yield: 57 %).



^{1}H and ^{13}C NMR spectra: Figure SI-2

^{1}H-NMR (500 MHz, $CDCl_3$)

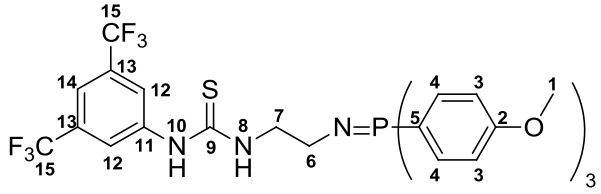
δ (ppm)= 3.67 (m, 2 H, $^1CH_2$), 3.83 (m, 2 H, $^2CH_2$), 6.44 (b, 1 H, ^{3}NH), 7.75 (s, 1 H, ^{9}CH), 7.80 (s, 2 H, ^{7}CH), 8.31 (b, 1 H, ^{5}NH)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 44.36 (1 C, $^2CH_2$), 50.28 (1 C, $^1CH_2$), 122.70 (q, 2 C, J_{CF} = 273 Hz, $^{10}CF_3$), 120.01 (1 C, ^{9}CH), 124.21 (2 C, ^{7}CH), 133.26 (t, 2 C, J_{CF} = 34 Hz, ^8C_q), 138.43 (1 C, ^6C_q), 181.14 (1 C, ^4C_q)

Step 2:

The 1-(2-azidoethyl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea from step 1 (1.00 g, 2.81 mmol) and tris(4-methoxy)phenyl phosphine (0.99 g, 2.81 mmol) were dissolved in anhydrous diethyl ether (9 mL) in a round-bottom flask. The mixture was stirred at room temperature under argon atmosphere overnight. The precipitated solid was filtrated, washed with *n*-pentane (30 mL) and dried under vacuum at room temperature to give a colorless solid (1.57 g, 2.30 mmol, yield: 82 %, mp. = 109 - 111°C).



^{1}H and ^{13}C NMR spectra: Figure SI-3

^{1}H-NMR (500 MHz, $CDCl_3$)

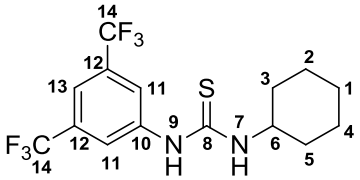
δ (ppm)= 3.08 (m, 2 H, $^{6}CH_2$), 3.63 (b, 2 H, $^{7}CH_2$), 3.83 (s, 9 H, $^{1}CH_3$), 6.96 (m, 6 H, ^{3}CH), 7.27 (s, 1 H, ^{14}CH), 7.46 (m, 6 H, ^{4}CH), 7.54 (s, 2 H, ^{12}CH)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 46.70 (d, 1 C, J_{CP}=14.6 Hz, $^{6}CH_2$), 47.00 (1 C, $^{7}CH_2$), 55.48(1 C, $^{1}CH_3$), 115.13 (d, 1 C, J_{cp}=85.9 Hz, ^{5}CH), 115.00 (d, 2 C, J_{CP}=13.6 Hz, ^{4}CH), 116.33, (1 C, ^{14}CH), 123.64 (q, 2 C, J_{CF}=272.7 Hz, $^{15}CF_3$), 124.20 (2 C, ^{12}CH), 130.54 (q, 2 C, J_{CF}=32.7 Hz, $^{13}C_q$), 134.69 (d, 2 C, J_{CP}=11.5 Hz, ^{3}CH), 149.09 (1 C, $^{11}C_q$), 163.65 (d, 1 C, J_{cp}=2.8 Hz, $^{2}C_q$)

3.4.3 Synthesis of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea[271]

Cyclohexaneamine (0.42 mL, 3.70 mmol) was added to a solution of 3,5-bis(trifluromethyl)phenyl isothiocyanate (0.68 mL, 3.70 mmol) in THF (4 mL). The mixture was then stirred at 30 °C for 2 h. THF was removed *in vacuo* and an off-white solid was obtained. The solid was washed with *n*-pentane (4x10 mL) to obtain a white solid (1.34 g, 3.62 mmol, yield: 98%, mp. = 167 - 168 °C).



^{1}H and ^{13}C NMR spectra: Figure SI-4

^{1}H-NMR (500 MHz, DMSO)

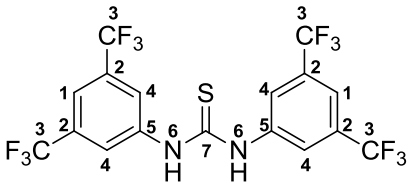
δ (ppm)= 1.20-1.94 (m, 10 H, $^{1\text{-}5}CH_2$), 4.12 (b, 1 H, ^{6}CH), 7.70 (s, 1 H, ^{13}CH), 8.13 (b, 1 H, ^{7}NH), 8.25 (b, 2 H, ^{11}CH), 9.84 (b, 1 H, ^{9}NH)

^{13}C-NMR (125 MHz, DMSO)

δ (ppm) = 24.88 (2 C, $^{2,4}CH_2$), 25.55 (1 C, $^{1}CH_2$), 32.06 (2 C, $^{3,5}CH_2$), 52.75 (1 C, ^{6}CH), 116.30 (1 C, ^{13}CH), 122.21 (2 C, ^{11}CH), 123.73 (q, 2 C, J_{CF}=272.8 Hz, $^{14}CF_3$), 130.56 (q, 2 C, J_{CF}=32.4 Hz, $^{12}C_q$), 142.51 (1 C, $^{10}C_q$), 179.68 (1 C, $^{8}C_q$)

3.4.4 Synthesis of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)thiourea[271]

3,5-Bis(trifluromethyl)phenyl isothiocyanate (0.5 mL, 2.70 mmol) was added to a solution of 3,5-bis(trifluromethyl)aniline (0.4 mL, 2.67 mmol) in THF (5 mL) in a 25 mL round-bottom flask. The mixture was then stirred at 50 °C for 4 d. THF was removed *in vacuo* and yellow oil was obtained. After the purification by flash chromatography over silica gel using ethyl acetate/*n*-hexane (2: 8, R_f = 0.41) a white solid was obtained (0.92 g, 1.81 mmol, yield: 70 %, mp. = 162 - 163 °C).



^{1}H and ^{13}C NMR spectra: Figure SI-5

^{1}H-NMR (500 MHz, DMSO)

δ (ppm) = 7.84 (s, 2 H, ^{6}NH), 8.23 (s, 4 H, ^{2}CH), 10.63 (s, 2 H, ^{1}CH)

^{13}C-NMR (125 MHz, DMSO)

δ (ppm) = 122.93 (4 C, ^{1}CH), 128.38 (q, 4 C, J_{CF}=272.7 Hz, $^{3}CF_3$), 129.30 (4 C, ^{4}CH),135.58 (q, 4 C, J_{CF}=33.0 Hz, $^{2}C_q$), 146.40 (2 C, $^{5}C_q$), 185.84 (1 C, $^{7}C_q$)

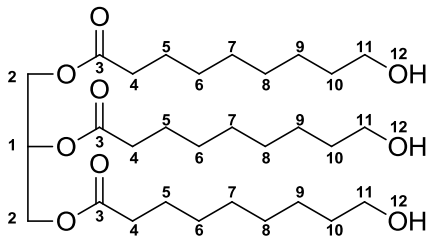
3.4.5 Ozonolysis of castor oil and soybean oil

In a three-necked flask with dichloromethane/methanol (4: 3), castor oil or soybean oil with a concentration of 0.1 g/ml was added. The reaction mixture was cooled to 0 - 3 °C using an ice/water bath. Ozonolysis was carried out by bubbling ozone/oxygen generated using an i-Fischer OZ 500/5 ozone generator with input oxygen pressure of 0.5 bar. After the ozonolysis finished, the mixture was bubbled with nitrogen for 10 min to remove unreacted ozone from solution.

3.4.6 Synthesis of triol from castor oil (TriOL-CO) and soybean oil (TriOL-SO)[208,209]

Sodium borohydride (1: 1 molar ratio with unsaturation in vegetable oil) was added slowly into the ozonolysis reaction mixture at a temperature below 15 °C. The reaction mixture was stirred for further 1 h to finish the reduction process. The reaction mixture was washed with brine until pH 7 was reached and dried over anhydrous magnesium sulfate. After removing the solvent, the triol was purified in a vacuum dry box at 120 °C and 1 x 10^{-3} mbar to remove the side products (e.g. 1-propanol, 1-nonanol, 1-heptanol, 1,3-propanediol and 1,3-nonanediol).

A white waxy solid was obtained as product with a yield of 95% and 88% for castor oil and soybean oil, respectively.



^{1}H spectrum: Figure SI-6

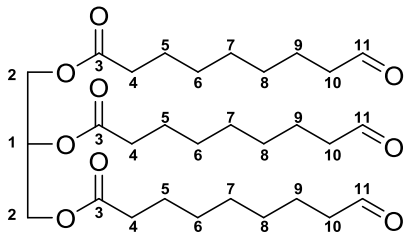
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 0.84 (m, 3 H, CH_3 from unreactive saturated chain), 1.00 – 1.75 (m, 36 H, $^{5\text{-}10}CH_2$), 2.24 (m, 9 H, $^{4}CH_2$, ^{12}OH), 3.57 (t, 6 H, $^{3}J_{HH}$ = 6.7 Hz ,$^{11}CH_2$), 4.10 – 4,25 (m, 4 H, $^{2}CH_2$), 5.22 (m, 1 H, ^{1}CH)

MS (ESI): m/z(theoretical) 560.392; m/z(found) 561.401 ($M + H^+$), 583.382 ($M + Na^+$).

3.4.7 Synthesis of trialdehyde from castor oil (TriAD-CO) and soybean oil(TriAD-SO)[210]

Zinc powder (2.5: 1 molar ratio with unsaturation in vegetable oil) was added into the ozonolysis reaction mixture at a temperature of 0 °C. Anhydrous acetic acid (2: 1 molar ratio with zinc) was then added slowly (strongly exothermal reaction, temperature should be maintained below 30 °C). The mixture was then stirred for 1 h at room temperature. After filtration of zinc salt, the organic phase was washed two times with sodium hydrogencarbonate solution (5 wt%) and with water until pH 7 was reached. The organic phase was dried over magnesium sulfate. After removing the solvent, the trialdehyde was purified under vacuum at 90 °C to remove the side products (e.g. 1-propyl aldehyde, 1-nonyl aldehyde, heptanal, malondialdehyde and 3-hydroxynonanal). A clear yellow liquid was obtained as product with a yield of 71% and 78% for castor oil and soybean oil, respectively.



^{1}H spectrum: Figure SI-7

^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 0.86 (m, 3 H, CH_3 from unreactive saturated chain), 1.00 – 1.75 (m, 30 H, $^{5\text{-}9}CH_2$), 2.29 (m, 6 H, $^{4}CH_2$), 2.40 (m, 6 H, $^{10}CH_2$), 4.10 – 4.30 (m, 4 H, $^{2}CH_2$), 5.24 (m, 1 H, ^{1}CH), 9.74 (t, $^{3}J_{HH}$ = 1.8 Hz, 3 H, ^{11}CHO).

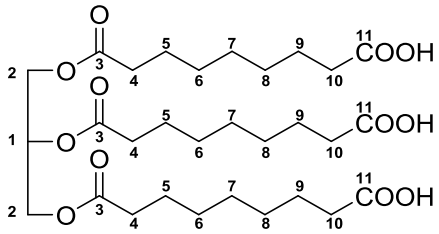
MS (ESI): m/z(theoretical) 554.346; m/z(found) 577.335 ($M + Na^{+}$).

3.4.8 Synthesis of tricarboxylic acid from soybean oil (TriAC-SO-Ozo) via ozonolysis

35% Hydrogen peroxide (5 mL pro 1 g soybean oil) and formic acid (5 mL pro 1 g soybean oil) were added into the ozonolysis reaction mixture at a temperature of 0 °C. The mixture was then stirred at 60 °C for 1 h and 70 °C for 30 min (strongly exothermal reaction, flask should be equipped with a reflux condenser). After cooling to room temperature, water was added to the mixture, and the organic layer was separated. The aqueous layer was extracted three times with dichloromethane. The organic phase was washed seven times with water and dried over magnesium sulfate. After removing the solvent, the tricarboxylic acid was purified under vacuum at room temperature overnight. A colorless liquid was obtained as product with a yield of 65%.

3.4.9 Synthesis of tricarboxylic acid via oxidation of trialdehyde from castor oil (TriAC-CO-Ox) and soybean oil (TriAC-SO-Ox)

In a round flask, TriAD, 35% hydrogen peroxide (5 mL pro 1 g trialdehyde) and formic acid (5 mL pro 1 g trialdehyde) were added. The mixture was stirred at 60 °C for 1 h and then at 70 °C for 30 min using a reflux condenser. After cooling to room temperature, dichloromethane and brine were added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted three times with dichloromethane. The organic phase was washed seven times with water and dried over magnesium sulfate. After removing the solvent, the tricarboxylic acid was purified under vacuum at room temperature overnight. A colorless liquid was obtained as product with a yield of 77% for castor oil and 78% for soybean oil.



^{1}H spectrum: Figure SI-8

^{1}H-NMR (500 MHz, DMSO)

δ (ppm) = 0.87 (m, 3 H, CH_3 from unreactive saturated chain), 1.00 – 1.75 (m, 30 H, $^{5\text{-}9}CH_2$), 2.18 (m, 6 H, $^{10}CH_2$), 2.28 (m, 6 H, $^{4}CH_2$), 4.10 – 4.30 (m, 4 H, $^{2}CH_2$), 5.18 (m, 1 H, ^{1}CH), 11.93 (b, 3 H, $^{11}COOH$).

MS (ESI): m/z(theoretical) 602.330; m/z(found) 625.320 ($M + Na^{+}$).

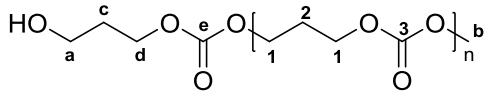
3.4.10 General procedure for polycondensation of diols and DMC via two-step polycondensation

In a two-necked flask connected to a Schlenk line with vacuum and argon gas lines diol, DMC and organic catalysts were added under argon atmosphere. The mixture was stirred in an oil bath at 130 °C until achieving the equilibrium determinated by ^{1}H NMR spectroscopy within 2 - 18 h. Before starting the second step, the flask was equipped with a vacuum distillation apparatus. In the second step the polycondensation was carried out under reduced pressure with the oil bath temperature maintained at 130 °C or increased to 170 °C. The polycondensation was conducted over night. The mixture was then cooled to room temperature and dissolved in chloroform. The polymer was isolated by precipitation in ethanol and dried under vacuum to give a white solid.

3.4.11 General procedure for the synthesis of linear aliphatic homo- and copolycarbonates from different diols and DMC via one-pot polycondensation

All polymerizations were carried out in a two-necked flask equipped with a pressure-equalized addition funnel filled with 16 g of 4 Å molecular sieve, a cold reflux condenser and connected to a Schlenk line with vacuum and argon gas lines. The diol(s) (23.4 mmol), DMC, catalyst and 1,4-dioxane were added to the flask under argon atmosphere. The reaction mixture was stirred under reflux (approximate oil bath temperature of 120 °C) for 72 or 96 h. The mixture was then cooled to room temperature and diluted with dichloromethane. The polymer was isolated via precipitation in methanol and dried in vacuum.

Poly(trimethylene carbonate) (PTMC)



^{1}H and ^{13}C NMR spectra: Figure SI-9

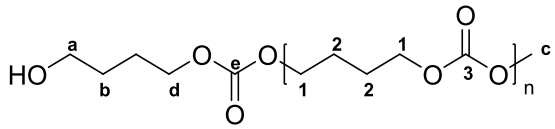
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 2.04 (m, 2 H, $^{2}CH_2$), 3.73 (t, 2 H, $^{3}J_{HH}$ = 5.8 Hz, $^{a}CH_2$), 3.77 (s, 3 H, O^{b}CH), 4.23 (t, 4 H, $^{3}J_{HH}$ = 6.2 Hz, $^{1}CH_2$)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 28.14 (1 C, $^{2}CH_2$), 37.13 (1 C, $^{c}CH_2$), 59.01 (1 C, $^{a}CH_2$), 64.37 (2 C, $^{1}CH_2$), 65.13 (1 C, $^{d}CH_2$), 154.97 (1 C, $^{3}C_q$), 155.35 (1 C, $^{e}C_q$)

Poly(butylene carbonate) (PBC)



^{1}H and ^{13}C NMR spectra: Figure SI-10

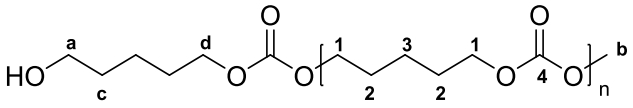
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.65 (m, 3 H, $^{b}CH_2$, OH), 1.76 (b, 4 H, $^{2}CH_2$), 3.67 (t, 2 H, $^{3}J_{HH}$ = 6.3 Hz, $^{a}CH_2$), 3.77 (s, 3 H, O$^{c}CH_3$), 4.15 (b, 4 H, $^{1}CH_2$)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 28.28 (2 C, $^{2}CH_2$), 29.04 (1 C, $^{b}CH_2$), 54.83 (1 C, $^{c}CH_3$), 62.39 (1 C, $^{a}CH_2$), 67.39 (2 C, $^{1}CH_2$), 67.89 (1 C, $^{d}CH_2$), 155.30 (1 C, $^{3}C_q$), 155.36 (1 C, $^{e}C_q$)

Poly(pentamethylene carbonate) (PPC)



^{1}H and ^{13}C NMR spectra: Figure SI-11

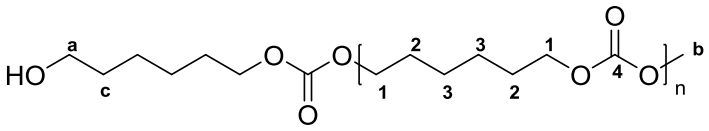
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.46 (m, 2 H, $^{3}CH_2$), 1.70 (m, 4 H, $^{2}CH_2$), 3.64 (t, 2 H, $^{3}J_{HH}$ = 6.5 Hz, $^{a}CH_2$), 3.76 (s, 3 H, $O^{b}CH_3$), 4.12 (t, 4 H, $^{3}J_{HH}$ = 6.6 Hz, $^{1}CH_2$)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 21.97 (1 C, $^{3}CH_2$), 28.19 (2 C, $^{2}CH_2$), 32.14 (1 C, $^{c}CH_2$), 62.51 (1 C, $^{a}CH_2$), 67.50 (2 C, $^{1}CH_2$), 67.71 (1 C, $^{d}CH_2$), 155.16 (1 C, $^{4}C_q$)

Poly(hexamethylene carbonate) (PHC)



^{1}H and ^{13}C NMR spectra: Figure SI-12

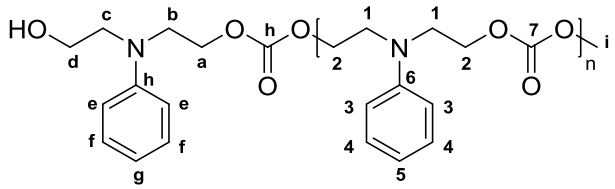
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.40 (m, 4 H, $^{3}CH_2$), 1.67 (m, 4 H, $^{2}CH_2$), 3.63 (t, 2 H, $^{3}J_{HH}$ = 6.5 Hz, $^{a}CH_2$), 3.77 (s, 3 H, $O^{b}CH_3$), 4.11 (t, 4 H, $^{3}J_{HH}$ = 6.7 Hz, $^{1}CH_2$)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 25.75 (2 C, $^{3}CH_2$), 28.93 (2 C, $^{2}CH_2$), 32.95 (1 C, $^{c}CH_2$), 55.00 (1 C, $^{b}CH_3$), 63.13 (1 C, $^{a}CH_2$), 68.14 (2 C, $^{1}CH_2$), 155.72 (1 C, $^{4}C_q$)

Poly(diethylphenylamine carbonate) (PDEAC)



^{1}H and ^{13}C NMR spectra: Figure SI-13

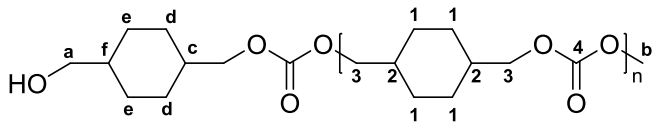
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 3.17 (t, 2 H, $^{3}J_{HH}$ = 4.8 Hz, $^{b}CH_2$), 3.54-3.70 (m, 4 H, $^{1}CH_2$), 3.50 (t, 2 H, $^{3}J_{HH}$ = 5.6 Hz, $^{c}CH_2$), 3.77 (t, 2 H, $^{3}J_{HH}$ = 5.6 Hz, $^{d}CH_2$), 3.87 (t, 2 H, $^{3}J_{HH}$ = 4.8 Hz, $^{a}CH_2$), 4.17-4.40 (m, 4 H, $^{2}CH_2$), 6.66-6.80 (m, 3 H, $^{3,5}CH$), 6.86-6.94 (m, 3 H, $^{e,g}CH$), 7.16-7.26 (m, 2 H, ^{4}CH), 7.26-7.31 (m, 2 H, ^{f}CH)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 49.52 (1 C, $^{b}CH_2$), 49.79 (2 C, $^{1}CH_2$), 50.64 (1 C, $^{c}CH_2$), 54.50 (1 C, $^{i}CH_3$), 60.30 (1 C, $^{d}CH_2$), 64.91 (2 C, $^{2}CH_2$), 67.07 (1 C, $^{a}CH_2$), 112.29, 117.44, 129.65, 147.06 (6 C, $^{3\text{-}6}C_{Ar}$), 113.08, 115.85, 120.17, 129.31, 129.53, 147.92 (6 C, $^{e,f,g,h}C_{Ar}$), 155.15 (1 C, $^{7}C_q$), 155.21 (1 C, $^{h}C_q$)

Poly(cyclohexan-1,4-dimethylene carbonate) (PCDMC)



^{1}H and ^{13}C NMR spectra: Figure SI-14

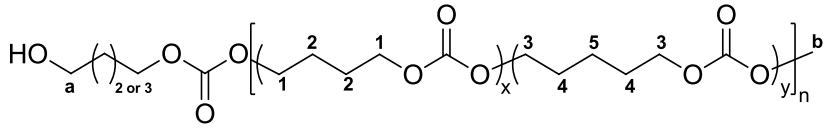
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 0.97-1.90 (m, 10 H, $^{1}CH_2$, ^{2}CH), 3.44-3.54 (m, 2 H, $^{a}CH_2$), 3.77 (s, 3 H, $O^{b}CH_3$), 3.93-4.04 (m, 4 H, $^{3}CH_2$)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 25.18, 28.64 (4 C, $^{1}CH_2$), 25.41 (2 C, $^{d}CH_2$), 28.90 (2 C, $^{e}CH_2$), 34.56, 37.12 (2 C, ^{2}CH), 37.39 (1 C, ^{c}CH), 40.42 (1 C, ^{f}CH), 54.72 (1 C, $^{b}CH_3$), 68.74, (1 C, $^{a}CH_2$), 70.66, 72.80 (2 C, $^{3}CH_2$), 155.55 (1 C, $^{4}C_q$)

Poly(butylene carbonate)-*co*-poly(pentamethylene carbonate) (PBC-*co*-PPC)

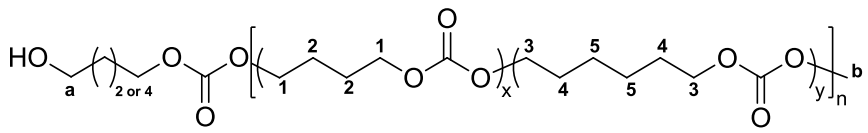


^{1}H NMR spectrum: Figure SI-15

^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.46 (m, 2 H, $^{5}CH_2$), 1.63-1.73 (m, 4 H, $^{4}CH_2$), 1.76 (m, 4 H, $^{2}CH_2$), 3.67 (m, 2 H, $^{a}CH_2$), 3.77 (s, 3 H, $O^{b}CH_3$), 4.10-4.20 (m, 4 H, $^{1}CH_2$; 4 H, $^{3}CH_2$)

Poly(butylene carbonate)-*co*-poly(hexamethylene carbonate) (PBC-*co*-PHC)

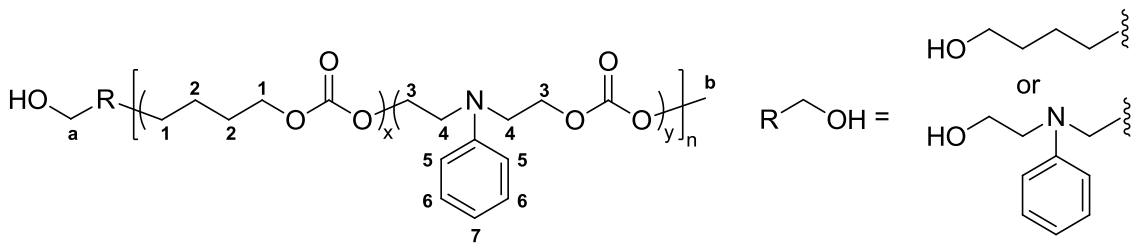


^{1}H NMR spectrum: Figure SI-16

^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.40 (m, 4 H, $^{5}CH_2$), 1.67 (m, 4 H, $^{4}CH_2$), 1.77 (m, 4 H, $^{2}CH_2$), 3.62-3.69 (m, 2 H, $^{a}CH_2$), 3.77-3.78 (m, 3 H, $O^{b}CH_3$), 4.00-4.27 (m, 4 H, $^{1}CH_2$; 4 H, $^{3}CH_2$)

Poly(butylene carbonate)-*co*-poly(diethylphenylamine carbonate) (PBC-*co*-PDEAC)

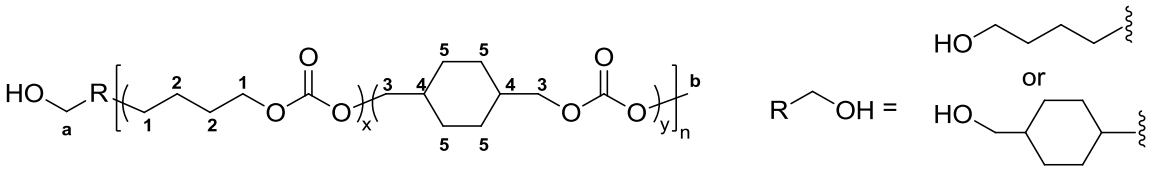


^{1}H NMR spectrum: Figure SI-17

^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 1.75 (m, 4 H, $^{2}CH_2$), 3.65 (m, 2 H, $^{a}CH_2$), 3.76 (b, 3 H, $O^{b}CH_3$), 4.14 (m, 4 H, $^{1}CH_2$), 4.26 (m, 4 H, $^{3}CH_2$), 6.73 (m, 3 H, $^{5,7}CH$), 7.21(m, 2 H, ^{6}CH)

Poly(butylene carbonate)-*co*-poly(cyclohexan-1,4-dimethylene carbonate) (PBC-*co*-PCDMC)



^{1}H NMR spectrum: Figure SI-18

^{1}H-NMR (500 MHz, $CDCl_3$)

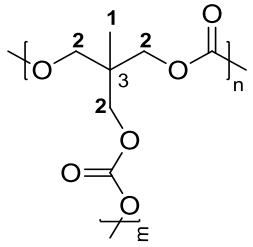
δ (ppm) = 0.90-1.90 (m, 4 H, $^2CH_2$; 10 H, ^4CH, $^5CH_2$), 3.66 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, $^aCH_2$), 3.75 (b, 3 H, O^bCH_3), 3.90-4.05 (m, 4 H, $^3CH_2$), 4.14 (m, 4 H, $^1CH_2$)

3.4.12 General procedure for the synthesis of HBPCs from different triols and DMC via one-pot polycondensation

In a two-necked flask equipped with the above-mentioned apparatus, triol (23.4 mmol), DMC, catalyst and solvent were added under argon atmosphere. The mixture was stirred under reflux (approximate oil bath temperature of 120 °C) for 2 to 18 h. The mixture was then cooled to room temperature and diluted with acetone or THF. The polymer was isolated by precipitation in water/methanol (v/v = 9: 1) or in water and centrifugation and dried in vacuum at room temperature to give a colorless solid.

Hyperbranched poly(1,1,1-tris(hydroxymethyl)ethyl carbonate) (PTHEC)

^{1}H and ^{13}C NMR spectra: Figure SI-19



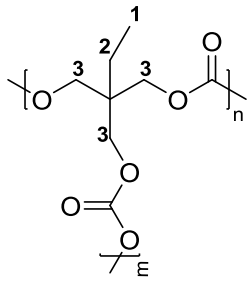
^{1}H-NMR (500 MHz, DMSO)

δ (ppm) = 0.75–1.05 (m, 3 H, $^{1}CH_3$), 3.20-3.35 (m. 2 H **CH_2**OH from alcohol end group), 3.69-3.72 (m, 3 H, OC(O)O**CH_3**, from methyl carbonate end group), 3.90-4.20 (m, 2 H, $^{2}CH_2$), 4.49 (b, CH_2**OH**, from alcohol end group), 4.80 (b, CH_2**OH**, from alcohol end group).

^{13}C-NMR (125 MHz, DMSO)

δ (ppm) = 16.44, 16.51, 16.55, 16.59 ($^{1}CH_3$), 25.99 ($^{3}C_q$), 39.12, 41.24 (**CH_2**OH from alcohol end group), 55.05, 55.21 (OC(O)O**CH_3**, from methyl carbonate end group), 63.08, 63.14, 63.75, 67.48, 69.15, 69.49, 69.70, 69.89, 70.22, 70.43 ($^{2}CH_3$), 154.68, 154.87, 155.06, 155.27, 155.33, 155.56 (C_q from carbonyl groups in polymer backbone and methyl carbonate end group)

Hyperbranched poly(1,1,1-tris(hydroxymethyl)propyl carbonate) (PTHPC)



^{1}H NMR spectrum: Figure SI-20

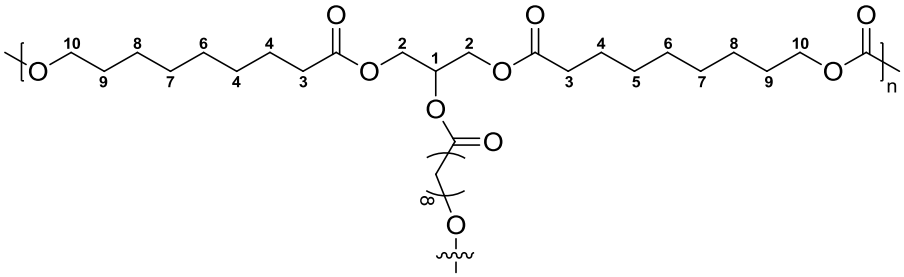
^{1}H-NMR (500 MHz, DMSO)

δ (ppm) = 0.8 (m, 3 H, $^{1}CH_3$), 1.2-1.5 (m, 2 H, $^{2}CH_3$), 3.20-3.35 (m. 2 H **CH_2**OH from alcohol end group), 3.65-3.75 (m, 3 H, OC(O)O**CH_3**, from methyl carbonate end group), 3.90-4.20 (m, 2 H, $^{2}CH_2$), 4.41 (b, CH_2**OH**, from alcohol end group), 4.73 (b, CH_2**OH**, from alcohol end group).

3.4.13 General procedure for the synthesis of hyperbranched polycarbonate (HBPC) from TriOL with diphenyl carbonate (DPC)

In a round bottom flask TriOL (0.7 g), DPC and 4-dimethylaminopyridine (DMAP) with various ratios were added. The mixture was stirred in an oil bath at 130 °C for 8 – 18 h. The mixture was then cooled to room temperature and dissolved in dichloromethane. The light-yellow

solution was washed five times with 1 M sodium hydroxide solution and five times with brine in order to remove the side product phenol. The organic phase was dried over magnesium sulfate. The organic solvent was evaporated to give HBPC as light yellow viscos liquid with a yield of 93%.



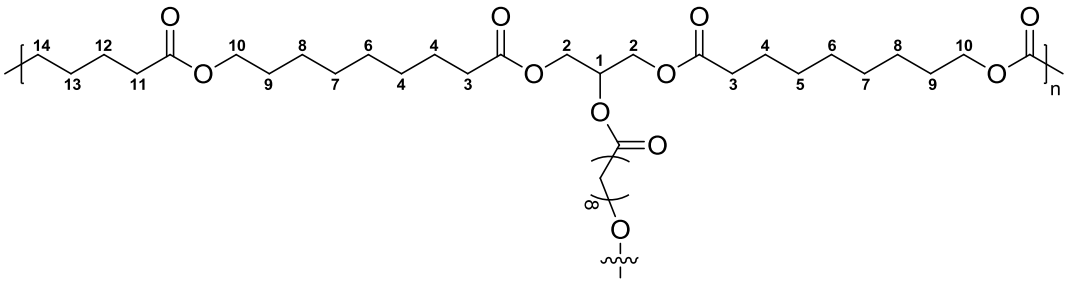
^{1}H NMR spectrum: Figure SI-21

^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 0.88 (m, CH_3 from unreactive saturated chain), 1.00 – 2.00 (m, $^{4\text{-}9}CH_2$), 2.31 (m, $^{3}CH_2$), 3.63 (m, CH_2OH (from hydroxyl end group)), 4.00 – 4,50 (m, $^{2}CH_2$, $^{10}CH_2$), 5.25 (b, ^{1}CH), 7.00 – 7.50 (m, CH_{phenyl} (from phenyl carbonate end group))

3.4.14 General procedure for the synthesis of hyperbranched polyester (HBPE) from TriOL with adipic acid (AA)

In a round flask, TriOL (0.7 g), AA and 0.15 wt% dibutyltin oxide (DBTO) with various ratios were added. The mixture was stirred at 150 °C for 1 h. Then the pressure was reduced to 20 mbar, and the condensation reaction was conducted for another 2 h. Finally, the polymerization was conducted for further 1.5 h with full evacuation (1.0 x 10^{-2} mbar). The mixture was cooled to room temperature and dissolved in dichloromethane. The solution was the washed three times with brine and three times with water. The organic phase was dried over magnesium sulfate. The organic solvent was evaporated to give HBPE as light yellow viscos liquid with a yield of 80%.



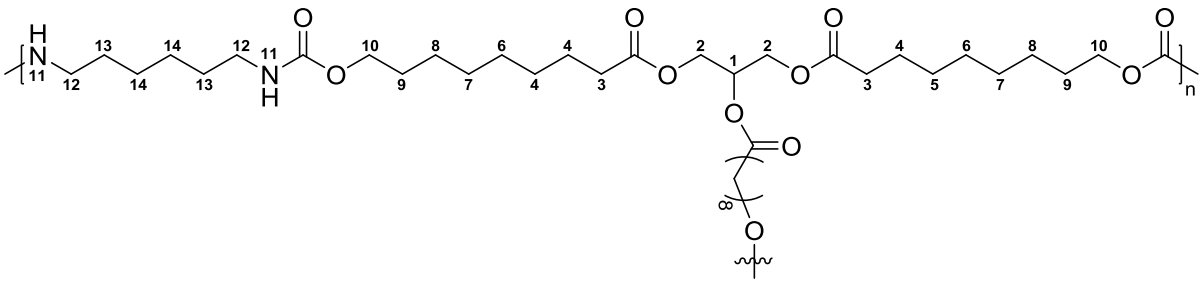
^{1}H NMR spectrum: Figure SI-22

^{1}H-NMR (500 MHz, DMSO)

δ (ppm) = 0.85 (m, CH_3 from unreactive saturated chain), 1.00 – 1.80 (m, $^{4\text{-}9,12,13}CH_2$), 2.00 - 2.40 (m, $^{3,11,14}CH_2$), 3.36 (m, CH_2OH (from hydroxyl end group)), 4.00 – 4,50 (m, $^{2}CH_2$, $^{10}CH_2$), 5.19 (b, ^{1}CH), 11.94 (b, COOH (from acid end group))

3.4.15 General procedure for the synthesis of hyperbranched polyurethane (HBPU) from TriOL with hexamethylene diisocyanate (HDI)

In a round flask, TriOL, two drops dibutyltin dilaurate (DBTD) were dissolved in anhydrous tetrahydrofuran under an argon atmosphere. A solution of HDI in anhydrous tetrahydrofuran was added dropwise to the flask. The reaction mixture was stirred at room temperature for 18 h. The HBPU was then isolated by precipitation in *n*-hexane and dried under vacuum to give a white solid with a yield of 99%.



^{1}H NMR spectrum: Figure SI-23

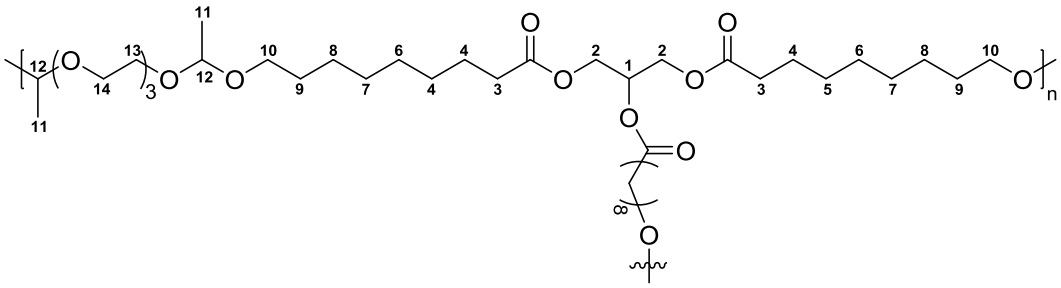
^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 0.86 (m, CH_3 from unreactive saturated chain), 1.00 – 2.00 (m, $^{4\text{-}9,12\text{-}14}CH_2$), 2.29 (m,

$^{3}CH_2$), 3.14 (m, $^{12}CH_2$), 3.61 (m, **CH_2**OH (from hydroxyl end groups)), 4.01 (b, $^{10}CH_2$), 4.10 – 4,30 (m, $^{2}CH_2$), 4.80 (b, ^{11}NH), 5.24 (m, 1 H, ^{1}CH)

3.4.16 General procedure for the synthesis of hyperbranched polyacetal (HBPA) from TriOL with tri(ethylene glycol) divinyl ether (TEDE)

In a round flask, TriOL, TEDE and pyridinium *p*-toluene sulphonate (PPTS) were dissolved in dichloromethane at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature for 2.5 h. The mixture was then diluted with ethyl acetate and washed with saturated sodium carbonate solution and two times with brine. The organic phase was dried over magnesium sulfate. The organic solvent was evaporated to give HBPA as light yellow viscos liquid with a yield of 79%.



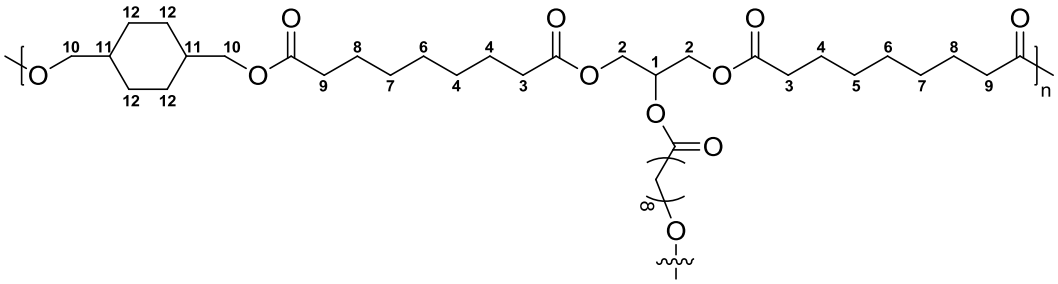
^{1}H NMR spectrum: Figure SI-24

^{1}H-NMR (500 MHz, $CDCl_3$)

δ (ppm) = 0.87 (m, CH_3 from unreactive saturated chain), 1.00 – 2.00 (m, $^{4\text{-}9,11}CH_2$), 2.30 (m, $^{3}CH_2$), 3.39 (m, **CH_2**OH (from hydroxyl end groups)), 3.50 - 3.80 (m, $^{10,13,14}CH_2$), 4.00 – 4,30 (m, $^{2}CH_2$), 4.50 - 4.80 (m, ^{12}CH), 5.24 (m, 1 H, ^{1}CH)

3.4.17 General procedure for the synthesis of hyperbranched polyester from TriAC with cyclohexanedimethanol (CHDM)

In a round flask, TriAC, CHDM and dibutyltin oxide (DBTO) were added under an argon atmosphere. The reaction mixture was stirred at 180 °C and atmospheric pressure for 1.5 h. Then the pressure was reduced to 20 mbar, and the condensation reaction was conducted for another 2.5 h. The mixture was cooled to room temperature and dissolved in dichloromethane. The solution was then washed three times with brine and three times with water. The organic phase was dried over magnesium sulfate. The organic solvent was evaporated to give hyperbranched polyester as light yellow viscos liquid with a yield of 70%.



^{1}H NMR spectrum: Figure SI-25

^{1}H-NMR (500 MHz, DMSO)

δ (ppm) = 0.75 – 1.00 (m, CH_3 from unreactive saturated chain), 1.00 – 1.80 (m, $^{4\text{-}8,11,12}CH_2$), 2.00 – 2.40 (m, $^{3,9}CH_2$), 3.40 – 3.60 (m, CH_2, from CH_2OH end group) 3.80 – 4.00 (m, $^{10}CH_2$), 4.00 – 4.40 (m, $^{2}CH_2$), 5.25 (b, ^{1}CH), 11.91 (b, COOH, from COOH end group).

4 Results and discussion

4.1 Synthesis of linear aliphatic polycarbonates by organo-catalysis

4.1.1 Catalyst screening

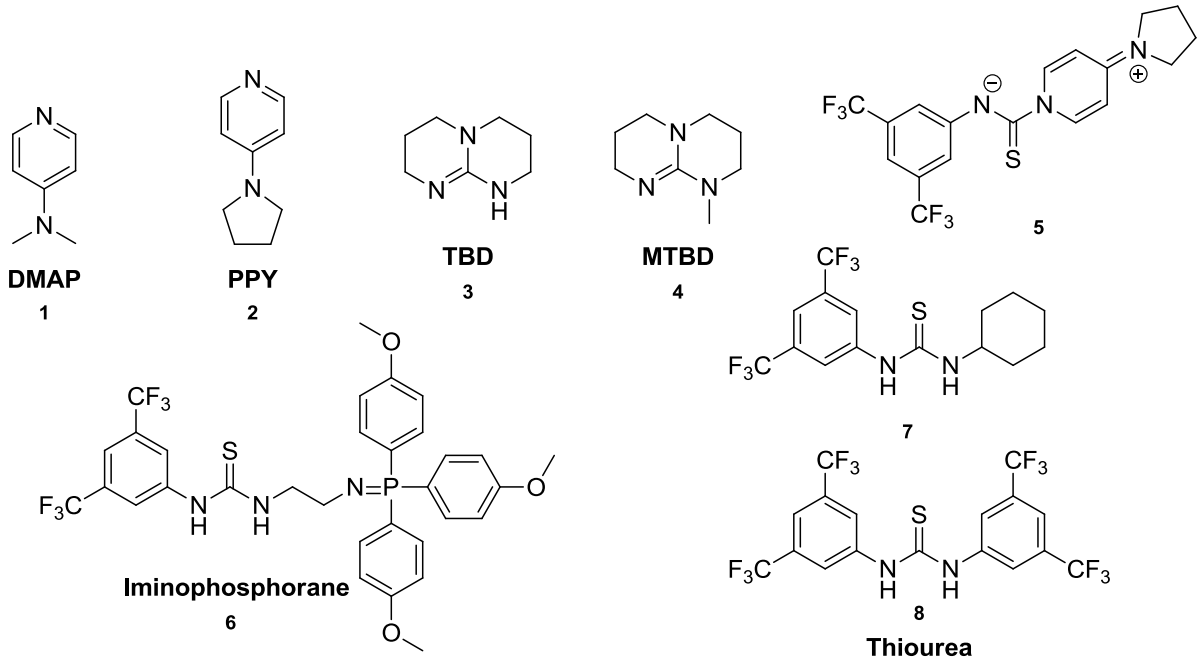


Figure 34. Organo-catalysts for the synthesis of aliphatic polycarbonates via the polycondensation method.

A variety of organo-catalysts (Figure 34) such as commercially available pyridines (DMAP (**1**) and PPY (**2**)), guanidines (TBD (**3**) and MTBD (**4**)), bifunctional arylaminothiocarbonylpyridinium salt (**5**) and iminophosphorane (**6**) have been used in the polycondensation of diols and DMC. Furthermore, DMAP was also investigated together with thioureas with mono-(**7**) and bi- (**8**) electron withdrawing 3,5-bis(trifluoromethyl)phenyl groups as cocatalysts. Such compounds were used in the ring opening polymerization of trimethylene carbonate successfully,[111,112,170] and it was of interest to test the influence of thiourea in the transesterification step and in the polycondensation. In the first step the transesterification reaction of DMC and diols is an equilibrium reaction. According to the Le

Chatelier's principle, the chemical equilibrium could only be affected by a change in the temperature or feed ratio. At the equilibrium point the conversions of $–CH_2OH$ to $–CH_2OC(O)O–$ groups should be constant, which is shown in the ^1H NMR spectrum of the reaction solution at this point as the constant peak area ratio of unreacted dimethyl carbonate (3.70 ppm in DMSO-d_6) and generated byproduct methanol (3.19 ppm in DMSO-d_6) (Figure. 35).

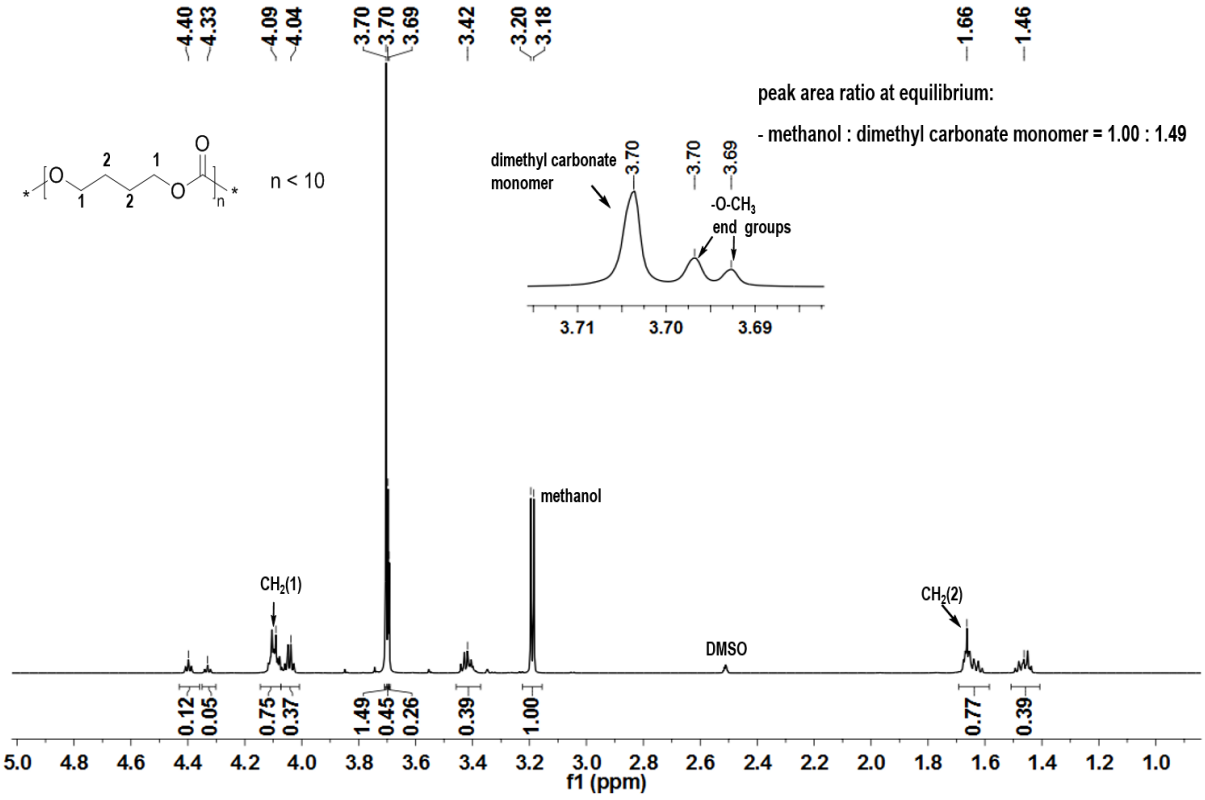


Figure 35. ^1H NMR spectrum of the reaction solution of BD and DMC using DMAP as catalyst at equilibrium

The catalytic activities of various organo-catalyst systems with respect to the transesterification step of 1,4-butanediol (BD) and DMC were evaluated by comparing the necessary time to achieve the equilibrium. The fewer time the system needed, the higher the activity of the system. Table 6 summarizes the results of the different catalyst systems in the transesterification step under argon atmosphere with a constant feed ratio of [BD]: [DMC]: [cat.] = 1: 1.2: 0.005 at 130 °C.

All catalyst systems investigated were active for the transesterification of BD and DMC. It was found that the transesterification reaction was carried out readily (< 1 h) in the presence of pyridine (cat. 3 and 4) and guanidine (cat. 5 and 6) catalysts. However, the same reaction catalyzed either by bifunctional catalysts including thioureas groups (cat. 1 and 2) or by DMAP with mono- or bi- electron withdrawing 3,5-bis(trifluromethyl)phenyl groups thiourea (cat. 7 and 8) cocatalysts proceeded much slower.

Table 6. Catalyst screening of polycondensation of BD and DMC

entry	catalyst systems	time to achieve equilibrium[1]	M_n[2](g/mol)	$Đ_M$ [2]
1	cat. 1	1.0 h	16000	1.66
2	cat. 2	1.0 h	7900	2.03
3	cat. 3	0.5 h	6200	2.18
4	cat. 4	< 0.5 h	17000	1.77
5	cat. 5	3.0 h	4100	2.40
6	cat. 6	over night	13000	1.68
7	cat. 4 + cat. 7	2.5 h	6900	2.16
8	cat. 4 + cat. 8	3.0 h	7500	1.80

BD: DMC: cat. = 1: 1.2: 0.005

Reaction time:

1. step: until equilibrium

2. step: over night

[1] determined using ^{1}H NMR spectroscopy

[2] determined using SEC in chloroform with PS standards

A proposed mechanism is shown in Figure 36. The thiourea is able for the direct activation of the carbonyl group by means of double hydrogen bonding. The activation may lead to a more stable intermediate, which may subsequently release the methanol difficultly. This also indicates why the thiourea based catalysts could be used in the ring opening polymerization of cyclic ester or carbonates and inhibiting simultaneously the transesterification side reaction.

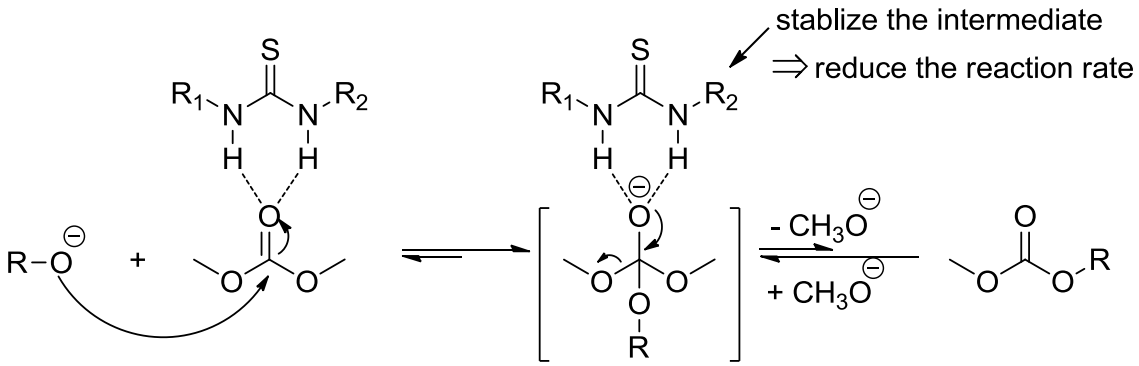


Figure 36. Possible mechanism of thioureas catalyzed transesterification reaction

Besides the transesterification step all catalyst systems were also investigated in the polymerization step after achieving the equilibrium in the 1. step. All catalyst systems were effective for the synthesis of PBC from BD and DMC and polycarbonates were obtained with M_n higher than 4100 g/mol and dispersities lower than 2.40. DMAP (cat. 1) and MTBD (cat. 4) showed the best results with the synthesized polycarbonate having a molar mass up to 17000 g/mol and dispersity of 1.66. Also in polycondensation step, thioureas as cocatalyst retarded the polymerization. Moreover, an experiment without any catalyst was also evaluated at 130 °C and 170 °C for 1. and 2. steps, respectively. However, the ^{1}H NMR spectrum after first step showed, that the transesterification reaction between DMC and BD did not occur. All of compounds in the reaction flask were distilled off after 30 min in the second step. That proved also the efficiency of all investigated catalyst systems.

4.1.2 Polycarbonate synthesis

The polymerization temperature and initial feed ratio of diol and DMC are further two important parameters. They can influence the final polymer properties significantly. In order to obtain polycarbonates with higher molar mass we optimized the polymerization conditions. The initial [BD]: [DMC] ratio was varied from 1: 1.2 up to 1: 2.0 and the temperatures in polycondensation step was set from 130 °C up to 170 °C. The aim of using excess dimethyl carbonate is enhancing the conversion of diols in the 1. step and obtaining oligomers with more methyl carbonate end group, which is more reactive than hydroxyl end group in the 2. step for transesterification reaction between two polymer chains and thus leading to higher molar masses. Excess of DMC was removed in the 2. step.[120]

Table 7 summarizes the most significant results of the polycarbonate synthesis under different polymerization conditions. As shown M_n increased significantly from 5900 g/mol to 11000 g/mol, respectively, while the feed ratio changed from 1: 1.5: 0.5 mol-% to 1: 2.0: 1 mol-% (entry 1 - 3). Indicating that the methyl carbonate end group is more reactive than the hydroxyl end group in the polycondensation step. With the feed ratio of 1: 2.0: 1 mol-% PBC, PPC and PHC samples with relatively high M_n values up to 23000 g/mol were obtained in the presence of more reactive catalyst DMAP (entry 9, 11 and 12). Yields were achieved up to 88 %, which was calculated by the following equation.

$$\text{Yield} = \frac{\frac{\text{mass of purified polymer}}{\text{molecular weight of repeating unit}}}{\text{mole of diol}} \times 100\ \% \qquad \text{(Eq. 1)}$$

whereby 116 g/mol, 128 g/mol and 140 g/mol are the molar mass of repeating units for PBC, PPC and PHC, respectively. Moreover, M_n values increased with increasing temperature from 130 °C to 170 °C (entry 9 and 10)

Table 7. Results of polycarbonate synthesis

	[diol]:[DMC]:[cat.]	Cat.	T (2. step) (°C)	Yields (%)	M_n[1] (g/mol)	$Đ_M$[1]	End groups[2] [-OCH_3]:[-OH]
PBC 1	1: 1.5: 0.005	cat. 5	130	60	5900	1.85	2: 98
PBC 2	1: 1.5: 0.01	cat. 5	130	70	9000	1.69	14: 86
PBC 3	1: 2.0: 0.01	cat. 5	130	65	11000	1.71	80: 20
PBC 4	1: 1.2: 0.005	cat. 1	130	57	16000	1.66	0: 100
PBC 5	1: 1.2: 0.005	cat. 2	130	59	7900	2.03	0: 100
PBC 6	1: 1.2: 0.005	cat. 4	130	61	17000	1.77	0: 100
PBC 7	1: 1.2: 0.005	cat. 5	130	57	4100	2.40	0: 100
PBC 8	1: 1.2: 0.005	cat. 6	130	53	13000	1.68	0: 100
PBC 9	1: 2.0: 0.01	cat. 1	130	85	23000	1.77	32: 68
PBC 10	1: 2.0: 0.01	cat. 1	170	79	52000	1.77	70: 30
PPC 1	1: 2.0: 0.01	cat. 1	130	77	22000	1.60	43: 57
PHC 1	1: 2.0: 0.01	cat. 1	130	88	23000	1.53	61: 39

[1] determined using SEC in chloroform with PS standards

[2] determined using ^{1}H NMR spectroscopy

Reaction time:

1. step: until equilibrium

2. step: over night

In addition, the end group ratio in the resulting polymers could be adjusted by changing the initial feed ratios, catalysts, or polymerization temperatures. The hydroxyl end group content decreases from 86% to 20% with increasing initial concentration of DMC (entry 2 and 3). When the polymerization was conducted using lower amount of catalyst, PBC with higher hydroxyl content (98% -OH end group) was obtained. The end group composition can also be controlled by using various catalysts due to their different catalytic activities (entry 3 and 9). Using cat. 5 leads to a PBC with 20% -OH end group, while a PBC with 68 % -OH end group could be

prepared at the same feed ratio of [diol]: [DMC]: [cat.] = 1: 2: 0.01, when DMAP (cat. 1) was used. Besides, polymerization temperature is also an important factor in controlling the end group composition. The hydroxyl content decreased from 68 % to 30 % with the temperature increasing from 130 °C to 170 °C (entry 9 and 10). By studying the preparation of polycarbonate with defined end group composition, we found that hydroxyl terminated PBCs, which are of great interest, especially for further terminal group modification, could be obtained by using different catalysts (0.5 mol-%) with the initial feed ratio of [BD]: [DMC] < 1: 1.2 (entry 4 - 8). Among them M_n determinated for the samples using DMAP and MTBD as catalysts (entry 4 and 6) were obtained up to 17000 g/mol and the dispersities were lower than 1.8. Polymers synthesized using PPY based catalysts (entry 5 and 7) showed lower M_n and higher $Đ_M$ ($Đ_M > 2$) in contrast to DMAP and MTBD. The lower catalytic activity of PPY based catalysts in the 2. step is probably reflective of the decreased nucleophilic properties for the transesterification reaction between two methyl carbonate end groups. According to our research results, polycarbonates with defined M_n, end group composition and low dispersity could be achieved by using alterable initial feed ratios, polymerization temperatures and catalysts with different activities.

The ^1H and ^{13}C NMR spectra of PBC 9 are shown in Figure 37. Two multiplet signals at 1.76 ppm and 4.15 ppm are attributed to the both CH_2-group in the polymer backbone. The small signals at 1.64 ppm and 3.67 ppm indicated the existence of terminal butanol group, while the singlet at 3.76 ppm is assigned to the terminal methyl carbonate group. The ^1H NMR spectroscopy indicated that no decarboxylation occurred because no ether linkage (CH_2-O-CH_2) at 3.4 - 3.5 ppm was detected. In addition, comparing the peak areas of the terminal butanol and methyl carbonate group the hydroxyl content could be calculated. For the samples with pure hydroxyl end group only two signals at 1.64 ppm and 3.67 ppm were detected, while the singlet peak at 3.76 ppm for -C(O)OCH_3 was not visible. In the ^{13}C NMR spectrum, the peaks around 25.14 ppm and 67.25 ppm correspond to C1 and C2 carbon atoms

of polymer backbone, respectively. The carbonate group is observed at 155.16 ppm. Signals of terminal groups are absent in ^{13}C NMR spectrum.

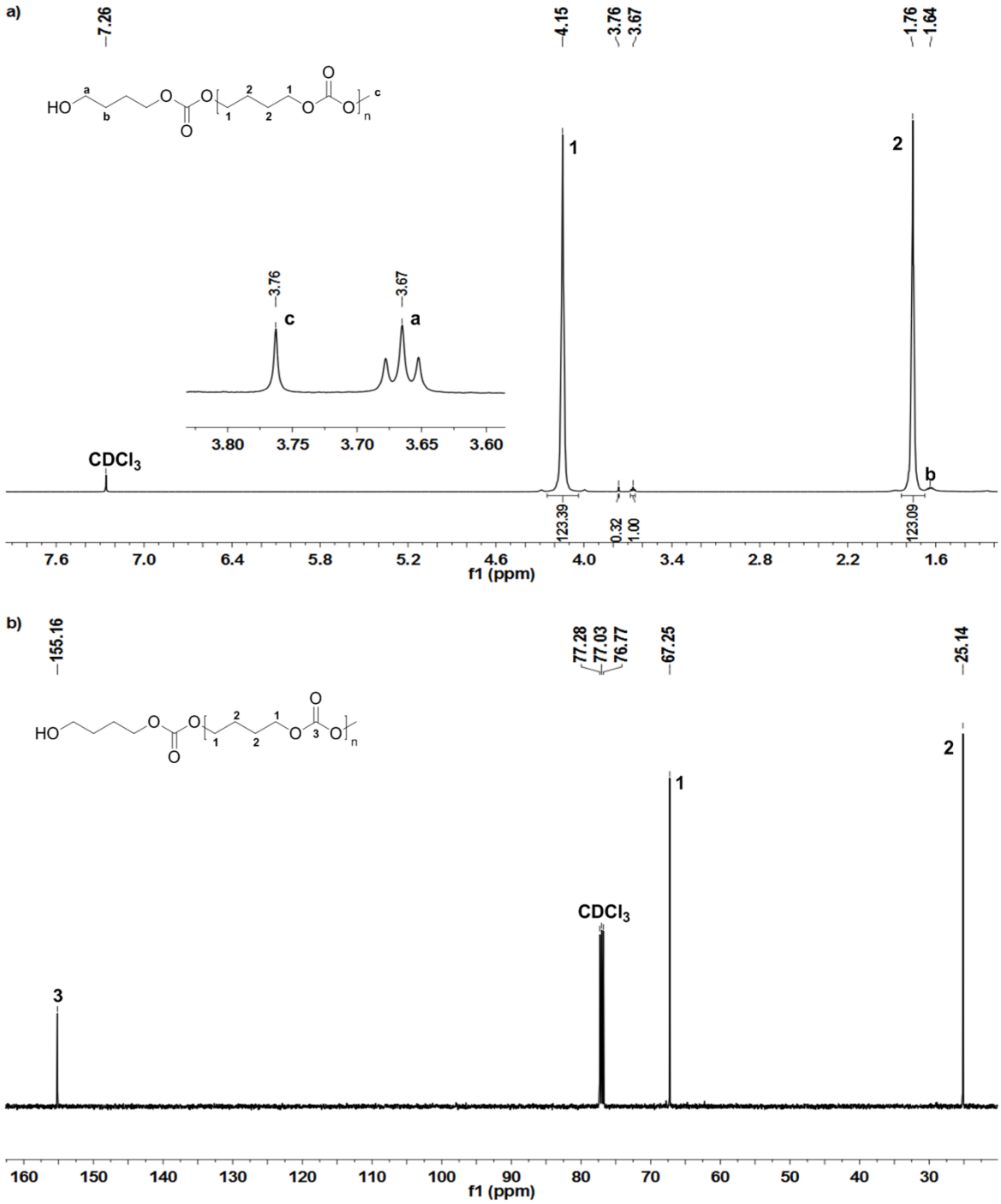


Figure 37. ^{1}H (a) and ^{13}C NMR (b) spectra of PBC 9

To determine the influence of polymerization times on the molar mass of PBC, a kinetic study of PBC 9 ([BD]: [DMC]: [DMAP] = 1: 2: 0.01, 130 °C) was carried out. Figure 38 shows molar mass and molar mass distribution data determined by SEC. The molar mass of the polymer increased rapidly throughout the initial 30 min. After a reaction time of 3 h, a molar mass of 14000 g/mol was obtained. When the condensation reaction was further conducted the molar mass increased slower up to finally M_n = 23000 g/mol for 24 h reaction time. The dispersity values remained below 1.8 during the condensation reaction.

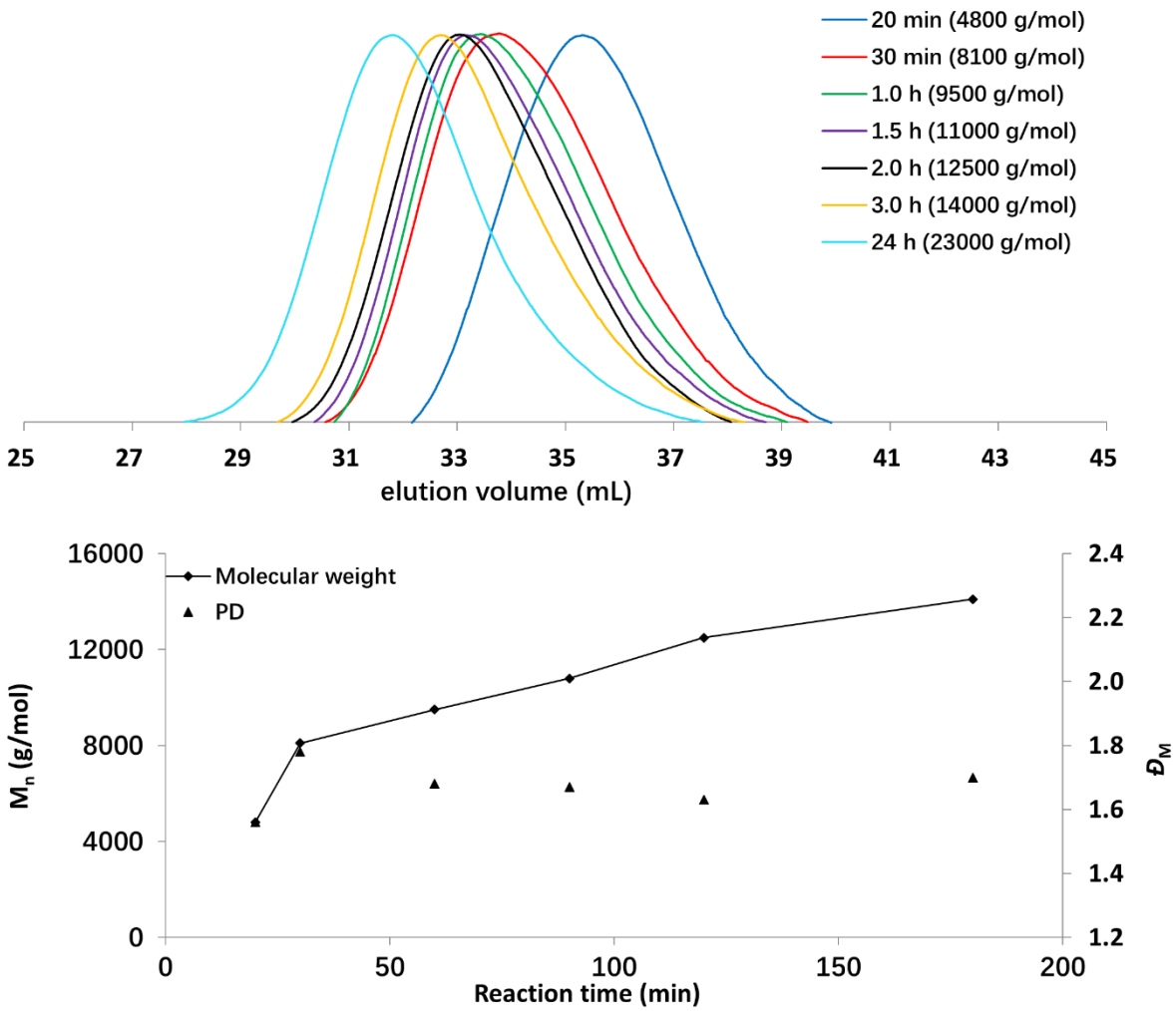


Figure 38. SEC traces and plot M_n (determined by SEC) and dispersity values of PBC 9 versus polymerization time in the 2. step.

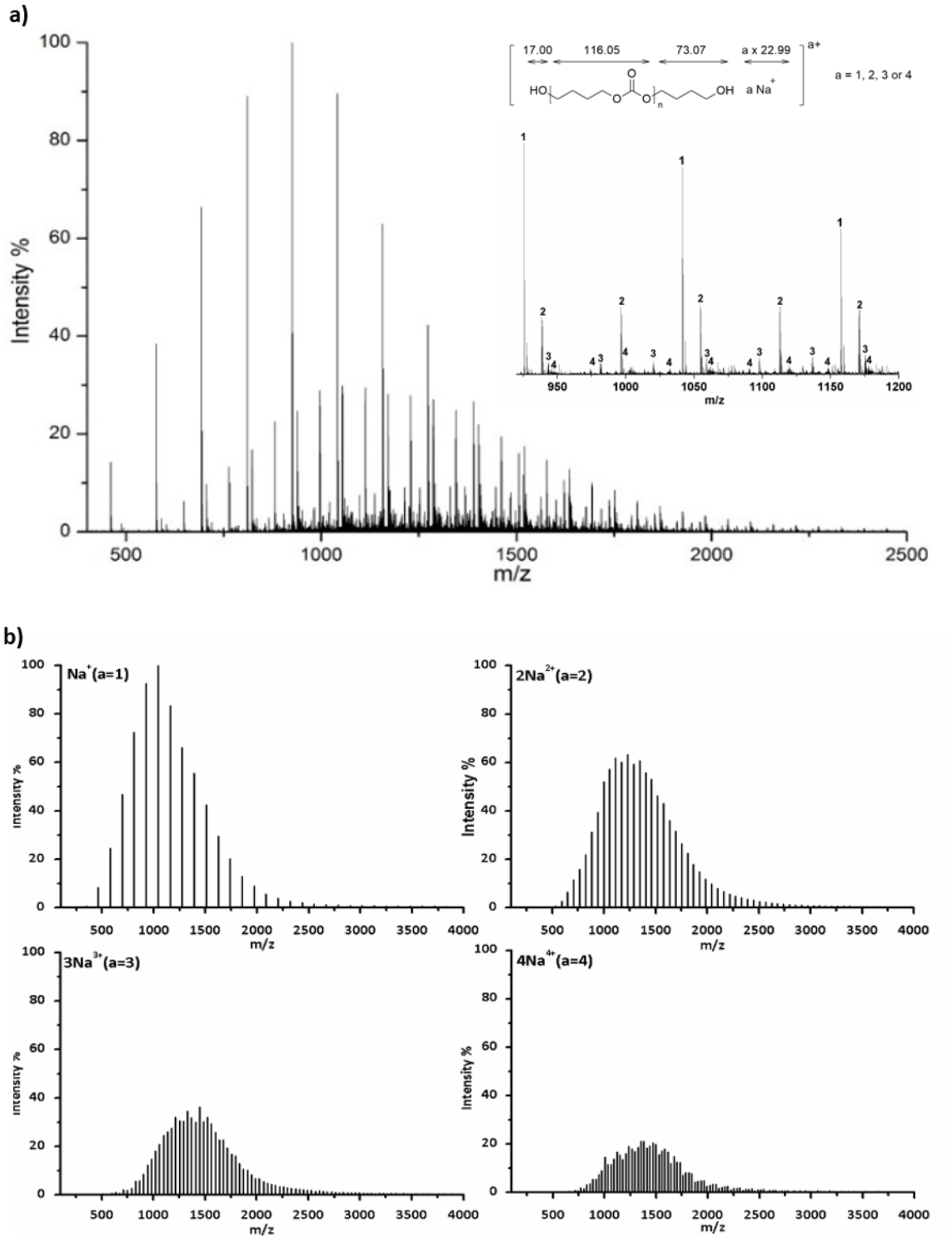


Figure 39. ESI-ToF mass spectrum of PBC 7 (Table 2, entry 7) terminated with hydroxyl group, a) complete spectrum and a part of the spectrum distinguished by carrying charges a = 1, 2, 3 and 4 in the region m/z 400 to 2500, and b) separated spectra with a = 1, 2, 3 and 4

Hydroxyl terminated PBCs (PBC 4 - 9 in Table 7) have also been investigated by ESI-ToF-MS to determine the end groups. Figure 39a shows a typical ESI-ToF-MS spectrum for hydroxyl terminated PBC. Polymers were multiply charged during the ionization. Separated spectra of up to tetraly charged polymers are shown in Figure 39b. Moreover, the pentaly and hexaly charged polymers were also detected but they are distributed with low intensity. ESI-ToF-MS spectra shows the presence of main series of polymer chains corresponding to (HO-PBC-C_4H_8OH a·Na)$^{a+}$ (a = 1, 2, 3 or 4) with repeating units of 116.05 Da, which is the molar mass of repeating PBC unit. For the doubly charged polymer with n = 20 (Table 8, entry 2), the measured value of 1229.36 Da corresponded to the calculated value of 1229.19 Da using Eq. 2. No further series could be seen, indicating that the polymer was only terminated with hydroxyl groups at the both chain ends. Hence, the organo-catalyzed synthesis of polycarbonates proceeds successfully without any side reaction, such as decarboxylation.

$$m/z = \frac{M(BD)+M(\text{monomer unit})\times n+a\times Na^+}{a}$$

Table 8. Calculated and experimental m/z in ESI-TOF mass spectrum of PBC 7 with different charges (a up to 4)

a	Calculated [Da]	Found [Da]	Calculated [Da]	Found [Da]	Difference [Da]
1	1042.01	1042.19 (n=8)	1158.12	1158.33 (n=9)	116.14
2	1229.19	1229.36 (n=20)	1287.24	1287.37 (n=21)	58.01
3	1214.18	1214.38 (n=30)	1252.88	1253.06 (n=31)	38.68
4	1206.67	1206.86 (n=40)	1235.69	1235.91 (n=41)	29.05

The thermal properties of PBC, PPC and PHC samples were evaluated by DSC as shown in Table 9. The PBC samples displayed glass transition temperatures (T_g) of -36 - -31°C and T_g increases with increasing molar mass. The T_g of PHC sample tended to lower T_g due to the higher chain flexibility. The melting temperatures (T_m) were observed at 56 - 62°C, while the PPC and PHC

showed lower T_m. In our case, the T_g were not visibly affected by the nature of chain end group compositions.

Table 9. Thermal properties of aliphatic polycarbonate samples

	M_n[1] (g/mol)	T_g (°C)[2]	T_m (°C)[2]
PBC 5	7900	[3]	59.9
PBC 4	16000	-35.9	61.6
PBC 9	23000	-33.2	59.0
PBC 10	52000	-31.9	56.4
PPC 1	22000	-42.4	54.2
PHC 1	23000	-38.6	55.5

[1] determined using SEC in chloroform with PS standards

[2] T_g and T_m were measured by DSC

[3] Not detected

4.1.3 Conclusions

In summary we demonstrated that the commercially available organo-catalysts DMAP, PPY, TBD and MTBD were suitable for the synthesis of aliphatic polycarbonates with high molar mass and low dispersities via a two-step polycondensation under relatively mild operating conditions. Poly(1,4-butylene carbonate) (PBC), poly(1,5-pentamethylene carbonate) (PPC) and poly(1,6-hexametylene carbonate) (PHC), were successfully prepared with M_n up to 23000 g/mol, dispersities below 1.80 and yields of > 80 % at 130 °C using 4-dimethylaminopyrridine (DMAP) as catalyst. At 170 °C molar mass of poly(1,4-butylene carbonate) increased up to 52000g/mol.

In addition, according to our results polycarbonate with defined M_n, end group composition and low dispersity could be achieved by changing initial feed ratios, polymerization temperatures and catalysts with different activities. Remarkably, depending on the initial feed

ratio ([BD]: [DMC] < 1 : 1.2), hydroxyl terminated polycarbonates with different molar mass can also be obtained with high molar mass (up to 17000 g/mol, $Đ_M$ = 1.77). These materials are of great interest, because the combination with other polymerization method, such as controlled radical polymerization (ATRP, RAFT or NMRP) for further application and thermal properties improvement is allowed by end group modification. Additionally, the thiourea based organo-catalysts retarded the transesterification and polycondensation steps. On the other hand, that also proved why the thiourea based catalysts could be used in the ring opening polymerization of cyclic ester or carbonates and inhibits simultaneously the transesterification side reaction.

4.2 One-pot process for the preparation of linear and hyperbranched polycarbonates of various diols and triols using dimethyl carbonate

4.2.1 Strategy for a one-pot polycondensation at atmospheric pressure

In a classic two-step polycondensation for the synthesis of polycarbonates, low molar mass oligomers (M_n < 1000 g/mol) are obtained in the first step. In the next step, the polymer chains are extended via transesterification reactions between hydroxyl and methyl carbonate (-OC(O)-OCH_3) chain ends or mainly between two methyl carbonate chain ends due to their higher reactivities than the hydroxyl end groups.[116,120] For this reason, excess DMC (e.g., diol: DMC = 1: 3)[75] is used in order to obtain oligomers mostly terminated with methyl carbonate groups. Polycondensation is then conducted at elevated temperature (170 – 200 °C) and under vacuum to remove the freshly generated major byproduct dimethyl carbonate and minor byproduct methanol to achieve high molar masses.

Here, we developed a new strategy for the preparation of linear and hyperbranched polycarbonates by a one-pot synthesis (Figure 40). In contrast to a classic two-step polycondensation (Figure 9), the polymerizations were carried out with equivalent amounts

of diol and DMC in bulk or in solution at atmospheric pressure in the presence of basic catalysts. The polymer chains grow by pure transesterification between hydroxyl (-OH) and methyl carbonate (-OC(O)-OCH_3) chain ends, and the methanol byproduct was removed using 4 Å molecular sieve in a pressure-equalized addition funnel.

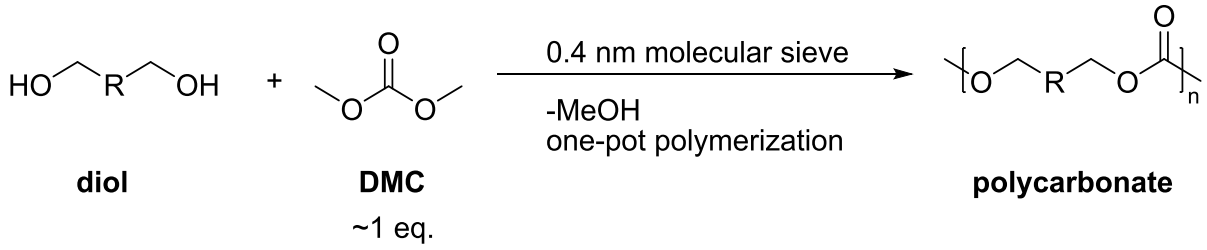


Figure 40. Strategy for the one-pot synthesis of polycarbonates

4.2.2 Polycarbonate synthesis from 1,4-butanediol

As mentioned above, various organo-catalysts showed activity for the synthesis of linear aliphatic polycarbonates. Among them, DMAP (1 mol% based on diol) showed the best catalytic activity. However, DMAP was not suitable for the synthesis of poly(trimethylene carbonate) (PTMC), leading to side reactions at high temperatures in the one-pot synthesis. Wang and Zheng reported that lithium acetylacetonate (LiAcac) was an effective catalyst for the synthesis of polycarbonate due to its strong coordination with carbonyl groups. According to their results, LiAcac at 0.1 percent by weight based on 1,4-BD (0.1 wt%) was also investigated.

In this work, a variety of polymerizations were evaluated to optimize the reaction conditions. Table 10 summarizes the most significant results of the one-pot polycarbonate syntheses based on 1,4-BD. The yields were calculated using Eq. 1.

Table 10. Results of optimizing polymerization conditions based on 1,4-BD

	Cat.	Solvents	[BD]: [DMC]: [cat.]	T (°C)	Time (h)	M_n (g/mol)[1]	$Đ_M$[1]	Yields (%)
PBC 1	DMAP	-	1: 1.2: 0.01	125	72	2300	1.36	42
PBC 2	LiAcac	-	1: 1.2: 0.1 wt%[2]	125/180	48/24	6300	1.70	60
PBC 3	LiAcac	DMSO	1: 1.2: 0.1 wt%[2]	125/180	48/24	-	-	-
PBC 4	LiAcac	DMF	1: 1.2: 0.1 wt%[2]	125/160	48/24	-	-	-
PBC 5	LiAcac	toluene	1: 1.2: 0.1 wt%[2]	130	72	-	-	-
PBC 6	LiAcac	1,4-dioxane	1: 1.2: 0.1 wt%[2]	120	72	1300	1.40	69
PBC 7	DMAP	1,4-dioxane	1: 1.2: 0.01	130	72	-	-	-
PBC 8	DMAP	1,4-dioxane	1: 1.2: 0.01	100	72	1500	1.33	33
PBC 9	DMAP	1,4-dioxane	1: 1.2: 0.01	120	72	4300	1.53	75
PBC 10	DMAP	1,4-dioxane	1: 1.1: 0.01	120	72	6300	1.67	77
PBC 11	DMAP	1,4-dioxane	1: 1.075: 0.01	120	72	7100	1.70	77
PBC 12	DMAP	1,4-dioxane	1: 1.05: 0.01	120	72	9800	1.66	77
PBC 13	DMAP	1,4-dioxane	1: 1.025: 0.01	120	72	14000	1.66	87
PBC 14	DMAP	1,4-dioxane	1: 1: 0.01	120	72	5300	1.67	74

[1]determined using SEC in chloroform solution with PS standards.

[2]0.1 wt% LiAcac based on 1,4-BD was used as the catalyst in PBC 2-6.

Initially, to determine the influence of the temperature and solvent on the molar mass, a number of polymerizations were carried out. DMAP and LiAcac were active for the one-pot synthesis after a reaction time of 72 h. A M_n of 2300 g/mol was recorded using DMAP as the catalyst in the bulk (PBC 1), while little product was formed at T > 125 °C because of the dominant side reactions. In contrast, LiAcac was more stable than DMAP even at a high temperature of 180 °C. The polycondensation using LiAcac was carried out initially at 125 °C for 48 h to avoid loss of DMC due to its low bowling point and then stirred at 180 °C for another

24 h. The resulting PBC had a higher molar mass of 6300 g/mol and a dispersity of 1.70 (PBC 2).

Solvents with high boiling points, such as dimethyl sulfoxide (DMSO, bp. = 189 °C), dimethylformamide (DMF, bp. = 153 °C), toluene (bp. = 111 °C) and 1,4-dioxane (bp. = 101 °C) were also investigated. The polycondensation could be carried out only in 1,4-dioxane solution, and samples with M_n of 1300 g/mol and 4300 g/mol were obtained using LiAcac and DMAP as catalysts, respectively, indicating that DMAP was more effective for synthesis of PBC under this polymerization condition. No polymer could be isolated after the reaction in the presence of DMSO, DMF and toluene. (PBC 3 - 8) Moreover, no product or polymer with low M_n formed in 1,4-dioxane solution at 130 °C and 100 °C, respectively.

To investigate the influence of the initial feed ratio on the polymer molar mass, the initial [DMC]: [BD] ratios were gradually varied from 1.2: 1 to 1: 1 (entries 8 - 13). The M_n increased slowly from 4300 g/mol to 7100 g/mol throughout the feed ratios from 1.2: 1 to 1.075: 1. Afterwards, the increase of M_n was more pronounced with M_n = 14000 g/mol for a polymerization with a feed ratio of 1.025: 1. When the initial feed ratio of [DMC]: [BD] was adjusted to 1.0, M_n decreased to 5300 g/mol. The last polymer possessed a high hydroxyl end group content of 94%, which could probably be attributed to a small loss of DMC due to the low boiling point. These results indicate that our strategy was effective for the synthesis of PBC, and with the initial feed ratios close to 1.0, the highest M_n of the resulting polymers could be achieved. All PBC samples generated at 120 °C had high yields (up to 87%) and dispersities below 1.70.

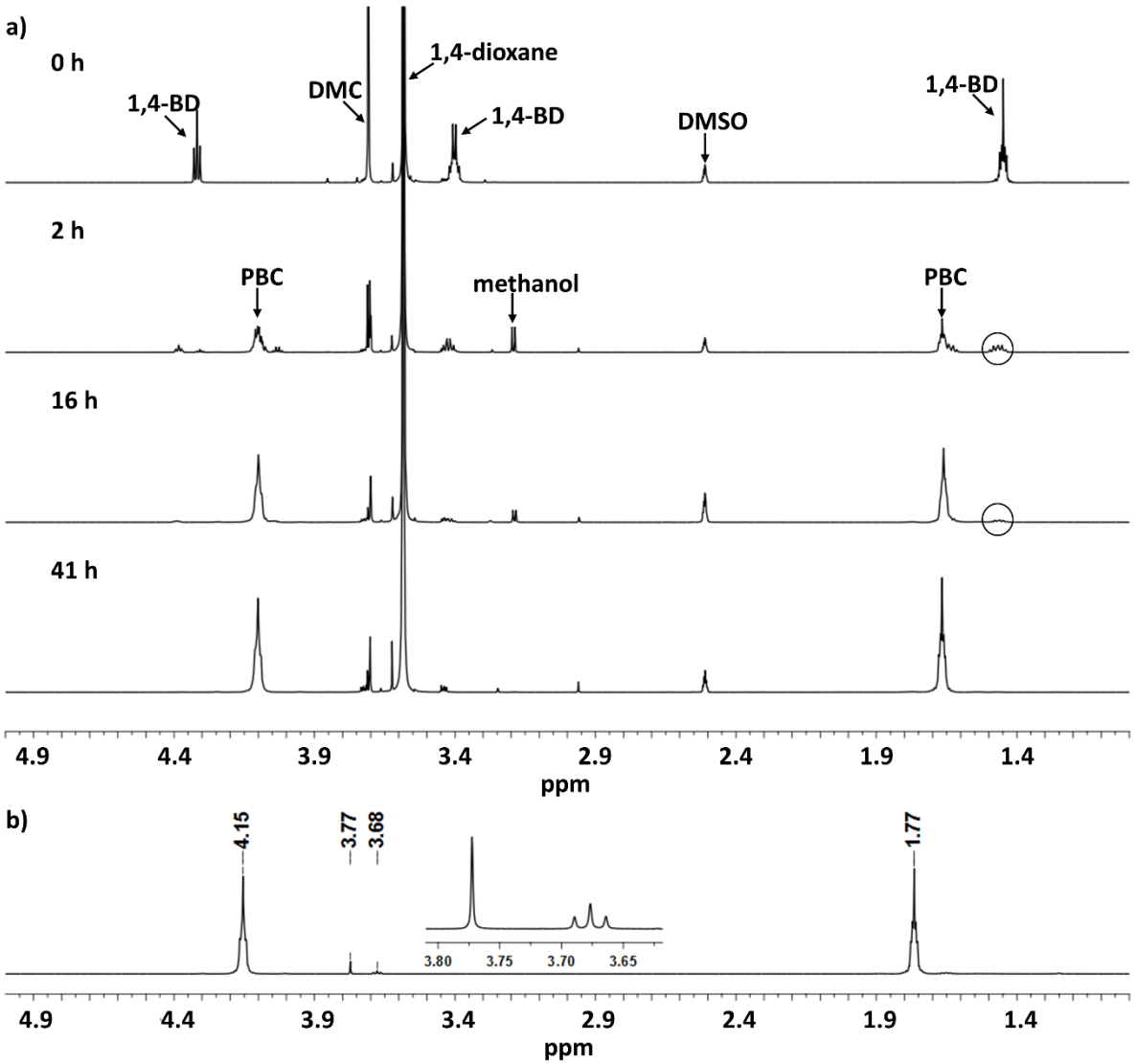


Figure 41. a) ^{1}H NMR spectra for the kinetic investigation of PBC 10 at different polymerization times (0, 2, 16 and 41 h) b) ^{1}H NMR spectrum of purified PBC 10.

Detailed information about the polymerization process was obtained using ^{1}H NMR spectroscopy (Figure 41a). After 2 h, the reaction signals from 1,4-butanediol at 1.47, 3.44 and 4.35 ppm decreased due to the formation of poly(butylene carbonate) oligomers, while the methanol side product was detected at 3.21 ppm as doublet signal. After 16 and 41 h, the intensities of the signals for 1,4-butanediol and methanol decreased continuously, indicating that the chain growth proceeded and the produced methanol was successfully removed using

4 Å molecular sieves. The ^{1}H NMR spectrum of purified PBC 10 is shown in Figure 41b. Both the CH_2-groups in the polymer backbone were detected at 1.77 and 4.15 ppm. The small signals at 3.68 and 3.77 ppm were attributed to terminal butanol groups and methyl carbonate groups, respectively. Moreover, a desorption process of used molecular sieve was conducted after the polymerization at 150 °C in vacuum. 1,52 g methanol were collected, which was close to the expected value (1.59 g at 100% conversion of DMC). Combining the result of the desorption investigation with the kinetic investigation, we confirm that, the generated methanol can be removed successfully from the reaction mixture using 4A molecular sieve.

A typical ESI-ToF-MS spectrum of PBC 9, which had about 95% methyl carbonate end group according to the ^{1}H NMR analysis, in the m/z region of 400 to 2000 Da is shown in Figure 42. The data were processed using Polymerix Software and peaks were assigned to different series (S1 – S6), which are shown in Figure 43 and 44 in detail. ESI-ToF-MS analysis shows main populations corresponding to methyl carbonate terminated $C_2H_3O_3$-$(PBC)_n$-CH_3·z Na^+ (z = 1 - 3) with repeating PBC units of 116.047 g/mol. The measured m/z of S1 and S2 are compared with calculated values. As shown in Figure 42, the measured m/z correspond very closely to the calculated values. For example, the most intense signal was detected at m/z: 925.350 Da, denoting the $C_2H_3O_3$-$(PBC)_n$-CH_3·Na^+ series containing 7 repeating monomer units and two methyl carbonate end groups, corresponding to m/z = [7 x 116.047(M_{PBC}) + 75.008(M_{C2H3O3}) + 15.024(M_{CH3})] + 22.990(M_{Na}). The second expected population (S5 and S6, SI-Figure 44) were attributed to PBC with both hydroxyl and methyl carbonate end groups. The structure analysis based on ESI-MS is consistent with ^{1}H NMR analysis. The obtained molar mass from ESI-MS was 3300 g/mol with $Đ_M$ of 1.2. In addition, cyclic polycarbonate with very low intensity was detected as well, indicating the presence of intramolecular transesterification side reaction.

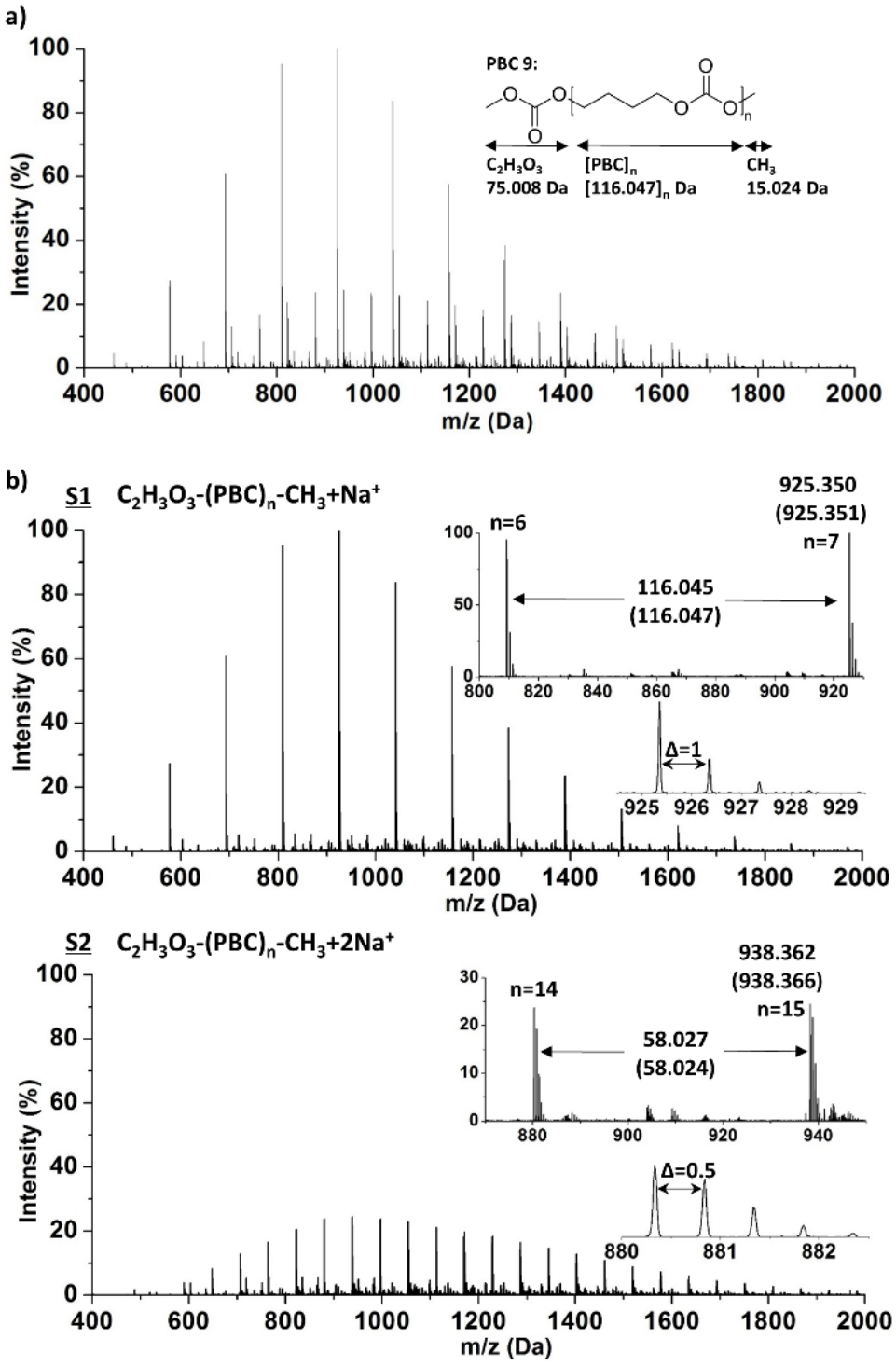


Figure 42. a) ESI-ToF mass spectrum of PBC 9 in the m/z region of 400 to 2000; b) Separated spectra (S1 and S2) using Polymerix Software in the m/z region of 400 to 2000 with measured and calculated (in parenthesis) values.

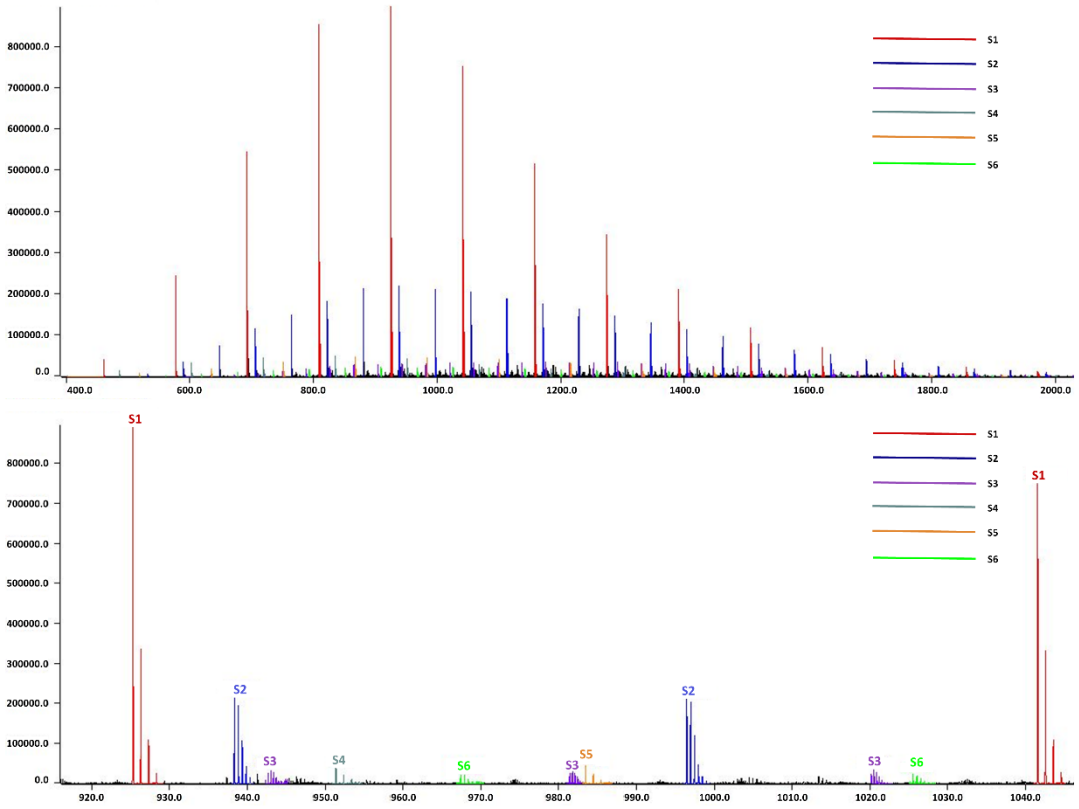
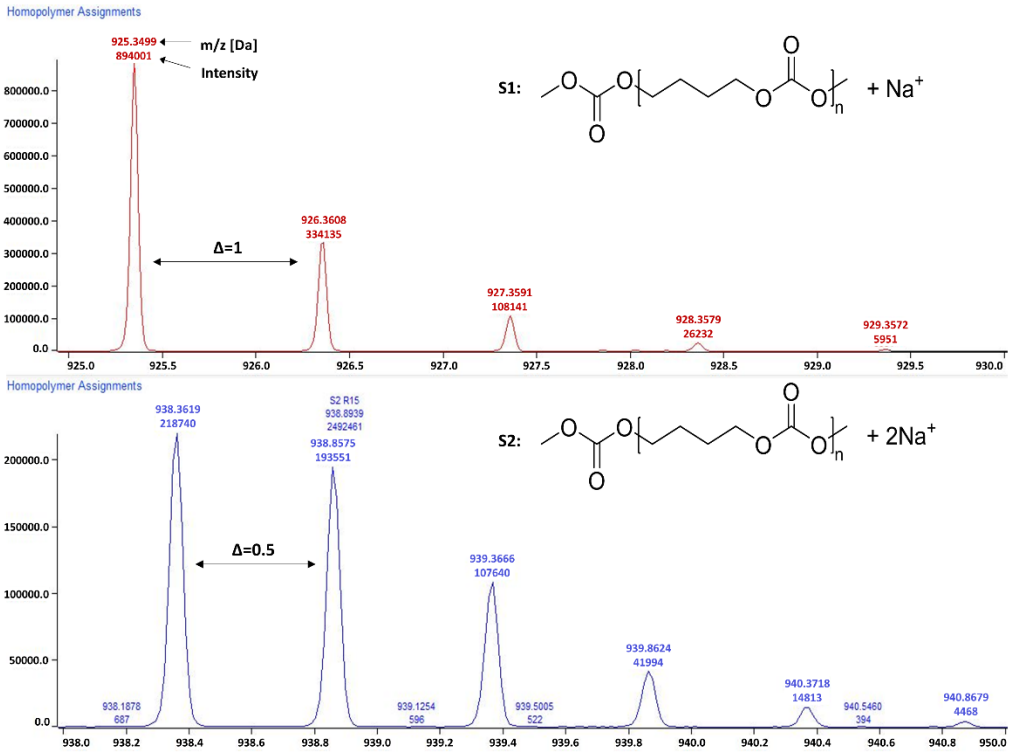


Figure 43. Whole spectrum of PBC 9 in the m/z region of 400 to 2000.



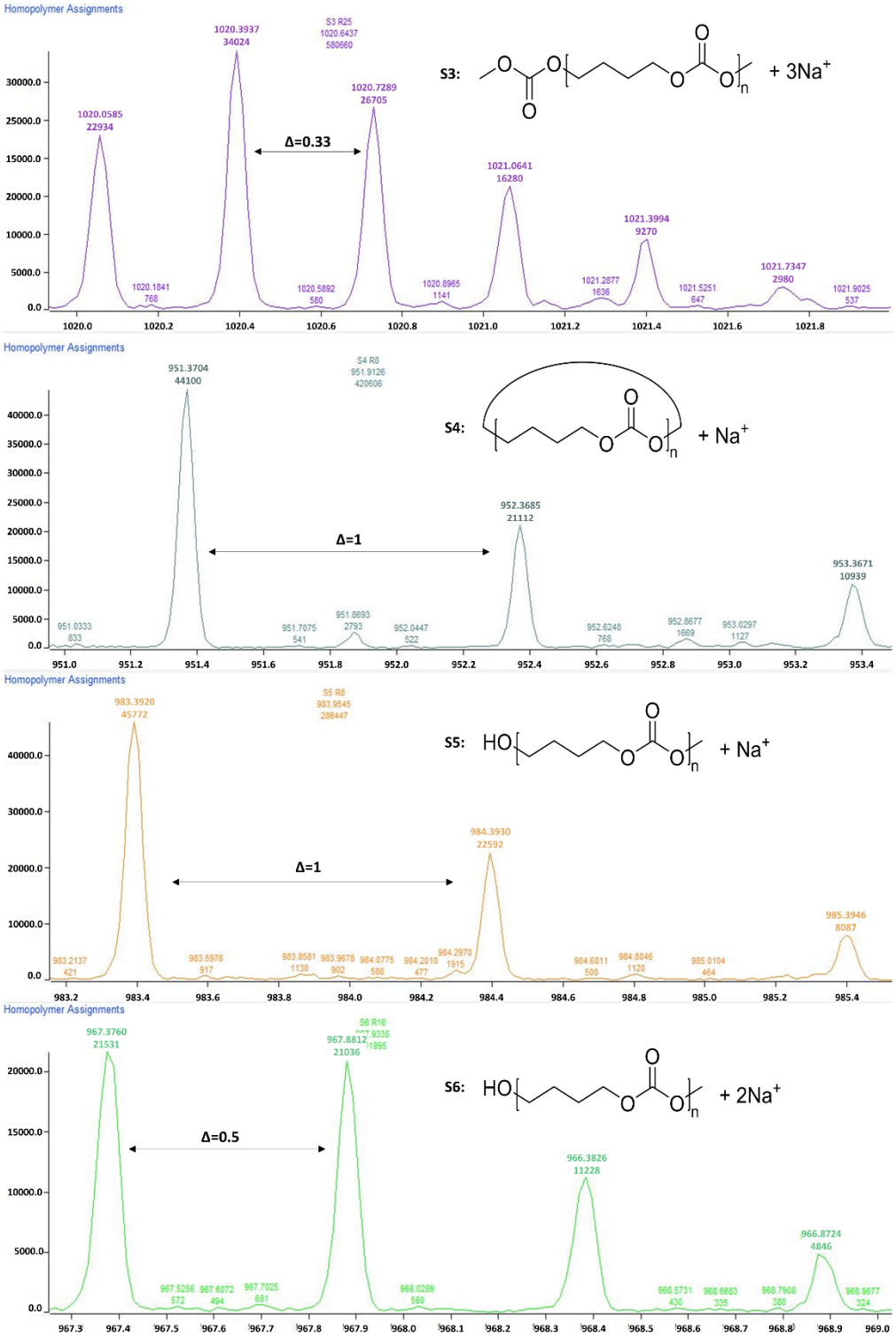


Figure 44. Detailed analysis of ESI-MS spectrum of PBC 9 (S1-S6)

4.2.3 Polycarbonate synthesis from other aliphatic diols with DMC

Additionally, to study the versatility of this new strategy, the synthesis of PTMC, PPC, PHC, poly(cyclohexan-1,4-dimethylene carbonate) (PCDMC) and poly(diethylphenylamine carbonate) (PDEAC) from commercially available aliphatic diols (Figure 45) with DMC were attempted. Because of the different purities of these diols, the initial [DMC]: [diol] ratio was adjusted to a slightly higher value of 1.05: 1. The polymerization temperature was maintained at 120 °C and the polymerization time for 1,5-pentanediol and 1,6-hexanediol was extended to 4 days in order to obtain higher molar masses of the resulting polymers. LiAcac was used as the catalyst for the preparation from 1,3-propanediol because when DMAP was used as the catalyst, the polymerization solution changed to dark brown and no polymer was isolated after purification. (Table 11, entry 1).

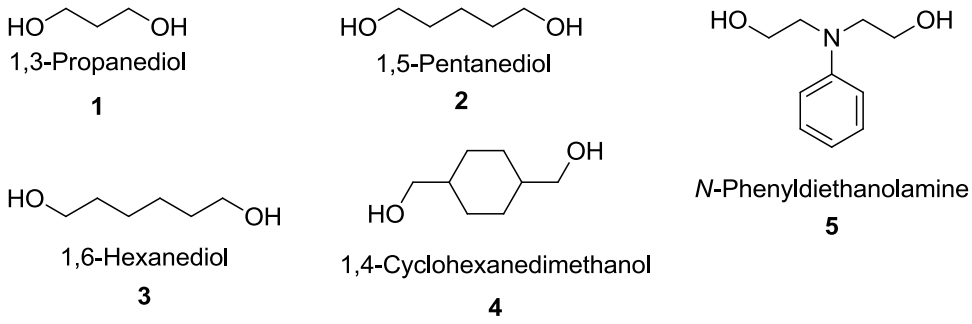


Figure 45. Various aliphatic diols used for the investigation of polycondensation

Using this method, PTMC with M_n of 5200 g/mol was generated. When 1,5-pentanediol and 1,6-hexanediol were used as monomers, after a polymerization time of 4 days, polycarbonates with higher molar masses (M_n = 16000 and 13000 g/mol, respectively) were also obtained, while lower M_n of 4400 g/mol and 8500 g/mol were obtained for PPC and PHC, respectively, after a polymerization time of 3 days only. For 1,4-cyclohexanedimethanol, polymers with M_n of 13000 g/mol formed within 3 days. The polycarbonate based on *N*-phenyldiethanolamine had a relatively low M_n of 4300 g/mol due to its lower reactivity. Conversions were achieved more than 95%, which were calculated according to the Carothers equation from M_n. The yields (> 70%) were lower than the conversions due to the loss in the purification step. All

polycarbonate samples generated in 1,4-dioxane solution possessed relatively narrow molar mass distributions ($Đ_M$ < 1.70).

Table 11. Results of polycarbonate synthesis from various diols and DMC at 120 °C in 1,4-dioxane solution using DMAP as the catalyst

	diol	[BD]:[DMC]:[cat.]	time	M_n[1] (g/mol)	$Đ_M$[1]	p[2] (%)	Yields (%)
PTMC 1	1	1: 1.025: 0.01	3 d	-	-	-	-
PTMC 2[3]	1	1: 1.025: 0.1 wt%	3 d	5200	1.69	98.5	70
PPC 3	2	1: 1.05: 0.01	4 d	16000	1.55	99.2	77
PHC 6	3	1: 1.05: 0.01	4 d	13000	1.55	98.9	80
PCDMC 1	4	1: 1.05: 0.01	3 d	13000	1.57	98.9	82
PDEAC 1	5	1: 1.05: 0.01	3 d	4300	1.56	95.2	70

[1]determined using SEC in chloroform solution with PS standards.

[2]conversion, calculated from Carothers equation using M_n from SEC.

[3]LiAcac was used as the catalyst.

4.2.4 Copolymerization from BD mixed with various diols and DMC

Copolycarbonates of 1,4-BD and different diols were also prepared by the one-pot polycondensation strategy in 1,4-dioxane solution. The feed ratio of [BD]: [diol]: [DMC] was maintained 0.8: 0.2: 1.05. The results are summarized in Table 12.

The molar masses were obtained in the range of 3500 g/mol and 7500 g/mol with dispersities below 1.70. The compositions of the resulting copolymers were determined by comparing the peak integrals of each repeating unit at 1.76 ppm for PBC and 1.46 ppm, 1.40 ppm, 1.01 ppm and 4.26 ppm for PPC, PHC, PCDMC and PDEAC, respectively. The calculated values correspond to the feed ratios fairly closely.

Table 12. Results of copolycarbonate synthesis using DMAP as the catalyst

	diol	M_n[1] (g/mol)	$Đ_M$[1]	Yields	BD/Diol[2]
PBC-*co*-PPC	2	6300	1.43	70	78: 22
PBC-*co*-PHC	3	7500	1.61	78	78: 22
PBC-*co*-PCDMC	4	7100	1.22	80	78: 22
PBC-*co*-PDEAC	5	3500	1.54	73	80: 20

[1]determined using SEC in chloroform solution with PS standards.

[2]calculated from ^{1}H NMR spectrum.

4.2.5 Synthesis of HBPCs from aliphatic triols

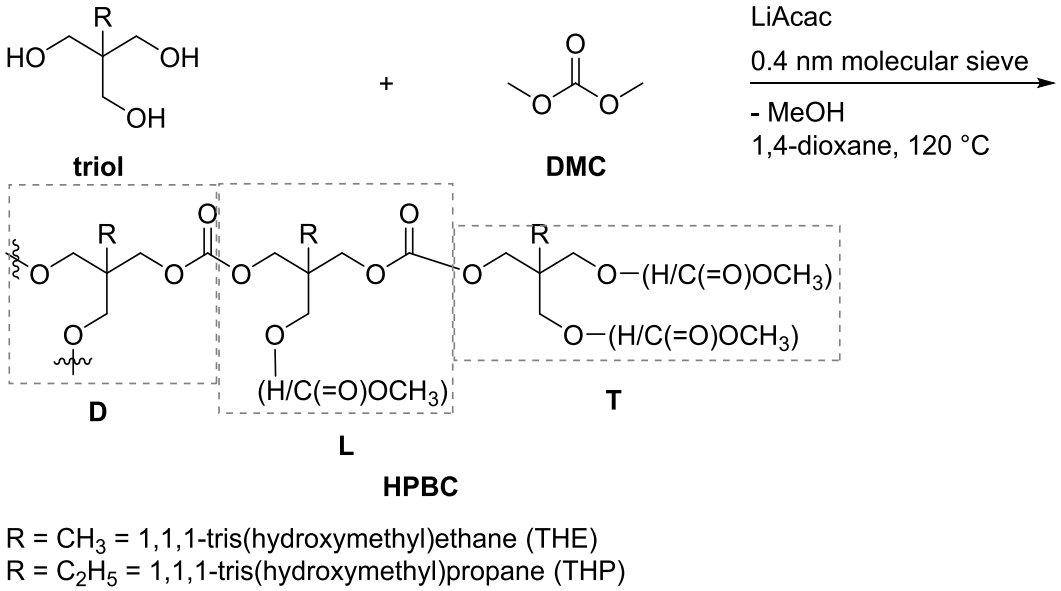


Figure 46. Strategy for the synthesis of HBPCs from triols and DMC

Due to fast gelation during the two-step polycondensation, the one-step procedure was applied for the synthesis of HBPCs. High-molecular weight HBPCs were obtained by feeding triols and DMC into a 1,4-dioxane solution at 120 °C. The reaction is depicted in Figure 46. Initially, various catalysts including organo-catalysts, such as DMAP, PPY and TBD, and metal salts, such as LiAcac, $Zn(OAc)_2$ and NaOMe were surveyed in the polycondensation of THE and

DMC in the bulk at 130 °C (data not shown). Most of them showed slow polymerization rates. After a polymerization time of 18 h, only HBPCs with low molar masses were obtained. However, LiAcac showed very high activity among them for this polycondensation (Table 13, entry 1). Hence, 0.1 wt% LiAcac (based on triol) was used as the catalyst instead of DMAP in these preparations. The products were obtained by dilution with acetone or THF and further precipitation in H_2O for THE and in H_2O/MeOH (v/v = 9: 1) for THP. The reaction conditions and results are summarized in Table 13.

Table 13. Results of HBPCs synthesis from triols and DMC using LiAcac as the catalyst

	[Triol]: [DMC]	Time	M_n (g/mol)[1]	M_w (g/mol)[1]	$Đ_M$[1]	DB[2]	Yield (%)	End group[2] (OH%)
PTHEC 1[3,4]	1: 1.5	18 h	4400	21000	4.87	0.50	42	81
PTHEC 2	1: 1.5	4 h	2900	4000	1.39	0.31	41	68
PTHEC 3	1: 1.5	6 h	2900	3800	1.33	0.31	36	74
PTHEC 4	1: 1.5	8 h	3000	5600	1.81	0.36	40	72
PTHEC 5	1: 1.5	10 h	8200	14000	1.67	0.43	42	73
PTHEC 6	1: 1.5	12 h	7200	123000	17.2	0.46	59	70
PTHEC 7	1: 1.0	18 h	10000	15000	1.47	0.46	25	94
PTHPC 1	1: 1.5	15 h	9300	64000	6.89	0.50	75	68

[1]Determined using SEC in DMAc solution with universal calibration.

[2]Calculated from the ^{1}H NMR spectrum.

[3]The polymerization was carried out in bulk at 130 °C.

[4]Gelation occurred after a polymerization time of 18 h, some solid precipitated and was not soluble in acetone.

DB = degree of branching

PTHEC = hyperbranched poly(1,1,1-tris(hydroxymethyl)ethyl carbonate)

PTHPC = hyperbranched poly(1,1,1-tris(hydroxymethyl)propyl carbonate)

Cross-linking phenomenon appeared in the bulk polymerization after a reaction time of 18 h. Some solid substances precipitated and were not soluble in acetone or THF. The resulting HBPC (acetone soluble part) had a M_n of 4400 g/mol and relatively broad dispersity ($Đ_M$ = 4.87). The cross-linking reaction was attributed to competitive intramolecular transesterification between the hydroxyl end groups and methyl carbonate end groups or polycarbonate backbone at high conversion. When 1,4-dioxane was used as the solvent for the same reaction, the molar masses increased significantly with narrower molar mass distributions (entries 2 – 7). Nevertheless, the prolonged reaction times lead to the generation of cross-linked gel products as well.

To determine the influence of the reaction time on the molar mass and cross-linking reaction, a kinetic study was performed (Table 13, entries 2 - 6). A series of polycondensations for THE and DMC were investigated with the same reaction conditions (120 °C, 1,4-dioxane) but with different reaction times from 4 to 12 h. The molar mass of the polymer was shown to increase very slowly throughout the initial 8 h. After a reaction time of 8 h, a M_n of 3000 g/mol with $Đ_M$ of 1.81 was obtained. When the polycondensation was further conducted for another 2 h, the increase in the molar mass became faster, with M_n = 8200 g/mol. Afterwards, an explosive increase in the dispersity ($Đ_M$ = 17.2) was observed because the gel product from the cross-linking reaction started to form. Moreover, with the feed ratio of 1: 1 a PTHEC sample with M_n = 10000 g/mol and $Đ_M$ = 1.47 was obtained.

The hydroxyl end group (-OH) contents could be calculated from the ^{1}H NMR spectra by comparing the integration of the hydroxyl and methyl carbonate end groups. For the polycondensation, the OH end group contents were approximately 70 % in 1,4-dioxane solution and 81 % in bulk. When the feed ratio of THE: DMC was 1: 1, the OH content increased to 94% but with a lower yield of 25 %, because increasing the hydroxyl end group content enhanced the solubility of HBPC in water. Using the same reaction conditions, an HBPC from THP was generated. The polymer formed within 15 h with M_n of 9300 g/mol, $Đ_M$ of 6.89 and OH end group content of 68 %. In contrast, a higher yield of 75% was obtained due to the more

hydrophobic property of the polymer backbone.

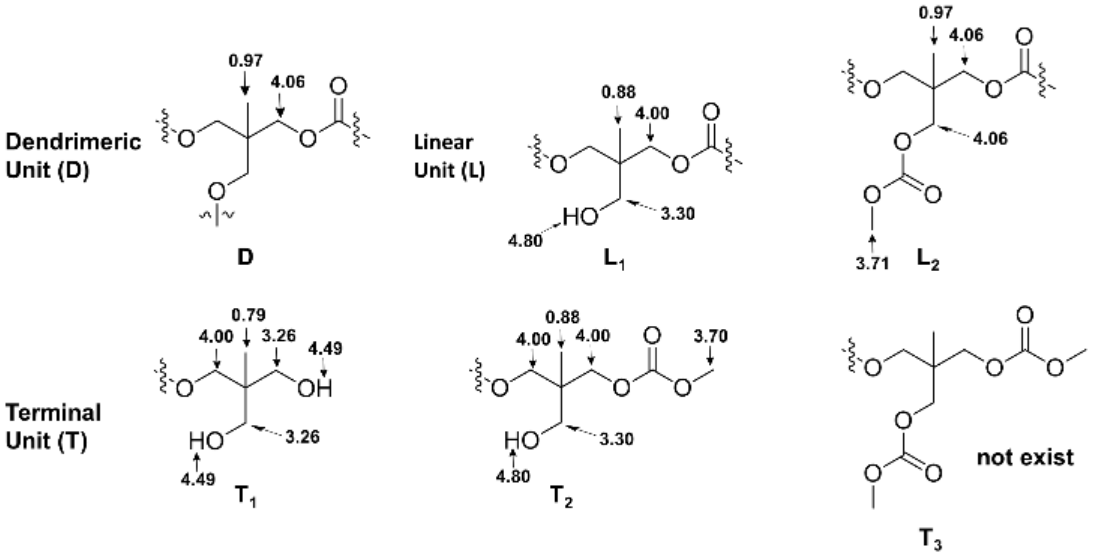


Figure 47. Possible chemical structures of PTHEC with chemical shifts (^{1}H NMR) in DMSO-d_6

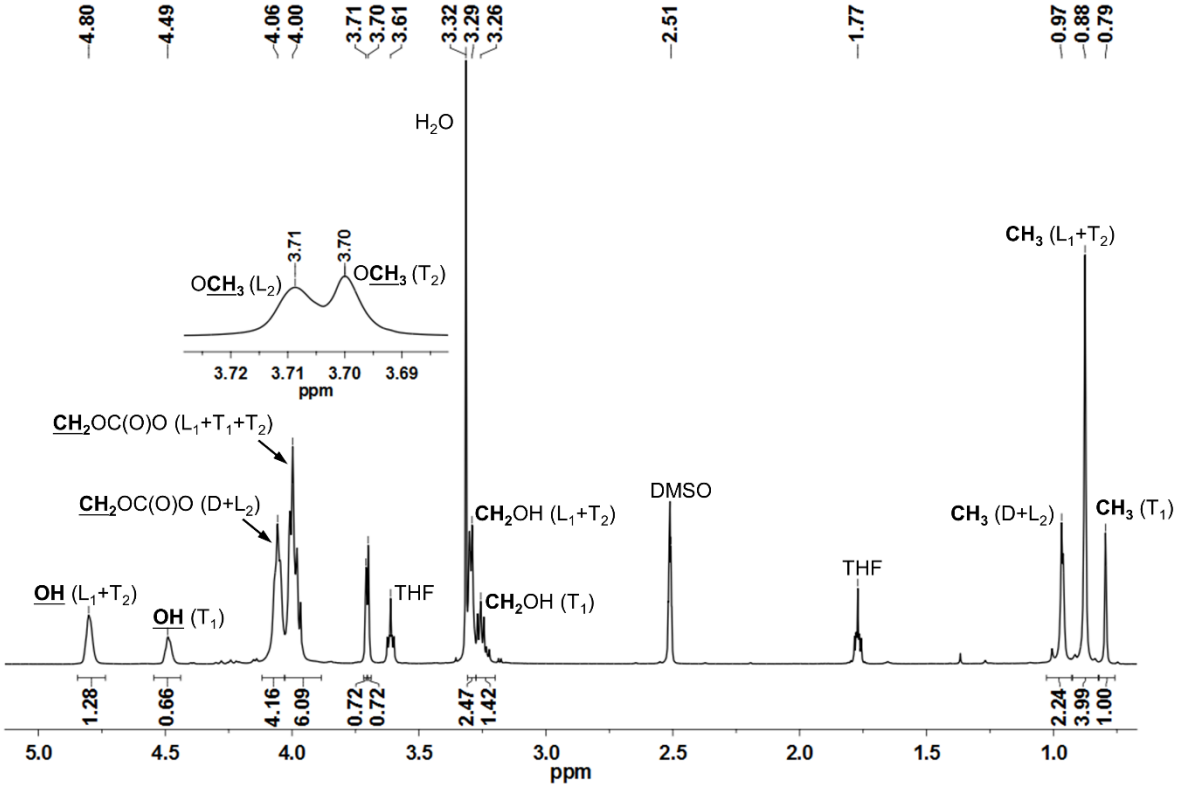


Figure 48. ^{1}H NMR spectrum of PTHEC

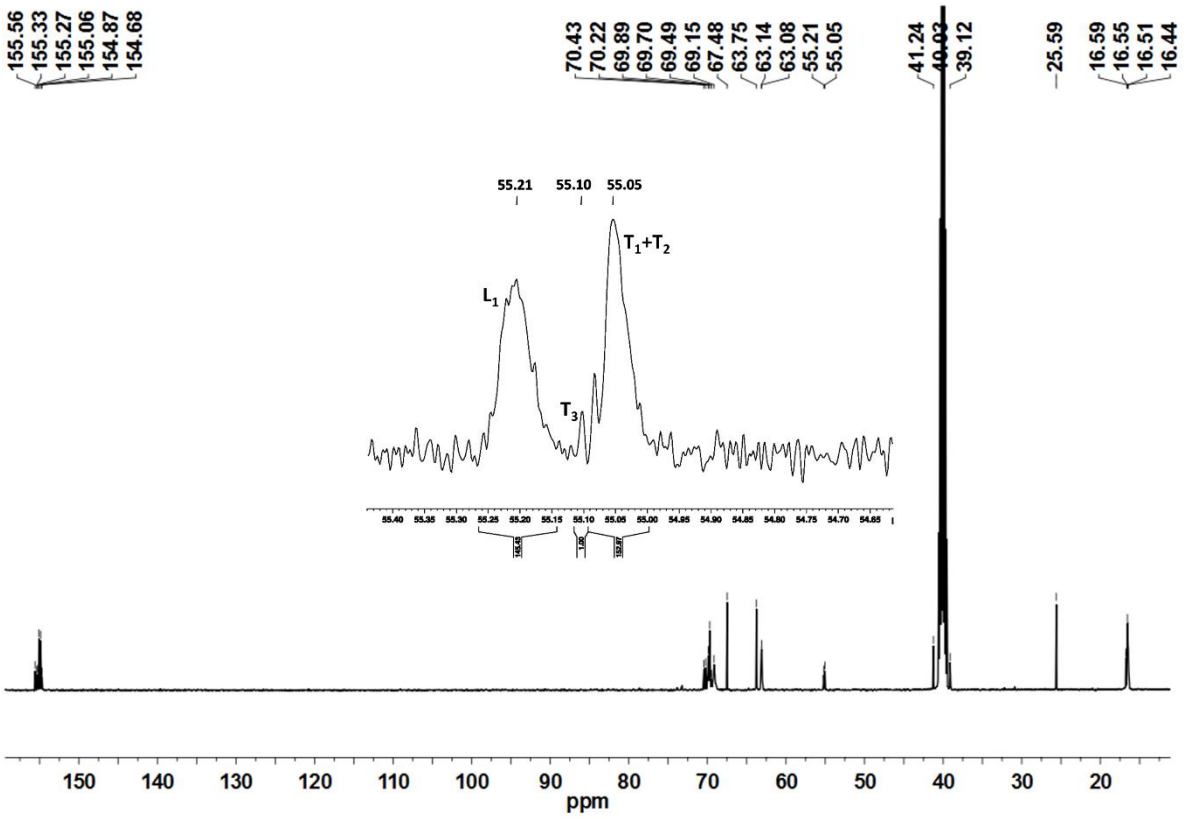


Figure 49. ^{13}C NMR spectrum of PTHEC

The fine structure of PTHEC was confirmed based on the analysis of the ^{1}H NMR spectrum. As Figure 47 shows, a hyperbranched polycarbonate structure consists of dendritic units (D), two linear structures (L) with hydroxyl (L_1) and methyl carbonate (L_2) side groups, respectively, and terminal units (T) including three possible structures. The terminal unit with two hydroxyl end groups (T_1) and a mixture of methyl carbonate and hydroxyl end groups (T_2) appeared in the ^{1}H NMR spectrum, while the two methyl carbonate terminated structure (T_3) could be neglected. This follows from the analysis of the ^{13}C NMR spectrum by comparing the peak integrals of the different structures (Figure 49).

The ^{1}H NMR spectrum of PTHEC 1 is shown in Figure 48. The three signals at 0.79 ppm, 0.88 ppm and 0.96 ppm were attributed to the methyl groups in the **T_1**, **L_1** + **T_2** and **D**+**L_2** structures, respectively. The signals between 3.20 ppm and 3.30 ppm were assigned to the **CH_2**OH groups.

Two singlet peaks at 3.70 ppm and 3.71 ppm indicated the existence of terminal methyl carbonate groups (O**CH$_3$**) in the **T$_2$** and **L$_2$** structures, respectively. The peaks between 3.90 ppm and 4.10 ppm corresponded to the **CH$_2$**OC(O)O groups in the polymer backbone. Furthermore, the hydroxyl end groups from **T$_1$** with two protons and **L$_1$** + **T$_2$** with one proton were observed at 4.49 ppm and 4.80 ppm as two broad peaks. The calculations of the contents of dendritic (**D**), linear (**L**) and terminal (**T**) units was possible using the following ^{1}H NMR analysis.

D = **CH$_3$**(**D** + **L2**) (0.97 ppm) – O**CH$_3$**(**L2**) (3.71 ppm) = 1.52

T = **CH$_3$**(**T1**) (0.79 ppm) + O**CH$_3$**(**T2**) (3.70 ppm) = 1.72

L = **CH$_3$**(**T1**) (0.79 ppm) + **CH$_3$**(**L1** + **T2**) (0.87 ppm) + **CH$_3$**(**D** + **L2**) (0.96 ppm) - **D** - **T** = 2.99

The degree of branching (DB) was calculated using ^{1}H NMR from the following Equation reported by Frey et al.

$$DB = \frac{2 \times \text{dendritic units (D)}}{2 \times \text{dendritic units (D)} + \text{linear units (L)}}$$

This equation is universally applicable for hyperbranched polymers with low and high molar masses. Using these calculated values, a DB for PTHEC 1 of 0.50 was obtained. According to the ^{1}H NMR analysis, DBs of 0.31 - 0.51 were calculated for the HBPC of THE. The DB was clearly influenced by the reaction time. With increasing reaction time, a higher DB was obtained.

4.2.6 Thermal properties of polycarbonates obtained by one-pot polycondensation

As shown in Table 5, the thermal properties of the synthesized linear and hyperbranched samples were evaluated using DSC measurements. The PTMC, PBC and PPC samples displayed T_g of -21 – -40 °C. The T_g decreased as the number of carbon atoms increased in repeating units and can be explained by the increase in chain flexibility. PDEAC and PCDMC tended to

higher T_g of 21 and 31 °C, respectively, due to their increasing rigidity from the phenyl side group in PDEAC and the rigid cyclic structure in the PCDMC backbone. By incorporating 20 mol% of a more flexible diol (1,5-propanediol and 1,6-hexanediol), with BD the T_g of the resulting polymers were decreased to -40 and -45 °C, respectively. In contrast, the polycarbonates based on PBC copolymerized with PDEAC and PCDMC have higher T_g detected at -23 and -32 °C, respectively. The PBC, PPC and PHC samples were semi-crystalline materials with melting points (T_m) of 63 °C, 49 °C and 55 °C, respectively, while the melting points of other homo- or copolycarbonates were not detected, indicating that the polymers were amorphous. For hyperbranched polycarbonates, PTHEC and PTHPC, higher T_g of 4 °C and -10 °C were observed compared to -38 °C for PBC sample. In comparison to linear polycarbonates, the T_g of HBPCs increased as a result of the large number of hydroxyl end groups in the hyperbranched structure, which lead to increases in polarity.[32]

Table 14. Thermal properties of linear and hyperbranched aliphatic polycarbonates

	M_n (g/mol)[1]	T_g (°C)[2]	T_m (°C)[2]
PTMC 2	5200	-21	n.d.
PBC 12	9800	-38	63
PPC 1	16000	-40	49
PHC 1	13000	n.d.	55
PDEAC 1	4300	21	n.d.
PCDMC 1	13000	31	n.d.
PBC-*co*-PPC	6300	-40	n.d.
PBC-*co*-PHC	7500	-45	n.d.
PBC-*co*-PDEAC	3500	-23	n.d.
PBC-*co*-PCDMC	7100	-32	n.d.
PTHEC 7	10000	4	n.d.
PTHPC 1	9300	-10	n.d.

[1]determined using SEC in chloroform with PS standards.

[2]T_g and T_m were measured by DSC.

n.d.: not detected.

4.2.7 Hydrolytic and enzymatic degradation

The hydrolytic and enzymatic degradations of the synthesized linear and hyperbranched polycarbonates were investigated under biological (37 °C, pH 7.4), accelerated (37 °C, pH from 1 to 13 or 55 °C, pH 13.0 °C) and enzymatic (37 °C, in lipase solution (pH 6.2)) conditions. The degradation process of the polycarbonates was monitored by the decrease in weight and molar mass after defined time intervals.

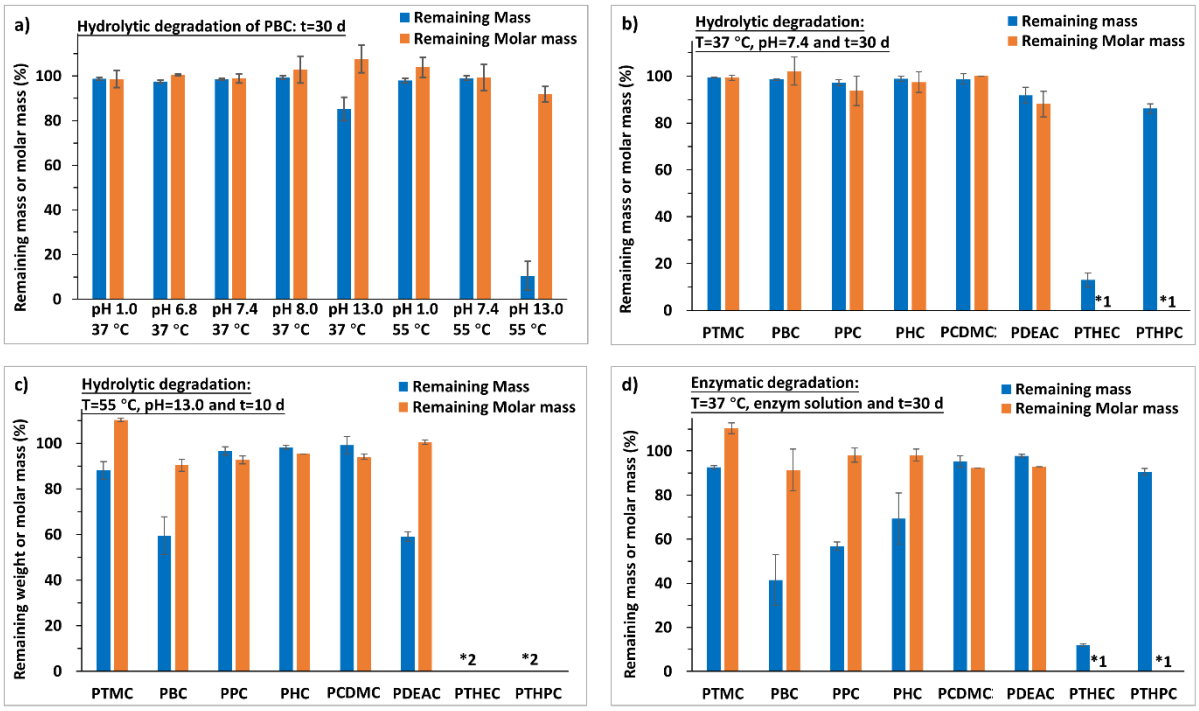


Figure 50. Results of the hydrolytic and enzymatic degradation for linear and hyperbranched polycarbonate specimens. a) Mass and molar mass loss of PBC specimen under different conditions after 30 days. b) Mass and molar mass loss of linear and hyperbranched polycarbonate specimens under the biological condition, 37 °C pH 7.4, after 30 days and c) under the accelerated condition, 55 °C pH 13.0, after 10 days. d) Mass and molar mass loss of linear and hyperbranched polycarbonate specimens in lipase solution after 30 days. *1, hyperbranched polymers were cross-linked after 30 days; *2, no polymer was recovered under this condition.

Firstly, the hydrolytic degradation of PBC specimen at 37 °C with pH values from 1.0 to 13.0 was investigated. The results in Figure 50a show that the PBC specimens did not degrade for up to 30 days in acidic or weakly basic conditions, but in the buffer solution with pH 13.0, a mass loss of 15% was observed. To highlight the effect of pH on the degradation of polycarbonates, an accelerated experiment was performed at 55 °C in buffer solutions with pH values of 1.0, 7.4 and 13.0. As shown in Figure 50a, the PBC specimens in the buffer solutions with pH values of 1.0 and 7.4 showed weight losses of 2.1 ± 0.9% and 0.3 ± 1.0%, respectively, after 30 days, while the specimen in basic condition with pH value of 13.0 showed a weight loss of 89.5 ± 6.3%. Moreover, the weight changes of PBC specimen during 30 d incubation at 37 °C, pH 7.4 and 55 °C pH 13.0 is compared in Figure 51. The results show that the sample weight remained constant at 37 °C and pH 7.4, while the PBC specimen was degraded at 55 °C pH 13.0 during 30 days according to zero order with an erosion rate of 2.9 wt%/day (correlation coefficient $R^2 = 0.9726$).

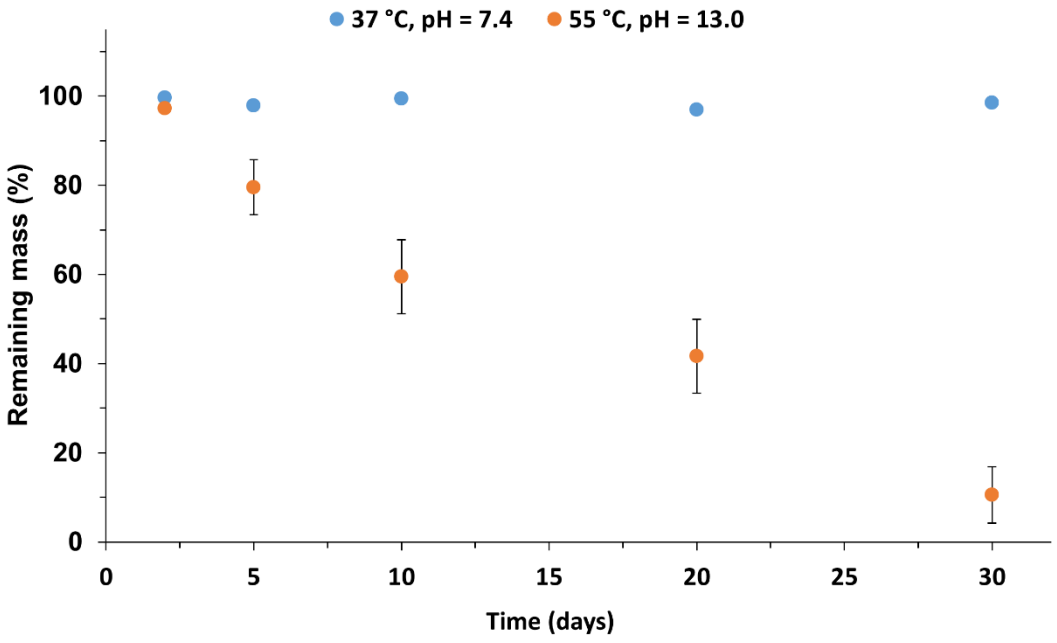


Figure 51. Mass loss of PBC specimen during 30 days under biological and accelerated conditions, i.e., 37 °C pH = 7.4 and 55 °C pH = 13.0.

All of the other linear and hyperbranched polycarbonates were also evaluated under the same conditions (at 37 °C pH 7.4 for 30 days and 55 °C pH 13.0 for 10 days) in order to determine the influence of polymer structures on the degradation rate. Figure 50b shows that most of the linear polycarbonate specimens showed no decrease in either weight or molar mass. An exception is that PDEAC lost 8.2 ± 3.5% weight, which is probably attributed to the heteroatom in the polycarbonate backbone. The two hyperbranched specimens presented completely different phenomena. Only 13.0 ± 2.8% weight was recovered for PTHEC, while PTHPC was found to show 86.2 ± 2.1% mass remaining on day 30. The huge mass loss could be ascribed to the more hydrophilic property of PTHEC, leading to the dissolution in buffer solution because of the lack of a methylene group on the side chain in comparison to the PTHPC specimen. Both hyperbranched polymers were cross-linked after the investigation and did not dissolve in acetone or THF.

As shown in Figure 50c, the degradation rate of the polycarbonates was also strongly influenced by the polymer structure. For linear polycarbonates under the accelerated condition, the mass losses of PTMC, PBC and PDEAC were 11.9 ± 3.8%, 40.5 ± 8.2% and 40.9 ± 2.1%, respectively, after 10 days. However, PPC, PHC and PCDMC showed higher stabilities under this condition. The hyperbranched polycarbonate specimens, PTHEC and PTHPC, were cooled to 0 °C for several hours after the degradation to reduce the error in the solubility. No hyperbranched polymer was recovered after 10 days, indicating that the hyperbranched structure could accelerate the hydrolytic degradation process probably due to its high density of functional groups in comparison to linear aliphatic polycarbonates.

Figure 50d shows the mass and molar mass losses of linear and hyperbranched polycarbonates specimens after 30 days incubation time using lipase from *Thermocyces languginosus* (solution from Sigma-Aldrich L0777, ≥100,000 U/g, pH 6.2). All linear polycarbonates except PDEAC showed more or less degradability in the enzymatic degradation investigation. PBC had the fastest degradation rate. After 30 days, 58.5 ± 11.4% of the weight had been lost. Enzymatic degradation rates could be significantly affected by polymer structures. Amorphous PTMC

showed only 7.4 ± 0.7% weight loss, which is consistent with previous literature.[100] In contrast, linear polycarbonates with higher crystallinity were degraded more quickly. The degradation rates decreased with the increase of carbon atoms of used alcohols (from PBC to PHC) and with the increase of rigidity (PCDMC). The mass losses of PPC, PHC and PCDMC were found to be 43.2 ± 1.8%, 30.6 ± 11.6% and 4,7 ± 2.6%, respectively. Different from other linear polycarbonates, PDEAC displayed higher stability and lower degradation rate in lipase solution. The possible reason is that the presence of nitrogen atoms in the polymer backbone reduced the lipase activity. Both the hyperbranched polycarbonates showed similar results as hydrolytic degradation at 37 °C and pH 7.4. Since significant losses of mass were observed while molar mass remained constant after the enzymatic and basic hydrolytic degradations, both the erosion processes must be considered as surface erosion process.

4.2.8 Conclusions

In summary, a universal new strategy for the synthesis of aliphatic linear and hyperbranched polycarbonates was developed. In contrast to the classic two-step polycondensation in melt requiring a high polymerization temperature and high vacuum to remove unreacted monomers and byproducts, in this work, the one-pot polycondensation was carried out in 1,4-dioxane solution and under relatively mild polymerization conditions (T = 120 °C and at atmospheric pressure) using DMAP or LiAcac as catalysts. The only side product was methanol, which was removed by using 4 Å molecular sieve in a pressure-equalized addition funnel. This study is the first to report a one-pot polycondensation at atmospheric pressure for the preparation of linear and hyperbranched polycarbonates using dimethyl carbonate (DMC) instead of phosgene. As expected, the polycarbonates were prepared only by the transesterification reaction between hydroxyl and methyl carbonate chain ends. Consequently, a nearly equal molar ratio of diol or triol to DMC was used to reach higher molar masses and avoid wasting excess DMC during the polycondensation. Using this strategy, poly(trimethylene carbonate) (PTMC), poly(1,4-tetramethylene carbonate) (PBC), poly(1,5-

pentamethylene carbonate) (PPC), poly(1,6-hexametylene carbonate) (PHC), poly(diethylphenylamine carbonate) (PDEAC) and poly(cyclohexan-1,4-dimethylene carbonate) (PCDMC) were successfully prepared with number averaged molar mass (M_n) up to 16000 g/mol, dispersities below 1.70 and high yields above 70%. Additionally, the hyperbranched polycarbonates based on 1,1,1-tris(hydroxymethyl)ethane (THE) and 1,1,1-tris(hydroxymethyl)propane (THP) were also obtained with M_n up to 10000 g/mol, M_w up to 64000 g/mol and high OH end group contents approximately 70%.

The hydrolytic degradations of the synthesized linear and hyperbranched polycarbonates were evaluated at 37 °C and 55 °C with various pH values, and the linear aliphatic polycarbonates were relatively stable under acidic to weakly basic conditions even at elevated temperature. In contrast, linear polycarbonates could only be hydrolytically degraded under strongly basic condition (pH 13.0). For the hyperbranched polycarbonates, no polymer was recovered after 10 days under the accelerated condition (55 °C, pH 13.0), indicating that the hyperbranched structure could accelerate the hydrolytic degradation process probably due to its high density of functional groups in comparison to linear aliphatic polycarbonates. Compared with hydrolytic degradation, linear polycarbonates were degraded much faster in lipase solution from *Thermocyces languginosus* at 37 °C. The degradation rates were strongly dependent on polymer structures. Both the enzymatic and basic hydrolytic degradations showed that linear polycarbonate specimens degraded by surface erosion.

In addition, this new strategy can theoretically be applied to synthesize other types of hyperbranched polymers, such as polyesters, via $A_2 + B_3$ polycondensation to obtain high molar masses and avoid cross-linking reactions with water or methanol as the byproduct.

4.3 Results of the synthesis of hyperbranched polymers from vegetable oil based monomers via ozonolysis pathway

4.3.1 Characterization of vegetable oil based B_3 monomers

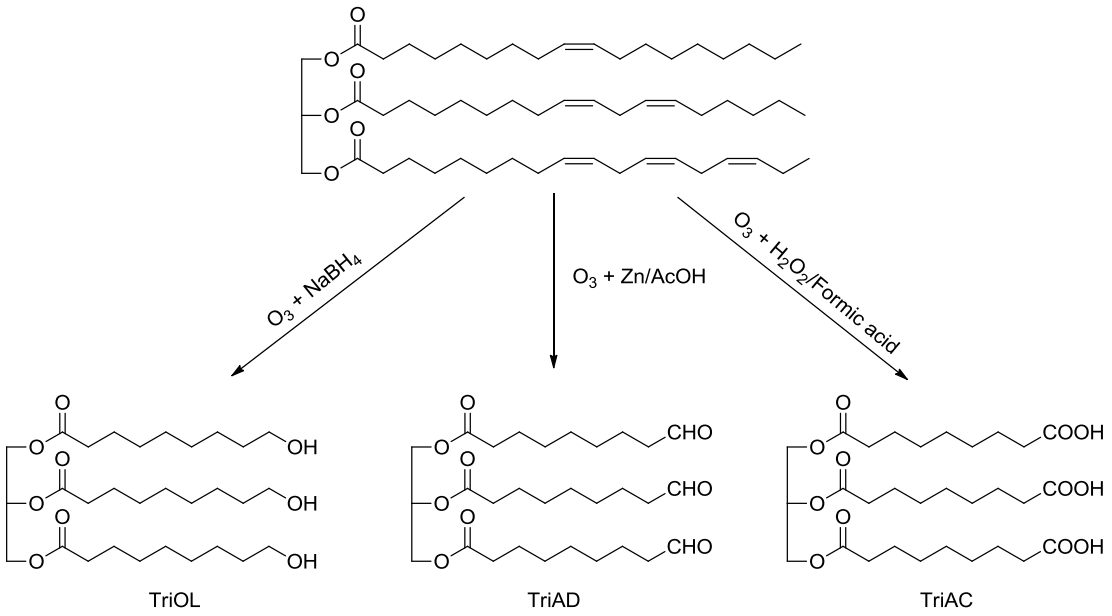


Figure 52. Ozonation of soybean oil to give TriOL, TriAD and TriAC

Trifunctional monomers were synthesized by ozonolysis in dichloromethane and methanol, followed by reductive or oxidative treatment resulting to TriOL, TriAD or TriAC (Figure 52). As shown in Table 15, the hydroxyl values of both the TriOLs (282.5 mg KOH/g and 215.1 mg KOH/g for TriOL-CO and TriOL-SO, respectively) were close to theoretical values. The functionality (f) was calculated by dividing the theoretical molar mass by the equivalent weight (EW). As expected, due to the higher content of unsaturated fatty acids in castor oil, the TriOL-CO had functionality of 2.9, while a lower functionality of 2.3 was obtained for TriOL-SO. In addition, unexpected carboxylic acids were formed during ozonolysis process (peroxide species) which cannot be reduced to alcohol by hydrogenation with $NaBH_4$. The acid values were 3.8 and 5.3 mg KOH/g for TriOL-CO and TriOL-SO, respectively.

Table 15. General parameters of TriOls and TriACs

B_3 monomers	OH no. (mg KOH/g)	theor. OH no. (mg KOH/g)	acid no. (mg KOH/g)	theor. acid no. (mg KOH/g)	EW (g/mol)	M_{th} (g/mol)	f
TriOL-CO	282.5	290	3.8	-	198	567	2.9
TriOL-SO	215.1	235	5.3	-	261	603	2.3
TriAC-SO-Ozo	-	-	198.5	222	283	641	2.3
TriAC-SO-Ox	-	-	226.1	222	248	641	2.6
TriAC-CO-Ox	-	-	255.3	271	220	607	2.8

EW = equivalent weight;

M_{th} = theoretical molar mass;

f = functionality (=M_{th}/EW)

Tricarboxylic acids were synthesized from soybean oil using two strategies, via direct ozonolysis with oxidative treatment (suffixed by "-Ozo") or via oxidation of trialdehyde (suffixed by "-Ox"). In the first method, formic acid and hydrogen peroxide were added into ozonolysis reaction mixture successively. The ozonation intermediate underwent an oxidation process and form a mixture of mono-, bi- and tricarboxylic acids. Low molecular weight compounds were then removed in vacuum. The latter method involved oxidation of purified TriAD using the combination of formic acid and hydrogen peroxide. Table 1 shows that the acid value of TriAC-SO-Ox (226.1 mg KOH/g) was higher than that of TriAC-SO-Ozo (198.5 mg KOH/g) and closer to the maximum value of 222 mg KOH/g. The low acid value of TriAC-SO-Ozo can be probably attributed to incomplete oxidation of the ozonation intermediates due to the presence of *in situ* generated methyl ester terminated triglycerides. Based on this result, tricarboxylic acid from castor oil was synthesized only via oxidation of trialdehyde (named TriAC-CO-Ox) with the acid value of 255.3 mg KOH/g. The equivalent weight (EW) is defined as the mass of a substance in grams that contains one mole functional groups. EW is an important parameter for further calculation of initial molar ratios, because the obtained

trifunctional monomers had a mixture of triglyceride structures. Using the following equation, EWs of B_3 monomers could be calculated.

$$EW = \frac{\text{molecular weight of KOH} \times 1000}{\text{OH no. (for triols) or acid no. (for tricarboxylic acids)}}$$

$$= \frac{56110}{\text{OH no. or acid no.}} \ {}^{g}/_{mol} \text{ of -OH or -COOH groups}$$

The EWs of 198, 289, 283, 248 and 220 g/mol were obtained for the TriOL-CO, TriOL-SO, TriAC-SO-Ozo, TriAC-SO-Ox and TriAC-CO-Ox, respectively.

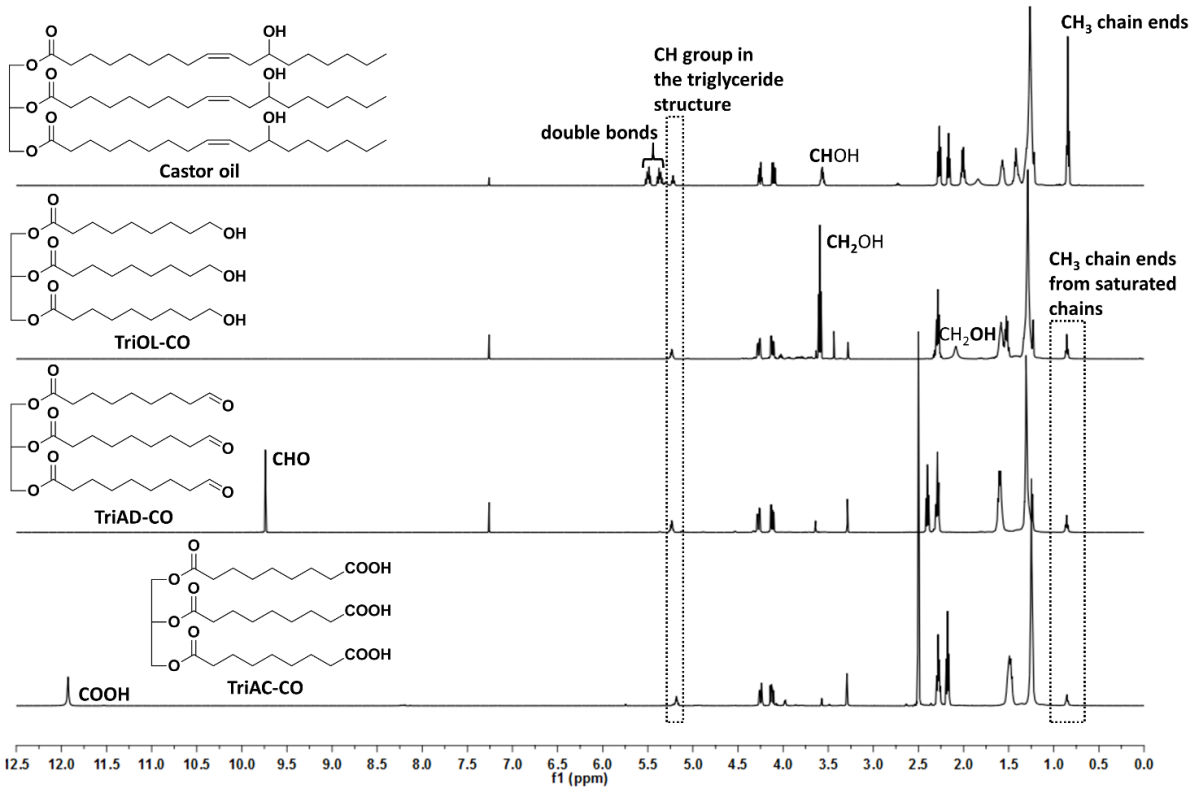


Figure 53. ^{1}H NMR spectra of castor oil, TriOL-CO, TriAD-CO (in $CDCl_3$-d) and TriAC-CO (in DMSO-d_6)

The ^{1}H NMR spectra of castor oil, TriOL-CO, TriAD-CO (in $CDCl_3$-d_1) and TriAC-CO (in DMSO-d_6) are shown in Figure 53. After the ozonolysis process, the signals for double bonds between 5.25 and 5.60 ppm disappeared. Further, the peak at 5.17 ppm for the CH group in the triglyceride structure remained unchanged, indicating that the ozonolysis proceeded completely and the triglyceride structure maintained integrity. Compared with the castor oil spectrum, three new signals at 2.45 ppm, 9.74 ppm and 11.93 ppm appeared corresponding to the –OH, -CHO and –COOH end groups in the TriOL-CO, TriAD-CO and TriAC-CO, respectively. In addition, the significant decrease of the signal at 0.85 ppm attributed to the CH_3 end groups shows that the byproducts were removed from the products successfully. The ^{1}H NMR spectra of the ozonolysis products from soybean oil were similar to that from castor oil.

The structures of ozonolysis products from castor oil, TriOL-CO, TriAD-CO and TriAC-CO, were further analyzed by ATR-FTIR spectroscopy (Figure 54). After the ozonolysis, the bands of C=C double bonds at 3010 cm^{-1} and 1654 cm^{-1} disappeared. The OH-group absorption band at 3340 cm^{-1} became broader and stronger indicating the new formation of primary hydroxyl groups and successful removal of 1,3-nonanediol byproduct. For the TriAD-CO and TriAC-CO products, the OH-group absorption band around 3400 cm^{-1} is clearly missing. Two absorption bands characteristic for the C=O group centered at 1722 and 1704 cm^{-1} were newly detected and assigned to the aldehyde (H**C=O**) and carboxylic acid (HO**C=O**), respectively. Moreover, the significant reduction of alkyl bands around 2900 cm^{-1} and 710 cm^{-1} indicates the absence of linear byproducts in the pure monomers. The FTIR results are in agreement with the ^{1}H NMR analysis. According to the results of ^{1}H NMR, FTIR and ESI-ToF-MS analysis, the synthesized B_3 monomers had high purity and were suitable to be applied in the further preparation of hyperbranched polymers.

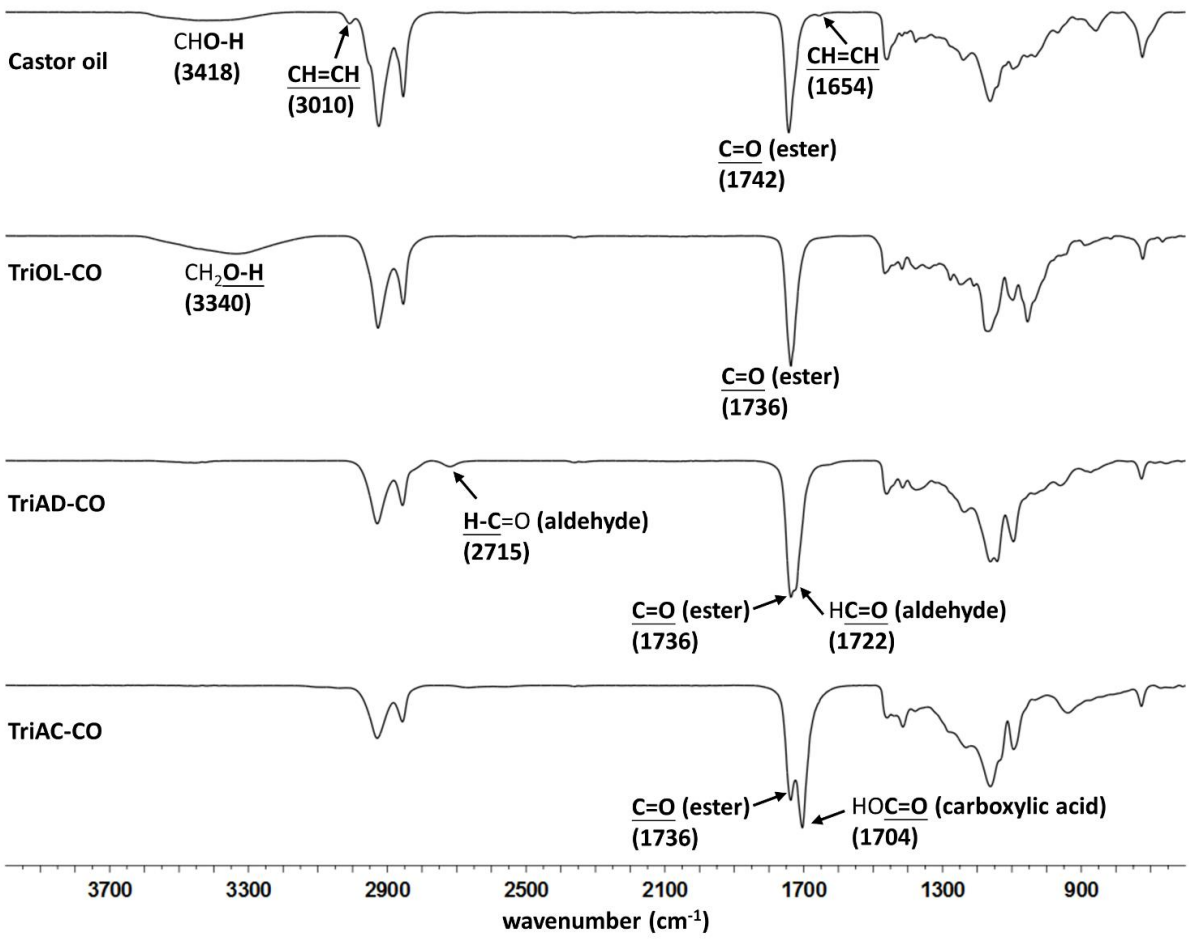


Figure 54. ATR-FTIR spectra of castor oil, TriOL-CO, TriAD-CO and TriAC-CO

4.3.2 Synthesis of hyperbranched polycarbonate from the vegetable oil based TriOLs

Starting from vegetable oil based TriOL monomers, a variety of hyperbranched polymers (HBPs), such as hyperbranched polycarbonate, polyester, polyurethane and polyacetal, can be obtained using A_2 + B_3 polycondensation (Figure 55). Their chemical, physical, mechanical properties and hydrolytic or enzymatic degradation rates of these HBPs can be varied, since different groups are introduced in polymer backbone.

As mentioned above, hyperbranched polycarbonates from triols and dimethyl carbonate (DMC) were successfully synthesized using a one-pot polycondensation. Unfortunately, in the presence of dimethyl carbonate and byproduct methanol, the ester bond decomposed during the polymerization. In the ^{1}H NMR spectrum the signal for the CH group at 5.20 ppm disappeared, which could be attributed to the transesterification of the ester bond with methanol or DMC (data not shown) forming a volatile side product. To avoid this problem, diphenyl carbonate (DPC), whose byproduct phenol has much lower nucleophilic property than methanol, was used instead of DMC.

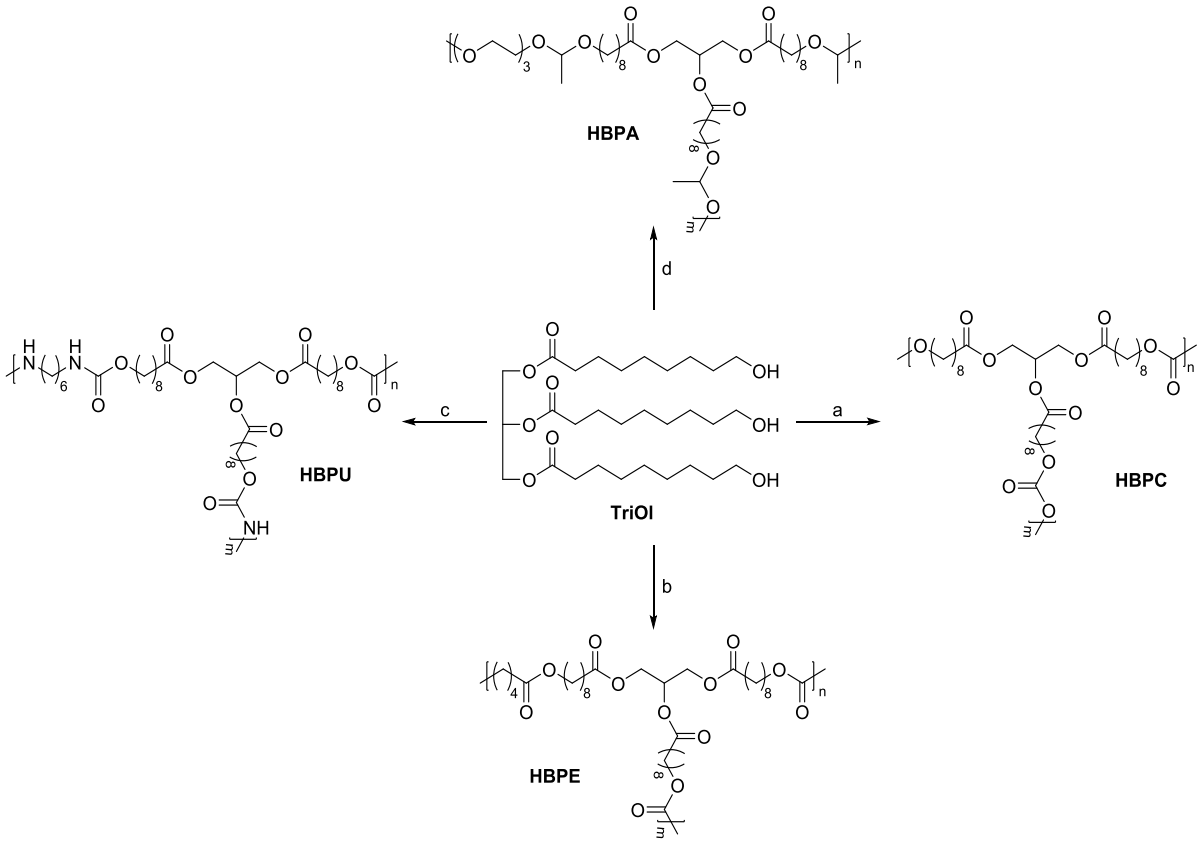


Figure 55. Overview of synthesis of hyperbranched polymers from the vegetable oil based TriOL. a: diphenyl carbonate (DPC), DMAP, 130 °C, in bulk; b: adipic acid (AA), DBTO, 150 °C, in bulk; c: hexamethylene diisocyanate (HDI), DBTD, rt, THF, argon; d: tri(ethylene glycol) divinyl ether (TEDE), PPTS, rt, DCM, argon.

Table 16. Results of hyperbranched polycarbonates from castor oil based TriOL monomers in bulk at 130 °C using DMAP as catalyst under argon atmosphere

	[TriOL]:[DPC]:[DMAP]	Time (h)	M_n[1] (g/mol)	M_w[1] (g/mol)	$Đ_M$[1]	OH-content[2] (%)
HBPC-CO-1	1.0: 0.8: 0.015	18	2700	6700	2.4	98
HBPC-CO-2	1.0: 1.0: 0.015	18	3700	14000	3.7	93
HBPC-CO-3	1.0: 1.1: 0.015	13	2700	6700	2.4	69
HBPC-CO-4	1.0: 1.2: 0.015	11	2300	4700	2.0	73
HBPC-CO-5	1.0: 1.3: 0.015	10	3800	15000	3.9	68
HBPC-CO-6	1.0: 1.5: 0.015	8	Cross-linked			
HBPC-CO-7	1.0: 2.0: 0.015	18	3100	8600	2.8	19
HPBC-SO-1	1.0: 1.0: 0.015	18	3600	10000	2.8	100

[1]determined using SEC in THF with PS standards

[2] determined using ^{1}H NMR spectroscopy.

Table 16 summarizes the most significant results of the hyperbranched polycarbonate synthesis from TriOL. The polymerization was carried out in bulk at 130 °C using DMAP as catalyst. TriOL-CO was used first to optimize the polymerization parameters, such as initial molar ratios ([TriOL]: mole of used [TriOL] = m_{TriOL}/M_{TriOL} = m_{TriOL}/3xEW, [DPC]: mole of used DPC and 0.015 mol% DMAP based on [TriOL] as catalyst) as well as polymerization times. The molar ratios of [TriOL-CO]: [DPC]: [DMAP] were varied from 1: 0.8: 0.015 to 1: 2.0: 0.015. As shown in Table 16, the number averaged molar mass (M_n) increased slightly from 2700 g/mol to 3800 g/mol throughout the feed ratios from 1: 0.8 to 1: 1.3, while weight averaged molar masses (M_w) up to 15000 g/mol were obtained. With molar ratio of 1.0: 1.5, a cross-linking reaction occurred within 8 h. The resulting polymer was a yellow gel and not soluble in common organic solvents. When the initial molar ratio was adjusted to 1: 2.0, no cross-linking reaction was observed due to the high content of phenyl carbonate end groups and a polymer with M_n of 3100 g/mol with dispersity $Đ_M$ of 2.8 was obtained. The polymerization times were

chosen based to obtain HBPC with high molar masses and avoid cross-linking reaction.

Hydroxyl terminated HBPCs are of great interest, because the OH end groups can be chemically modified for further application and improvement of thermal properties. There is a significant influence of the initial molar ratio [TriOL-CO]: [DPC] on the end group composition in the final polymers. The OH end group content decreases from 98 % to 19 % with increasing feed ratio [TriOL-CO]: [DPC] from 1: 0.8 to 1: 2.0. HBPC-CO with OH end group content more than 90 % could be obtained with the initial molar ratio [TriOL-CO]: [DPC] < 1: 1.0, while the HBPCs had around 70% OH end groups, when the molar ratio was greater than 1: 1.0. Based on the results of HBPC synthesis, a sample of HBPC from soybean oil based TriOL using [TriOL-SO]: [DPC] = 1: 1.0 was obtained with M_n of 3600 g/mol, M_w of 10000 g/mol and 100% OH end group content.

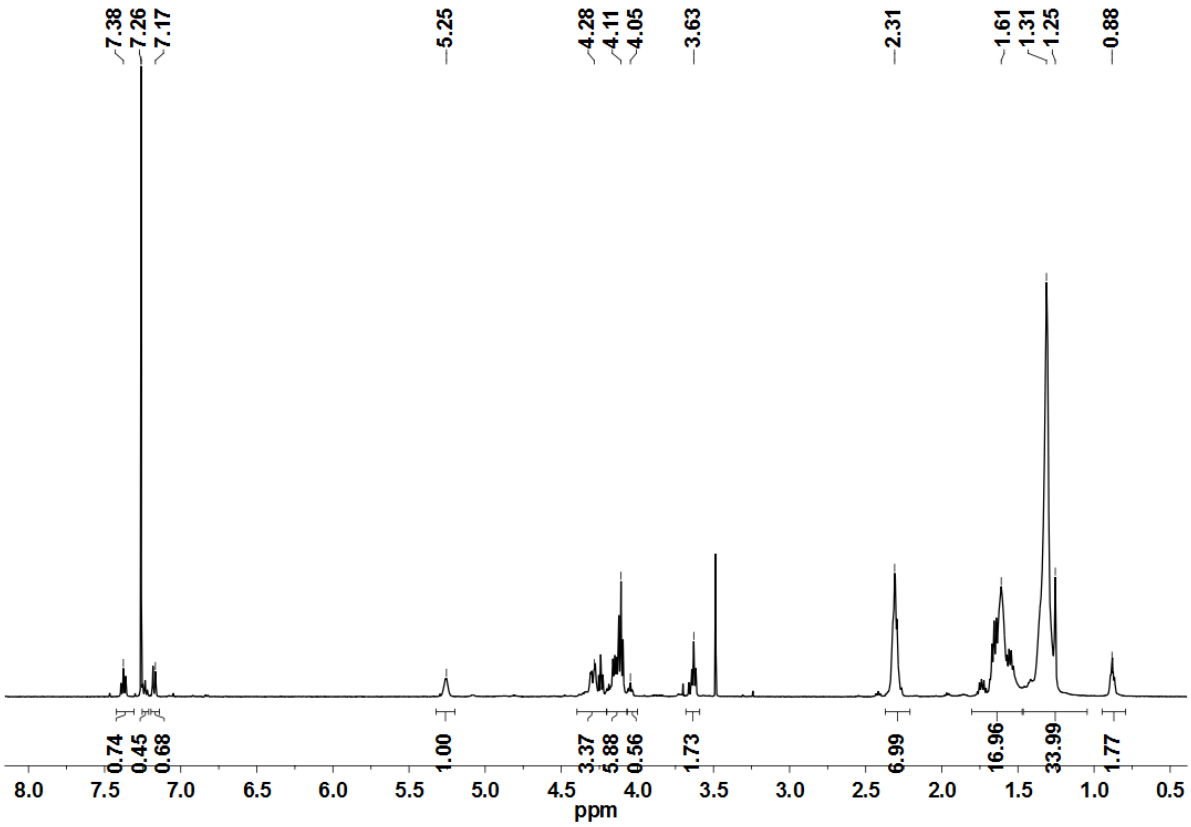


Figure 56. ^{1}H NMR spectrum of HBPC-CO-3 (in $CDCl_3$-d)

Figure 56 shows a typical ^{1}H NMR spectrum of HBPC-CO. The signal at 0.88 ppm is attributed to the CH_3 end group from unreactive saturated fatty acids as dangling chains in the final polymer. Signals between 1.00 and 2.00 ppm correspond to CH_2 groups not bonded to hydroxyl or ester groups. The multiplet peak at 3.63 ppm indicates the existence of **$\underline{CH_2}$**OH end groups. The two **$\underline{CH_2}$**OC(O)- ester groups and newly produced carbonate groups **$\underline{CH_2}$**OC(O)O are detected between 4.00 and 4.50 ppm. The CH-group of each repeating unit is observed at 5.25 ppm. The peak area ratio of the CH group and unreactive CH_3 group kept unchanged indicating that no decomposition of the ester bond from triglyceride occurred. In addition, the OH end group contents could be calculated from ^{1}H NMR spectrum comparing the integration of **CH_2**OH at 3.55 ppm and phenyl carbonate –OC(O)O**Ph** around 7.25 ppm. Degree of branching is an important parameter for HBPs. However, in this work, signals of terminal (T), linear (L) and dendritic (D) units cannot be distinguished in ^{1}H and ^{13}C spectra due to their similar chemical shifts.

4.3.3 Synthesis of HBPE, HBPU and HBPA from vegetable oil based TriOL

In addition to HBPC a variety of hyperbranched polymers can be obtained from vegetable oil based TriOL monomers. To study the versatility of this new strategy, the synthesis of HBPEs, HBPUs and HBPAs were attempted from commercially available A_2 monomers with TriOLs via a $A_2 + B_3$ polycondensation. The results of the synthesis are summarized in Tables 17 – 19. HBPEs were prepared from TriOL monomers with adipic acid at 150 °C by melt-polycondensation yielding highly viscos liquid. Polymers with M_n in the range 3500 g/mol to 4000 g/mol with dispersities between 5.0 and 8.0 were obtained. The molar masses were not affected by monomer ratios. However, the OH end group content increased from 59% to 100% with decreasing initial concentration of adipic acid.

Table 17. Results of HBPE synthesis in bulk at 150 °C using DBTO as catalyst via two step polycondensation

	[TriOL]: [AA]: [DBTO]	Time (h)	M_n[1] (g/mol)	M_w[1] (g/mol)	$Đ_M$[1]	OH-content[2] (%)
HBPE-CO-1	1.0: 0.9: 0.15 wt%	4.5	3600	27000	7.9	100
HBPE-CO-2	1.0: 1.0: 0.15 wt%	4.5	3600	18000	5.1	92
HBPE-CO-3	1.0: 1.1: 0.15 wt%	4.5	3900	20000	5.1	71
HBPE-CO-4	1.0: 1.2: 0.15 wt%	4.5	3500	21000	6.0	59
HBPE-SO-1	1.0: 1.0: 0.15 wt%	4.5	2400	4500	1.9	70

[1] determined using SEC in THF with PS standards;

[2] determined using ^{1}H NMR spectroscopy.

Table 18. Results of HBPU synthesis in THF at room temperature using DBTD as catalyst under argon atmosphere

	[TriOL]: [HDI]	Time (h)	M_n[1] (g/mol)	M_w[1] (g/mol)	$Đ_M$[1]	OH-content[2] (%)
HBPU-CO-1	1.0: 0.9	18	5800	21000	3.6	100
HBPU-CO-2	1.0: 1.0	18	7300	40000	5.5	100
HBPU-CO-3	1.0: 1.1	18	9400	17000	1.8	100
HBPU-CO-4	1.0: 1.2	18	cross-linked			
HBPU-SO-1	1.0: 1.0	18	8000	19000	2.4	100

[1] determined using SEC in THF with PS standards

[2] determined using ^{1}H NMR spectroscopy.

Table 19. Results of HBPA synthesis in dichloromethane at room temperature using DBTD as catalyst under argon atmosphere

	[TriOL]: [TEDE]: [PPTS]	Time (h)	M_n[1] (g/mol)	M_w[1] (g/mol)	$Đ_M$[1]
HBPA-CO-1	1.0: 0.9: 0.05	2.5	3500	11000	3.1
HBPA-CO-2	1.0: 1.0: 0.05	2.5	4700	23000	4.9
HBPA-CO-3	1.0: 1.1: 0.05	2.5	5300	36000	6.8
HBPA-SO-1	1.0: 1.0: 0.05	2.5	1300	1600	1.2

[1] determined using SEC in THF with PS standards

OH contents cannot be determined due to overlapping of ether bond and OH end groups

Compared to the synthesis of HBPE, higher M_n were obtained by the preparation of HBPU and HBPA, because the polymerizations were performed in the presence of solvent. M_n of HBPU and HBPA increased significantly with increasing initial concentrations of HDI and TEDE. M_n up to 9400 g/mol and 5300 g/mol were obtained for HBPU and HBPA, respectively. Due to the high reactivity of HDI the OH end group contents of HBPU and HBPA are observably higher than HBPE and HBPC. For HBPUs, hydroxyl terminated polymers have been obtained in all cases. However, the cross-linking reaction took place rapidly if [TriOL]: [HDI] was greater than 1: 1.1. In comparison to the HBPs from TriOL-CO, the soybean oil based HBPs (HBPC-SO-1, HBPE-SO-1 and HBPU-SO-1) had similar M_n, however, with lower dispersities due to the increased content of linear segments. Using the same polymerization conditions of HBPA-CO, the synthesized HBPA-SO had only low M_n. The ^{1}H NMR analysis confirmed as well, that the conversion of TEDE was very low. This phenomenon can be explained probably by the lower reactivity of TriOL-SO due to its higher saturated fatty acid contents (about 15%). Moreover, all the obtained HBPs are well soluble in common organic solvents.

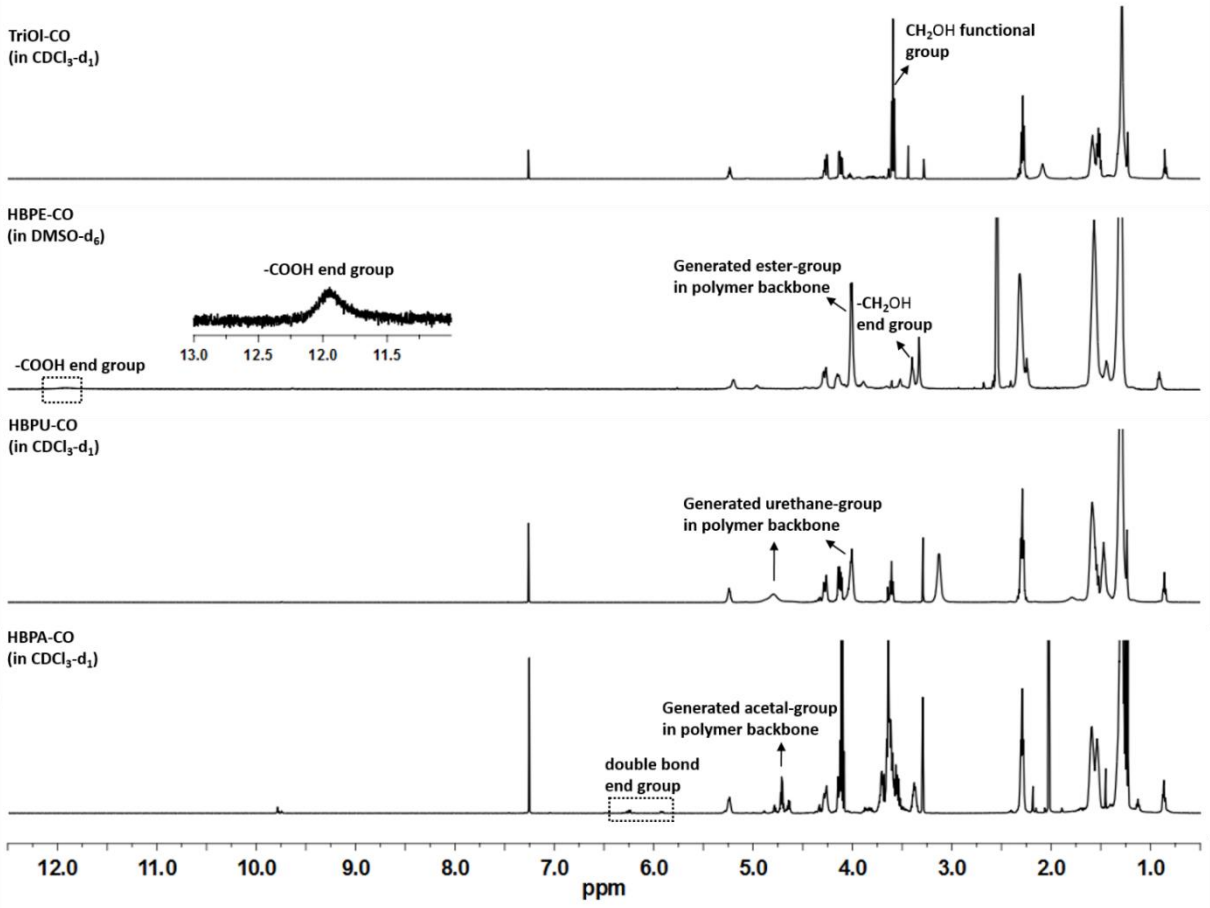
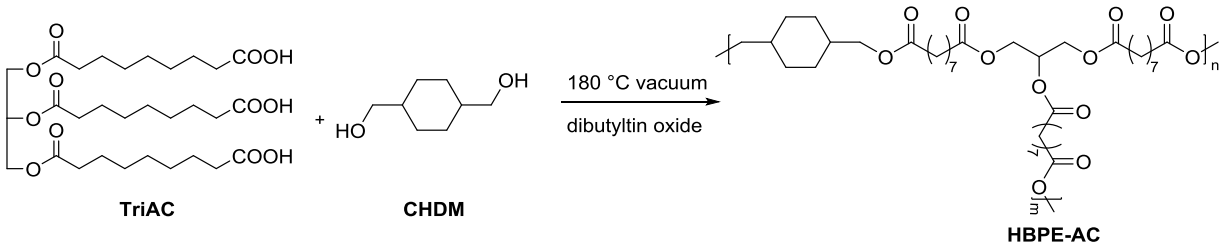


Figure 57. ^{1}H NMR spectra of TriOL-CO (in $CDCl_3$-d), HBPE-CO (in DMSO-d_6), HBPU-CO and HBPA-CO(in $CDCl_3$-d)

The ^{1}H NMR spectra of TriOL-CO monomer, HBPE-CO, HBPU-CO and HBPA-CO are shown in Figure 57. Compared with TriOL-CO spectrum, the main change is the conversion of OH-groups at 3.55 ppm to ester, urethane and acetal groups. Different from other samples, HBPE-CO was measured in DMSO-d_6 solution to calculate the end group compositions. For HBPEs, the newly generated ester group is observed at around 4.00 ppm. The hydroxyl (**CH_2**OH) and carboxylic acid (CO**OH**) end groups are found at 3.36 ppm and 11.94 ppm as broad signals, respectively. In the HBPU-CO spectrum, three new signals at 3.14 ppm (**CH_2**-NH-C(O)-O-CH_2), 4.01 ppm (CH_2-NH-C(O)-O-**CH_2**) and 4.80 ppm (CH_2-**NH**-C(O)-O-CH_2) emerged corresponding to the urethane group. No isocyanate group (**-CH_2**-NCO) was detected around 3.35 ppm, indicating that isocyanate groups have completely reacted and only OH end groups existed in the

resulting polymers. The formation of acetal bonds were achieved by the reaction of hydroxyl group with the double bond of vinyl ether. The signals around 4.70 ppm can be attributed to the acetal groups, -O**CH**(CH_3)O-, and the large signal between 3.60 ppm and 3.70 ppm corresponds to the ether bond, -**CH_2**-O-, which was transformed from the hydroxyl groups. The signals between 5.75 ppm and 6.25 ppm are assigned to the vinyl ether end groups. However, the end group compositions of hydroxyl and vinyl ether groups cannot be calculated, because the signals of the ether linkage in polymer backbone, -**CH_2**-O-, and the hydroxyl end groups, -**CH_2**OH, overlapped. Due to the low intensity of vinyl ether end groups, we speculated, that the OH end group content was more than 90% for all the HBPAs.

4.3.4 Synthesis HBPE from vegetable oil based tricarboxylic acid



Scheme 58. Synthesis of carboxylic acid terminated polyester HBPE-AC from tricarboxylic acid with cyclohexanedimethanol (CHDM) at 180 °C using DBTO as catalyst

Table 20. Results of HBPE-AC synthesis in bulk at 180 °C using DBTO as catalyst

	[TriAC]: [CHDM]: [DBTO]	Time (h)	M_n[1] (g/mol)	M_w[1] (g/mol)	$Đ_M$[1]	COOH content[2] (%)
HBPE-AC-SO-1	1.0: 1.0: 0.15 wt%	4	3900	15000	3.9	90
HBPE-AC-CO-2	1.0: 1.1: 0.15 wt%	4	4600	20000	4.2	87
HBPE-AC-CO-3	1.0: 1.2: 0.15 wt%	4	4100	19000	4.7	85
HBPE-AC-SO-1	1.0: 1.0: 0.15 wt%	4	3300	12000	3.7	84

[1] determined using SEC in THF with PS standards

[2] determined using ^{1}H NMR spectroscopy

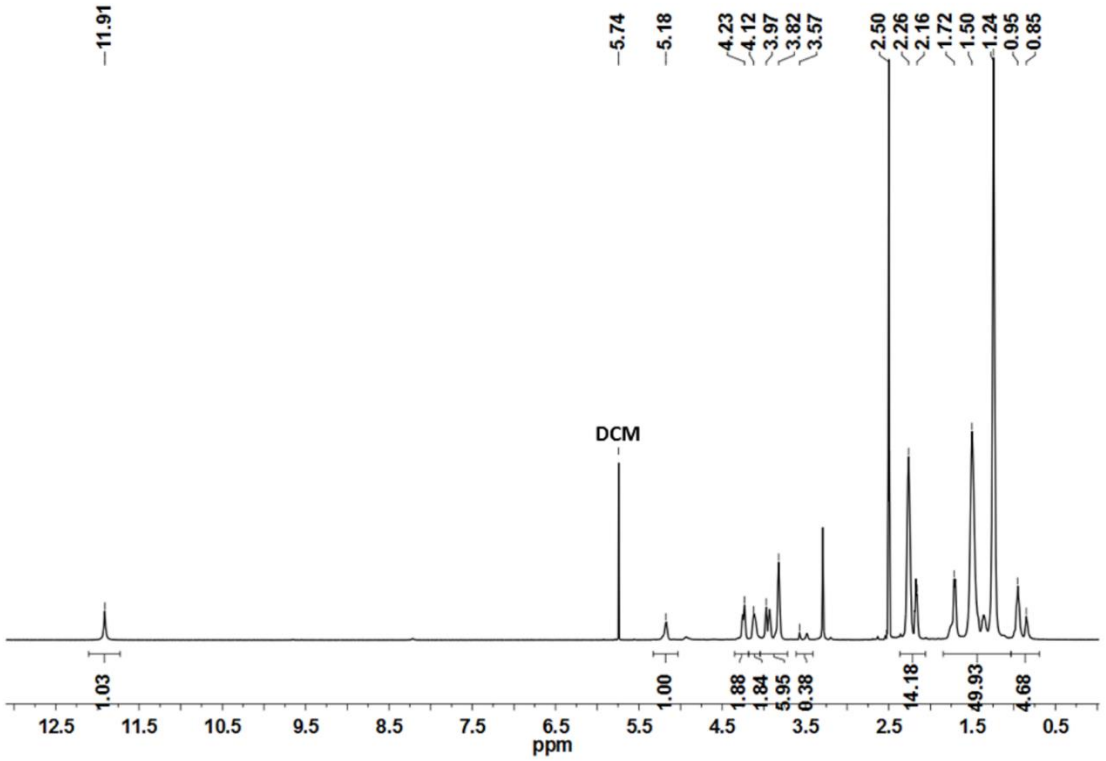


Figure 59. ^{1}H NMR spectrum of HBPE-AC from TriAC (in DMSO-d_6)

Here, another possibility to obtain carboxylic acid terminated polyesters (HBPE-AC) is represented, which were synthesized from vegetable oil based tricarboxylic acids with commercially available cyclohexanedimethanol (CHDM) as diol. The polycondensation was conducted at 180 °C in vacuum using DBTO as catalyst for 4 h. The results of HBPE-AC samples are summarized in Table 20. All the HBPE-AC samples had M_n values around 4000 g/mol with dispersities in the range of 3.7 to 4.7. The change of carboxylic acid end group content was unobvious with increasing initial molar ratios [TriAC]: [CHDM] from 1: 1.0 to 1: 1.2. Furthermore, due to the rigid structure of CHDM, the resulting HBPE-AC had higher viscosity than the HBPE obtained from TriOL with adipic acid. The ^{1}H NMR spectrum of HBPE-AC is shown in Figure 59. Because CHDM was a mixture of cis and trans isomers, two signals were detected in the ^{1}H NMR spectrum for each group of CHDM in HBPE-AC structure. The two small multiplet signals between 3.40 and 3.55 ppm were assigned to the terminal hydroxyl group from CHDM. The formed ester linkages $CH_2C(O)O\underline{\mathbf{CH_2}}$ were detected as two multiplet signals between 3.80 – 4.00 ppm. The broad signal at 12.91 ppm was attributed to the terminal

carboxylic acid group. With the integral of both end group signals the carboxylic acid end group content could be determined.

4.3.5 Thermal properties of obtained vegetable oil based HBPs

Table 21. DSC Results of HBPCs, HBPEs, HBPUs, HBPAs and HBPC-ACs

	M_n[1] (g/mol)	M_w[1] (g/mol)	T_g[2] (°C)	T_m[2] (°C)
HBPC-CO-5	3800	15000	-48.4	n.d.
HBPE-CO-2	3600	18000	-52.0	14,8
HBPU-CO-2	7300	40000	-47.2	60,0
HBPA-CO-2	4700	23000	-39,6	n.d.
HBPE-AC-CO-2	4600	20000	-44.6	n.d.
HBPC-SO-1	3600	10000	-46.2	7.2
HBPE-SO-1	2400	4500		12.4
HBPU-SO-1	8000	19000	-16.1	80.6
HBPE-AC-SO-1	3300	12000	-39.2	3.8

[1] determined using SEC in THF with PS standards

[2] determined using DSC (-90 °C – 90 °C, 2. measurement)

n.d.: not detected

As shown in Table 21, the thermal properties of HBPs were evaluated using DSC measurements. HBPA-SO-1 was not measured due to its extremely low molar mass. Except HBPU-SO-1, all HBPs displayed relatively low T_g of -39 °C to -52°C. In our case, the T_g was not visibly affected by polymer types. Among them, only HBPU-SO-1 tended to higher T_g of -16 °C. Generally, T_g of soybean oil based HBPs were slightly higher than HBPs obtained from TriOL-CO due to the higher content of linear segments in TriOL-SO. In contrast, melting temperatures (T_m) were strongly dependent on polymer types. Both HBPU-CO and HBPU-SO showed T_m higher than 60 °C as a result of the large number of intermolecular or intramolecular hydrogen bonds between urethane groups. Other HBPs were viscos liquid at room temperature and showed T_m

lower than 15 °C.

4.3.6 Conclusion

A strategy for the preparation of different kinds of hyperbranched polymers from vegetable oil based monomers was established. Due to the high hydroxyl end group content, these hyperbranched polymers can be used alone or in combination with other prepolymers for preparation of cross-linked materials using different chemical curing agents. This strategy is also suitable for utilization of other A_2 monomers and provides a great opportunity to obtain hyperbranched polymers with designed properties.

Furthermore, linear fatty acid based polyester and polyanhydride have been investigated for their injectable drug delivery application. However, there are still few works concerning vegetable oil based hyperbranched polymers as drug carrier.(section 2.3.4.1) For drug delivery application, polymeric materials should meet the following key conditions: good biocompatibility, high hydrophobicity, good biodegradation, low melting point (< 100 °C), good solubility in common organic solvents, high flexibility and low cost. The vegetable oil based hyperbranched polymers satisfy all above mentioned properties and should be suitable applied as drug carrier. Due to the presence of inherent ester bonding, tricarboxylic acids and carboxylic acid terminated polyesters (HBPE-AC) could be used for preparation of hyperbranched poly(ester-anhydride), which include two biodegradable bonds in the polymer backbone. Poly(ester-anhydride)s display two degradation stages: water-sensitive anhydride bonds are rapidly cleaved by hydrolysis to polyester prepolymers which have a much slower degradation rate. These polymers have been widely used for biomedical applications such as drug delivery system and tissue engineering.

In summary, the preparation of hyperbranched polymers from castor oil (CO) and soybean oil (SO) via ozonolysis pathway was presented in this part, followed by the A_2 + B_3 polycondensation. Firstly, B_3 monomers triols (TriOL), trialdehydes (TriAD) and tricarboxylic acids (TriAC) were successfully obtained by ozonolysis of CO and SO with following reductive

or oxidative treatment. Their structures were well characterized by ^{1}H NMR spectroscopy, ATR-FTIR spectroscopy and ESI-ToF mass spectroscopy. These monomers had very high purity according to the characterization results. These B_3 monomers were polymerized with different A_2 monomers to give hyperbranched polycarbonate (HBPC), hydroxyl or carboxylic acid terminated polyester (HBPE), polyurethane (HBPU) and polyacetal (HBPA) with M_n up to 9400 g/mol and M_w up to 40000 g/mol. This work established the basic strategy to obtain hyperbranched polymers from vegetable oils via ozonolysis and A_2 + B_3 polycondensation. Based on this strategy, a wide range of hyperbranched polymers can be prepared from vegetable oils to achieve designed properties and applications.

5 Conclusion

The present work summarizes investigations of the preparation of linear and hyperbranched polycarbonates from diol and triol monomers with eco-friendly dimethyl carbonate (DMC) via classic two-step polycondensation or newly developed one-pot polycondensation, as well as the synthesis of hyperbranched polymers from vegetable oil based trifunctional monomers (B_3 monomers) via $A_2 + B_3$ polycondensation. Polycondensation is the best strategy for large-scale preparation of polycarbonates with different structures, while the other two common strategies, ring opening polymerization of cyclic carbonates and copolymerization of carbon dioxide and epoxy, are limited by many parameters for large-scale use, such as extreme polymerization conditions, expensive monomers or catalysts, restrictive polymer structures etc.

The first part mainly dealt with the investigation of the application of organo-catalkysts (pyridines, guanidines, bifunctional arylaminothiocarbonylpyridinium salt, iminophosphorane and thioureas) in the synthesis of linear aliphatic polycarbonate by two-step polycondensation of different diols and DMC. Poly(1,4-butylene carbonate) (PBC), poly(1,5-pentamethylene carbonate) (PPC) and poly(1,6-hexametylene carbonate) (PHC), were successfully prepared with M_n up to 23000 g/mol, dispersities below 1.80 and yields of > 80 % at 130 °C using 4-dimethylaminopyrridine (DMAP) as catalyst. At 170 °C molar mass of PBC increased up to 52000g/mol. The hydroxyl terminated polycarbonates with M_n up to 17000 g/mol were synthesized using the initial ratio of [diol]: [DMC] ≤ 1.2: 1 as well. These materials are of great interest, because the combination with other polymerization method, such as controlled radical polymerization (ATRP, RAFT or NMRP) for further application and thermal properties improvement is allowed by end group modification. Unfortunately, the two-step polycondensation for the synthesis of hyperbranched polycarbonates (HBPCs) did not work due to the very fast gelation in the second step under reduced pressure.

To solve the cross-linking problems during the synthesis of hyperbranched polycarbonates via

classic polycondensation, a novel one-pot method to obtain linear and hyperbranched polycarbonates under relatively mild polymerization conditions was developed in the second part. Different from other works using toxic phosgene based carbonates to obtain hyperbranched polycarbonates, eco-friendly DMC was used in this work. The one-pot polycondensation in this work was carried out at a relatively low temperature and atmospheric pressure in 1,4-dioxane solution, and the methanol byproduct was removed via adsorption on molecular sieves instead of vacuum distillation at high temperature. Moreover, an equimolar amount of DMC was used to avoid waste and the disposal of excess DMC. Using this strategy, poly(trimethylene carbonate) (PTMC), poly(butylene carbonate) (PBC), poly(pentamethylene carbonate) (PPC), poly(hexamethylene carbonate) (PHC), poly(diethylphenylamine carbonate) (PDEAC) and poly(cyclohexan-1,4-dimethylene carbonate) (PCDMC) were successfully prepared with M_n up to 16000 g/mol, dispersities below 1.70 and high yields above 70%. Additionally, the hyperbranched polycarbonates based on 1,1,1-tris(hydroxymethyl)ethane (THE) and 1,1,1-tris(hydroxymethyl)propane (THP) were also obtained with M_n up to 10000 g/mol, M_w up to 64000 g/mol and high OH end group contents approximately 70%. Polycarbonates are well-known as biodegradable polymeric materials. Hydrolytic and enzymatic degradation were investigated for linear and hyperbranched polycarbonates obtained in this work under different conditions. The hydrolytic degradation was carried out at 37 °C and 55 °C with various pH values (from 1.0 to 13.0) for 30 d. The results showed, that the linear polycarbonate samples were relatively stable under acid to weak basic conditions, but could be rapidly degraded under strong basic condition. Hyperbranched polycarbonates degraded faster than linear polycarbonates under the same condition probably due to its high density of functional groups in comparison to linear aliphatic polycarbonates. Compared with hydrolytic degradation, linear polycarbonates were degraded much faster in lipase solution from *Thermocyces languginosus* at 37 °C. The degradation rates were strongly dependent on polymer structures. Both the enzymatic and basic hydrolytic degradations showed that linear polycarbonate specimens degraded by surface erosion.

The use of renewable feedstock, such as vegetable oils, instead of petroleum in material science has drawn great attention in recent years. There are many methods to introduce functional groups into vegetable oil structures by treating the double bonds, such as epoxidation, hydroformylation and ozonolysis. Among them, ozonolysis is the only way to obtain primarily terminal functional groups. In the last part of this work, B_3 monomers, triols, trialdehydes and tricarboxylic acids, were successfully obtained from soybean oil and castor oil via ozonolysis process with high purity according to the results of ^{1}H NMR spectroscopy, ATR-FTIR spectrometry as well as ESI-ToF-mass spectrosmetry. Using these monomers, a variety of vegetable oil based hyperbranched polymers, such as hyperbranched polycarbonate (HBPC), polyester(HBPE), polyacetal (HBPA) and polyurethane (HBPU), were synthesized with M_n up to 9400 g/mol and M_w up to 40000 g/mol. Their thermal properties were studied by DSC.

6 Outlook

The obtained linear and hyperbranched polymers in this work form the basis of further investigations. (i): Hydroxyl terminated linear aliphatic polycarbonates can be modified by combining various treatments, such as controlled radical polymerizations, to produce ABA-blockcopolymers for designed applications (e.g. biomedical application). (ii): All hyperbranched polymers (HBPCs produced by one-pot polycondensation or vegetable oil based HBPs) have potential application for producing biodegradable cross-linked materials by curing with chemical agents, such as diisocyanate or multifunctional epoxide, because these HBPs have high hydroxyl end group content. Through investigating their thermal, physical, mechanical and biodegradable properties, some potential applications of these materials can be probably discovered. (iii) Despite different kinds of HBPs have been successfully prepared, only small-scale synthesis was investigated in the present work. Polymerization conditions for preparation of HBPs in large-scale are probably required. (iv): It has been found in the study of synthesis of hyperbranched polyimine that cross-linked polyimine can form in several minutes after mixing TriAD and diamine monomers. It would be also interesting to investigate this cross-linked material for biomedical applications.

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1. Jingjiang Sun and Dirk Kuckling, “Synthesis of high-molecular-weight aliphatic polycarbonates by organo-catalysis”, *Polymer Chemistry* **2016**, *7*, 1642 - 1649.
2. Jingjiang Sun and Dirk Kuckling, “Biodegradable polymers from monomers based on vegetable oils”, *in Biodegradable polymers: recent developments and new perspectives,* edited by Geraldine Rohman, IAPC-OBP, IAPC publishing, Zagreb, Croatia, accepted.
3. Jingjiang Sun, Kamal Ibrahim Aly and Dirk Kuckling, “A novel one-pot process for the preparation of linear and hyperbranched polycarbonates of various diols and triols using dimethyl carbonate”, *RSC advances* ***2017***, 12550 – 12560.
4. Jingjiang Sun, Kamal Ibrahim Aly and Dirk Kuckling, “Synthesis of hyperbranched polymers from vegetable oil based monomers via ozonolysis pathway”, Journal of polymer science part A: polymer chemistry, submitted.

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Anerkennung der Promotionsordnung

Hiermit erkenne ich die Promotionsordnung der Fakultät für Naturwissenschaften der Universität Paderborn vom 12. November 2012 an. Erlassen von der Universität Paderborn aufgrund des § 2 Abs. 4 und des § 67 Abs. 3 des Gesetzes über die Hochschulen des Landes Nordrhein-Westfalen (Hochschulgesetz – HG) vom 31. Oktober 2006 (GV.NRW. 2006 S. 474), zuletzt geändert durch Art. 1 des Gesetzes zur Änderung des Hochschulgesetzes, des Kunsthochschulgesetzes und weiterer Vorschriften vom 31. Januar 2012 (GV.NRW. 2012 S. 90).

(Jingjiang Sun)

Eidestattliche Erklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

(Jingjiang Sun)

8 Appendix

8.1 Abbreviation

1,4-BD	1,4-Butane diol
1,5-PD	1,5-Pentane diol
1,6-HD	1,6-Hexane diol
AA	Adipic acid
AESO	Acrylated epoxidized soybean oil
AESO-AZ	Multiaziridine-containing acrylated epoxidized soybean oil
Al-SBO	Allyl alcohol modified soybean oil
APC	Aliphatic polycarbonate
Az-SBO	Azide-containing polyols from soybean oil
Bis-MPA	Bis(hydroxy methyl) propionic acid
BPA	Bis-phenol A
BMIM-2-CO_2	1-*n*-Butyl-3-methylimidazol-2- carboxylate
CHDM	Cyclohexanedimethanol
CMM	Couple-monomer methodology
CSBO	Carbonated soybean oil
D	Dendritic units
DB	Degree of branching
DBTC	Di-*tert*-butyl tricarbonate
DBTD	Dibutyltin dilaurate
DBTO	Dibutyltin oxide
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
$Đ_M$	Dispersity
DMAc	Dimethyl acetamide

DMAE	Dimethylaminoethanol
DMAEB	2-(Dimethylamino)ethyl benzoate
DMAP	4-Dimethylaminopyridine
DMC	Dimethyl carbonate
DMF	Dimethyl formamide
DMM	Double-monomer methodology
DMSO	Dimethyl sulfoxide
DPC	Diphenyl carbonate
DSC	Differential scanning calorimetry
EHDO	5-ethyl-5-hydroxymethyl-1,3-dioxan-2-one
Eq.	Equition
ESBO	Epoxidized soybean oil
ESI-MS	Electrospray ionization mass spectrometry
FAO	Food and Agriculture Organization of the United Nations
FIR	Far infrared
GC	Gas chromatography
HBP	Hyperbranched polymer
HBPA	Hyperbranched polyacetal
HBPC	Hyperbranched polycarbonate
HBPE	Hyperbranched polyester
HBPP	Hyperbranched polyester polyol
HBPU	Hyperbranched polyurethane
HBR	Hyperbranched resin
HDI	Hexamethylene diisocyanate
HOTf	Trifluoromethanesulfonic acid
HPLC	High performance liquid chromatography
HSAS	12-Hydroxystearic acid succinate

HX-SBO	HCl and HBr modified soybean oil
IPN	Interpenetrating polymer network
L	Linear units
LA	Lactic acid
LiAcac	Lithium acetylacetonate
MALDI-ToF-MS	Matrix-assisted laser desorption/ionization time of flight mass spectroscopy
Ma-SBO	Maleic acid modified soybean oil
MBROP	Multibranching ring-opening polymerization
MHSBO	Ethylene glycol modified soybean oil
MIR	Mid infrared
M_n	Number-averaged molar mass
MSA	Methanesulfonic acid
MTBD	7-Methyl-1,5,7-triazabicyclo[4.4.0] dec-5-ene
M_w	Weight averaged molar mass
NIR	Near infrared
NMR	Nuclear magnetic resonance
NHC	N-heterocyclic carbene
PBC	Poly(butylene carbonate)
PBC-*co*-PCDMC	Poly(butylene carbonate)-*co*-poly(cyclohexan-1,4-dimethylene carbonate)
PBC-*co*-PDEAC	Poly(butylene carbonate)-*co*-poly(diethylphenylamine carbonate)
PBC-*co*-PPC	Poly(butylene carbonate)-*co*-poly(pentamethylene carbonate)
PBC-*co*-PHC	Poly(butylene carbonate)-*co*-poly(hexamethylene carbonate)
PCDMC	Poly(cyclohexan-1,4-dimethylene carbonate)
PCL	Polycaprolactone

PDEAC	Poly(diethylphenylamine carbonate)
P(FAD-SA)	Poly(fatty acid dimer:sebacic acid)
PHC	Poly(hexamethylene carbonate)
PLA	Poly(lactic acid)
PLGA	Poly(lactic/glycolic acid)
PNL	Polynonanolactone
PPC	Poly(pentamethylene carbonate)
PPTS	Pyridinium *p*-toluene sulphonate
PPY	4-Pyrrolidinopyridine
PS	Polystyrene
PTHEC	Hyperbranched poly(1,1,1-tris(hydroxymethyl)ethyl carbonate)
PTHPC	Hyperbranched poly(1,1,1-tris(hydroxymethyl)propyl carbonate)
PTMC	Poly(trimethylene carbonate)
p-TSA	p-Toluenesulfonic acid
QAP	Quaternary ammonium salts containing soybean oil
RA	Ricinoleic acid
RAM	Ricinoleic acid maleate
RAS	Ricinoleic acid succinate
R_f	Retardation factors
ROP	Ring opening polymerization
SA/V	Surface area to volume ratio
SCROP	Self-condensing ring-opening polymerization
SEC	Size exclusion chromatography
SMM	Single-monomer methodology
T	Terminal units
TBAB	Tetrabutylammonium bromide

TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
TEDE	Tri(ethylene glycol) diviniyl ether
TFA	Triflic acid
T_g	Glass temperature
THF	Tetrahydrofuran
THE	1,1,1-Tris(hydroxymethyl)ethane
THP	1,1,1-Tris(hydroxymethyl)propane
THPE	1,1,1-Tris(4-hydroxyphenyl)ethane
TLC	Thin layer chromatography
T_m	Melting points
TMC	1,3-Dioxan-2-one
TMP	Trimethylolpropane
TOF	Turnover frequency
TriAC	Vegetable oil based tricarboxylic acid monomer
TriAC-CO	Tricarboxylic acid obtained from castor oil
TriAC-CO-Ox	Tricarboxylic acid obtained from castor oil using oxidation method
TriAC-SO	Tricarboxylic acid obtained from soybean oil
TriAC-SO-Ox	Tricarboxylic acid obtained from soybean oil using oxidation method
TriAC-SO-Ozo	Tricarboxylic acid obtained from soybean oil using ozonolysis method with oxidative treatment
TriAD	Vegetable oil based trialdehyde monomer
TriAD-CO	Trialdehyde obtained from castor oil
TriAD-SO	Trialdehyde obtained from soybean oil
TriOL	Vegetable oil based triol monomer
TriOL-CO	Triol obtained from castor oil

TriOL-SO	Triol obtained from soybean oil
TSP-44	TiO_2/SiO_2-poly(vinyl pyrrolidone)-based catalyst
TU	Thiourea
UV	Ultraviolet
Vis	Visible

8.2 NMR spectra of low molecular weight compounds and polymers

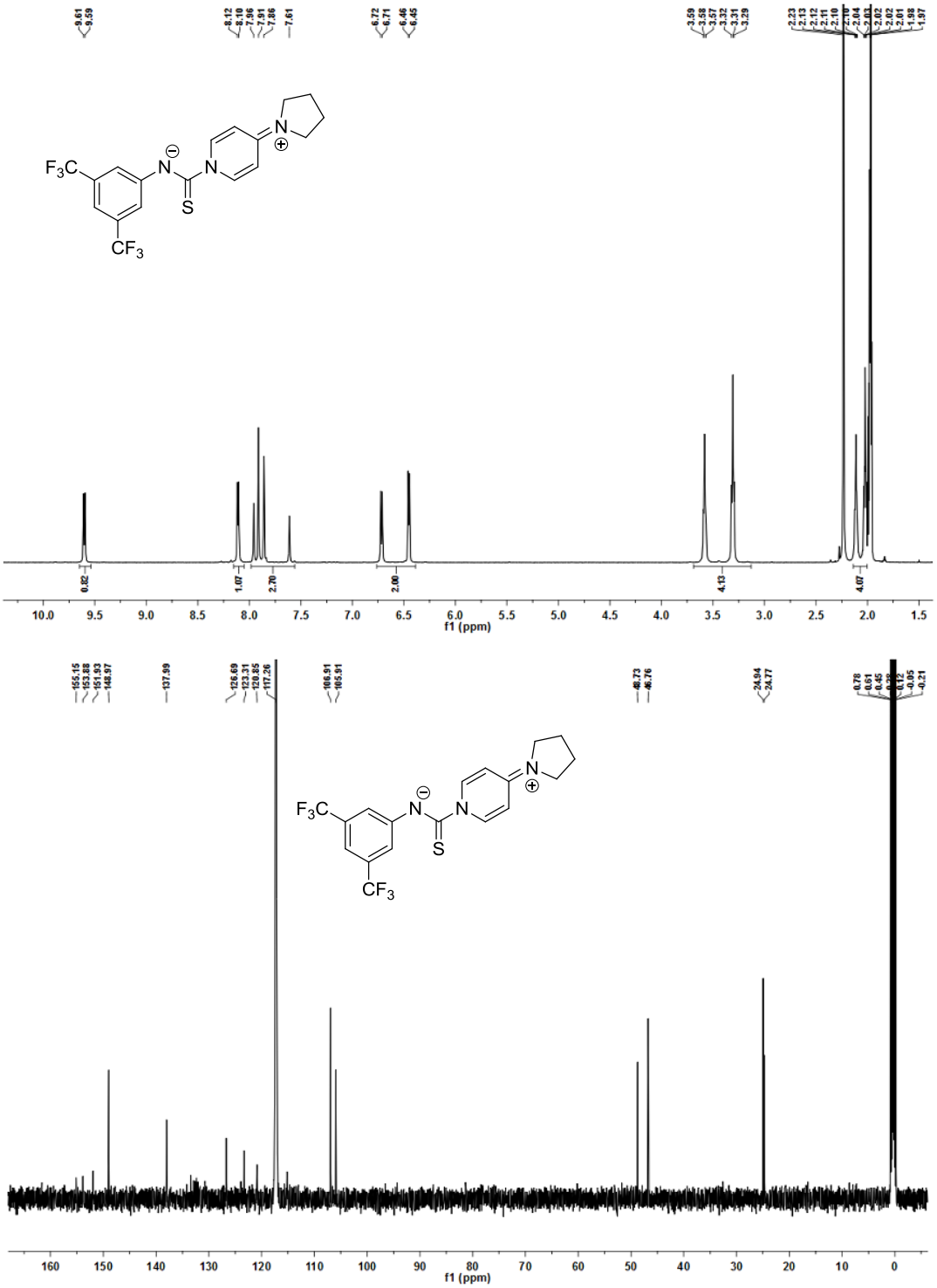

Figure SI-1. ^{1}H and ^{13}C NMR spectra of (3,5-bis(trifluoromethyl)phenyl)(4-(pyrrolidin-1-ium-1-ylidene)-1,4-dihydropyridine-1-carbonothioyl)amide (in CD_3CN-d_3)

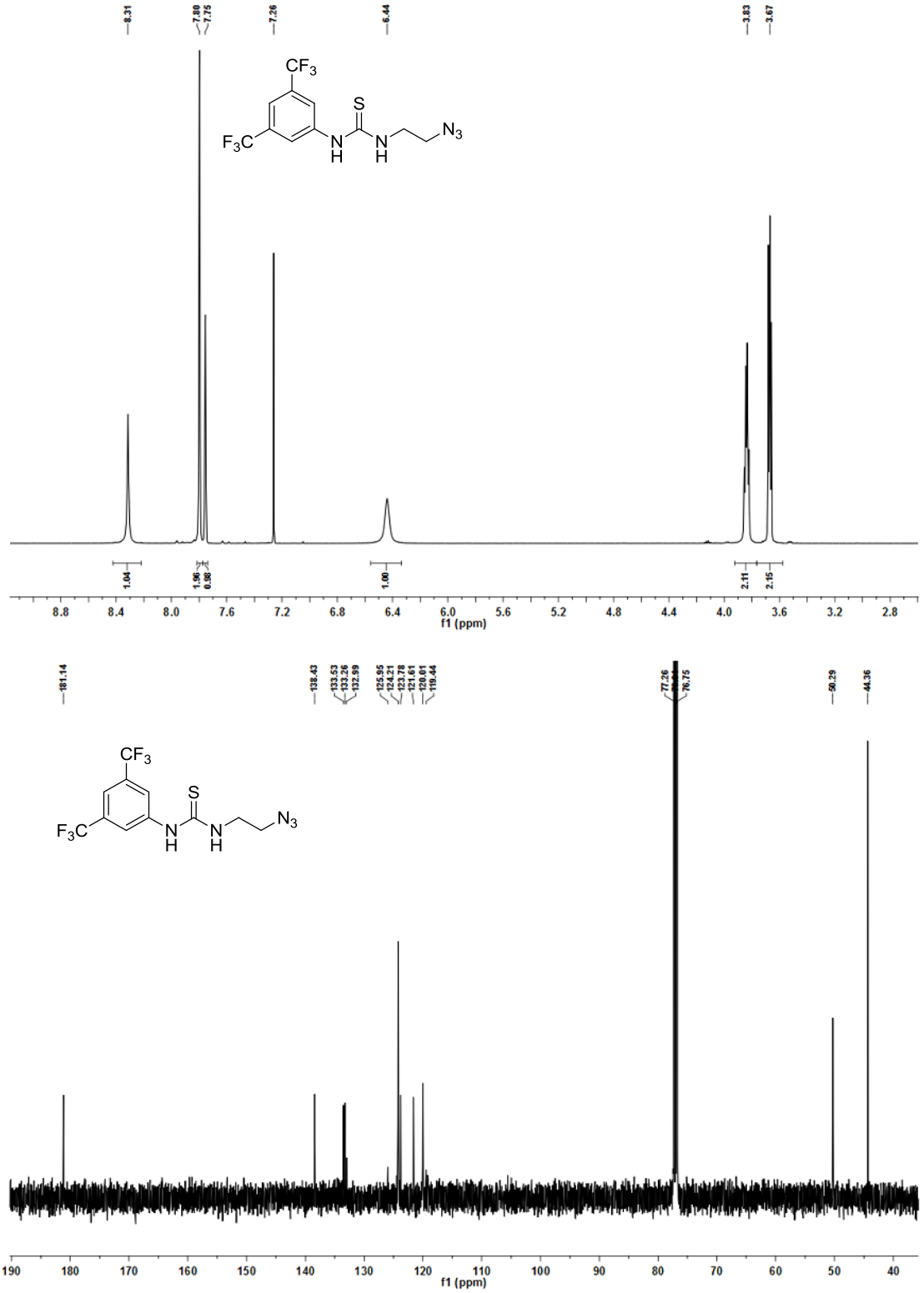

Figure SI-2. ^{1}H and ^{13}C NMR spectra of 1-(2-azidoethyl)-3-(3,5-bis(trifluoromethyl)-phenyl)thiourea (in $CDCl_3$-*d*)

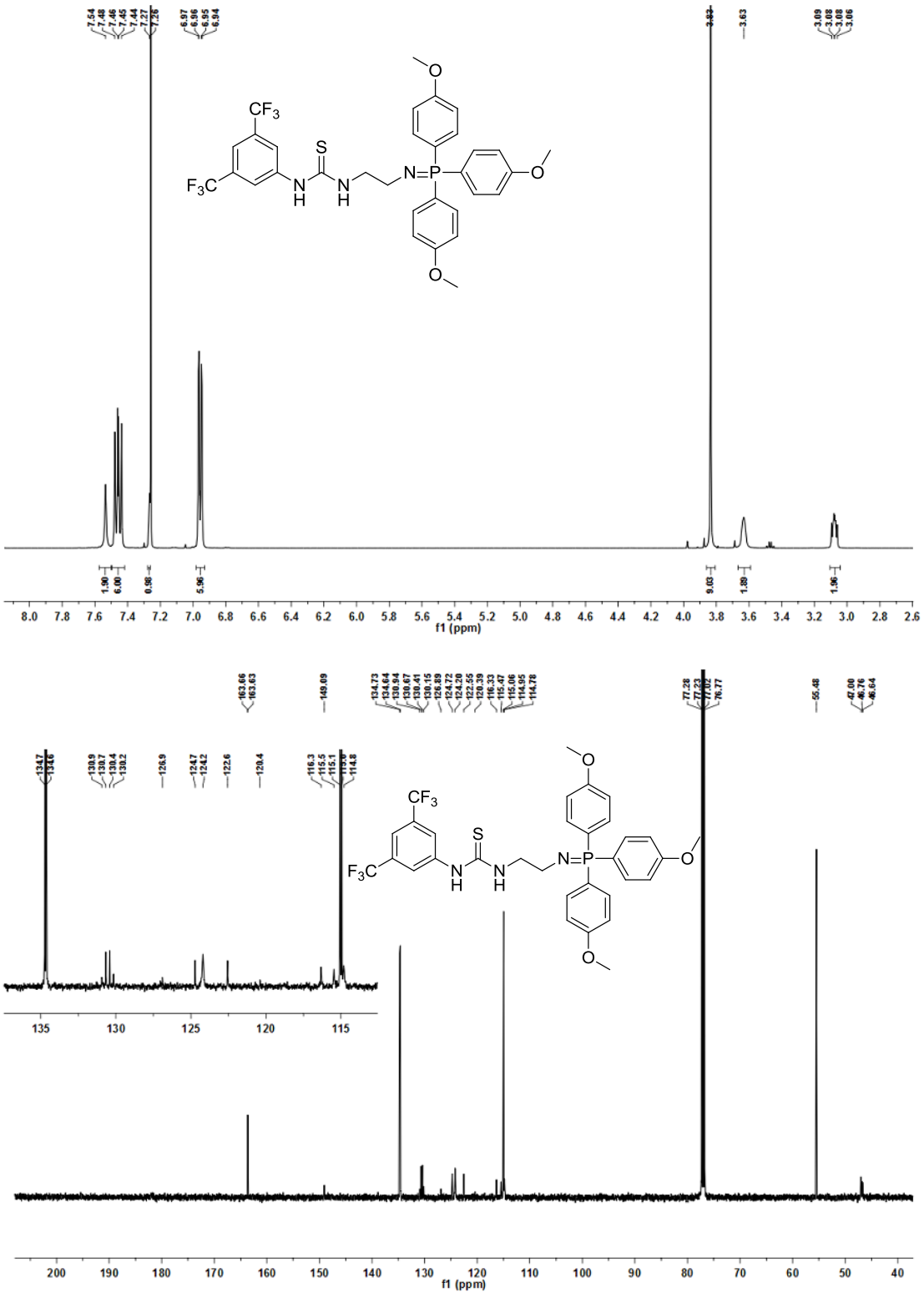

Figure SI-3. ^{1}H and ^{13}C NMR spectra of 1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(((4-methoxyphenyl)-phosphinylidene)amino)ethyl)thiourea (in $CDCl_3$-*d*)

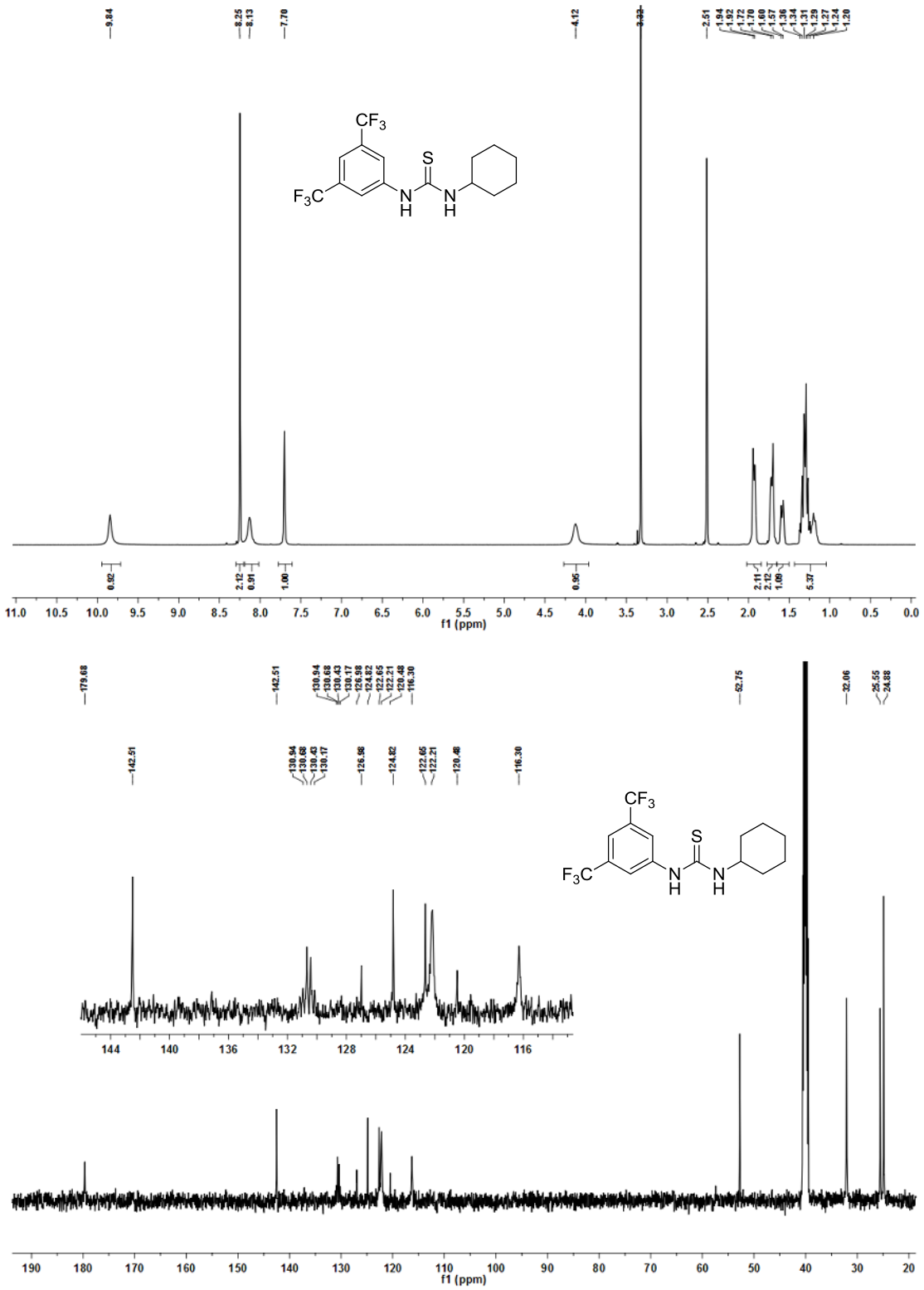

Figure SI-4. ^{1}H and ^{13}C NMR spectra of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (in DMSO-d_6)

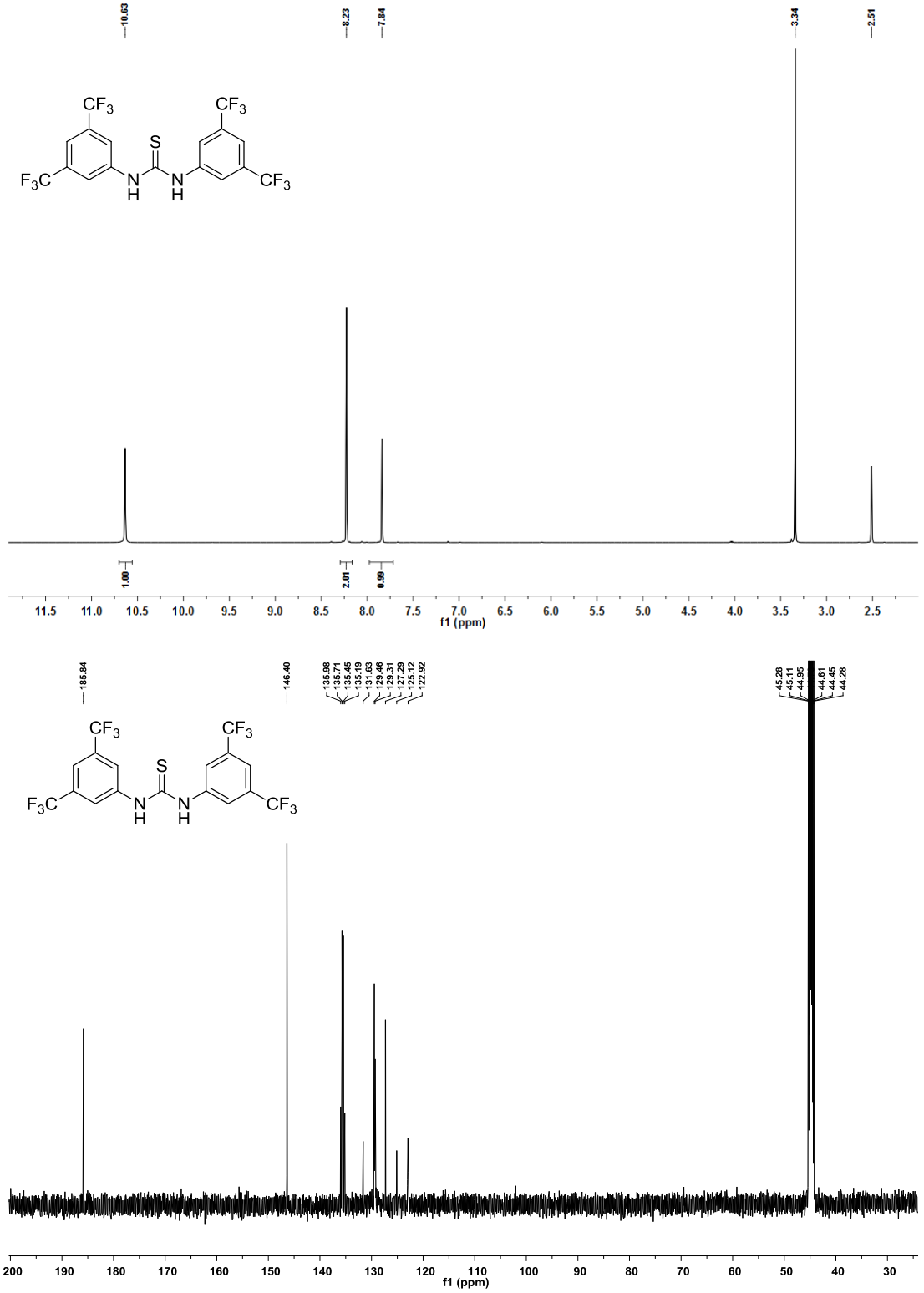

Figure SI-5. ^{1}H and ^{13}C NMR spectra of 1,3-bis(3,5-bis(trifluoromethyl)phenyl)thiourea (in DMSO-d_6)

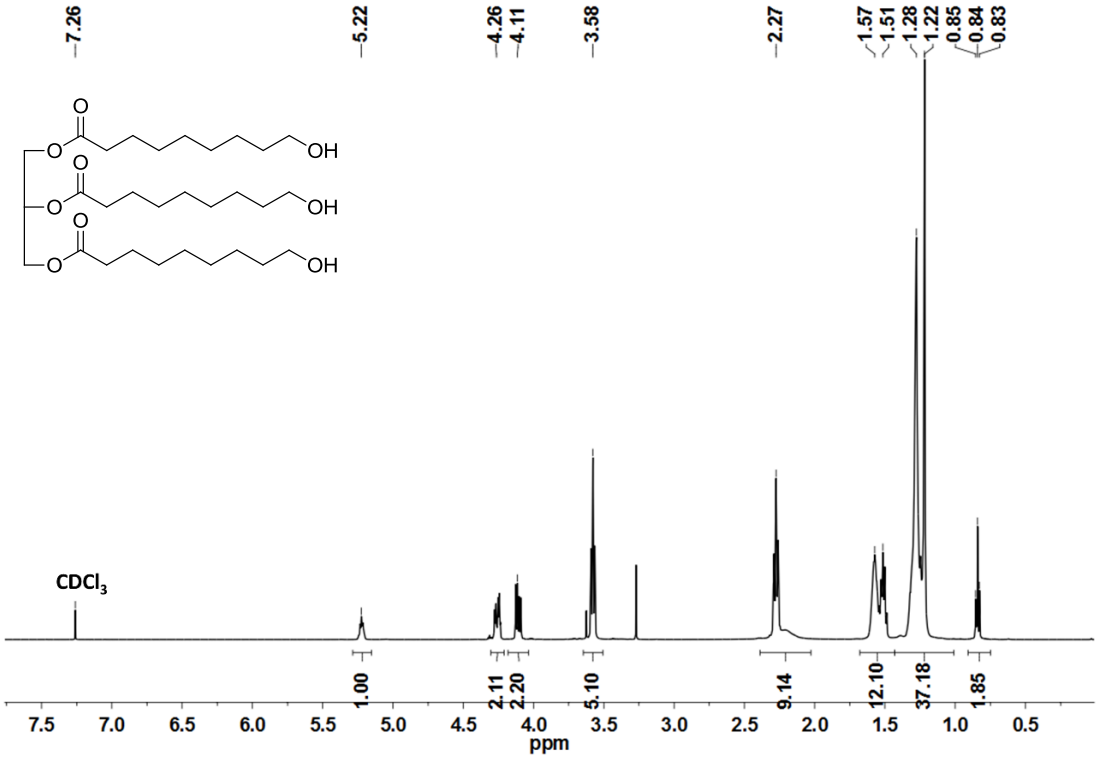

Figure SI-6. ^{1}H NMR of TriOl (in $CDCl_3$-*d*)

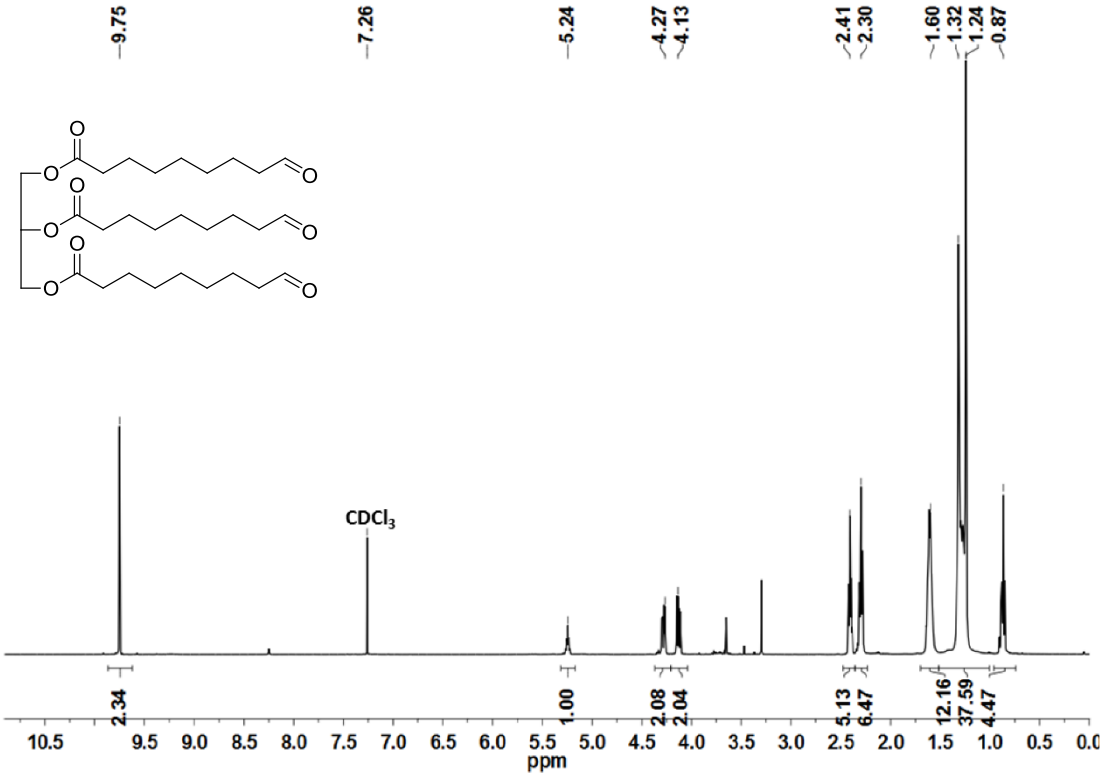

Figure SI-7. ^{1}H NMR of TriAD (in $CDCl_3$-*d*)

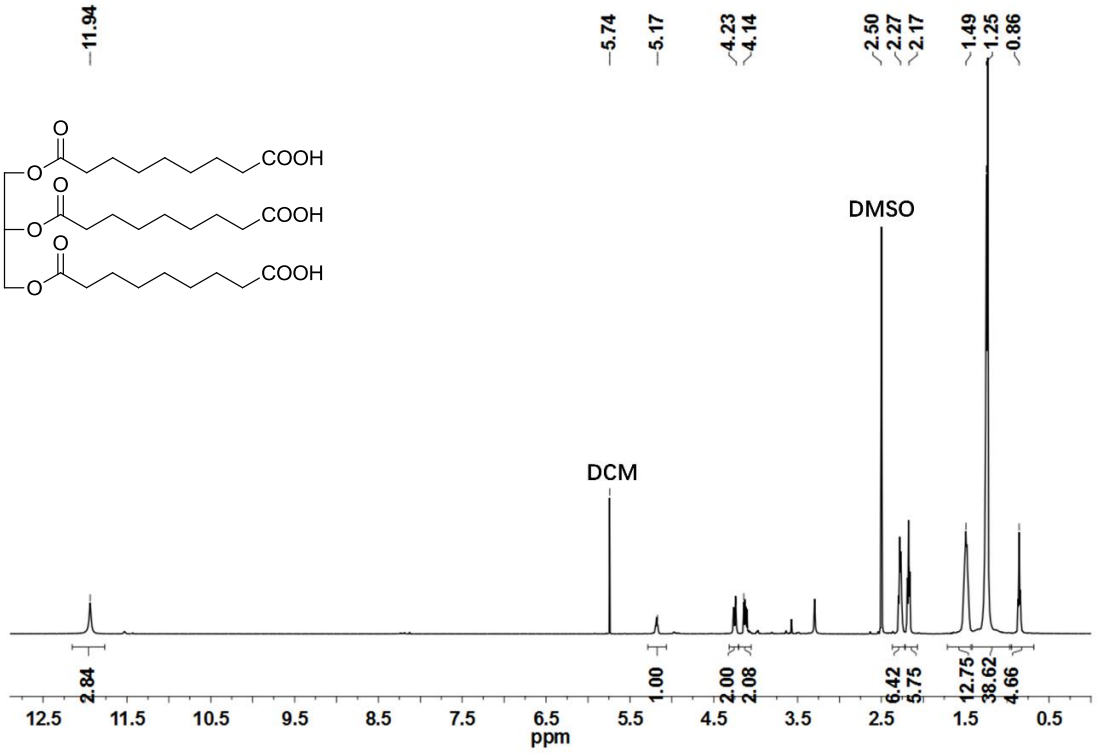

Figure SI-8. ^{1}H NMR of TriAC (in DMSO-d_6)

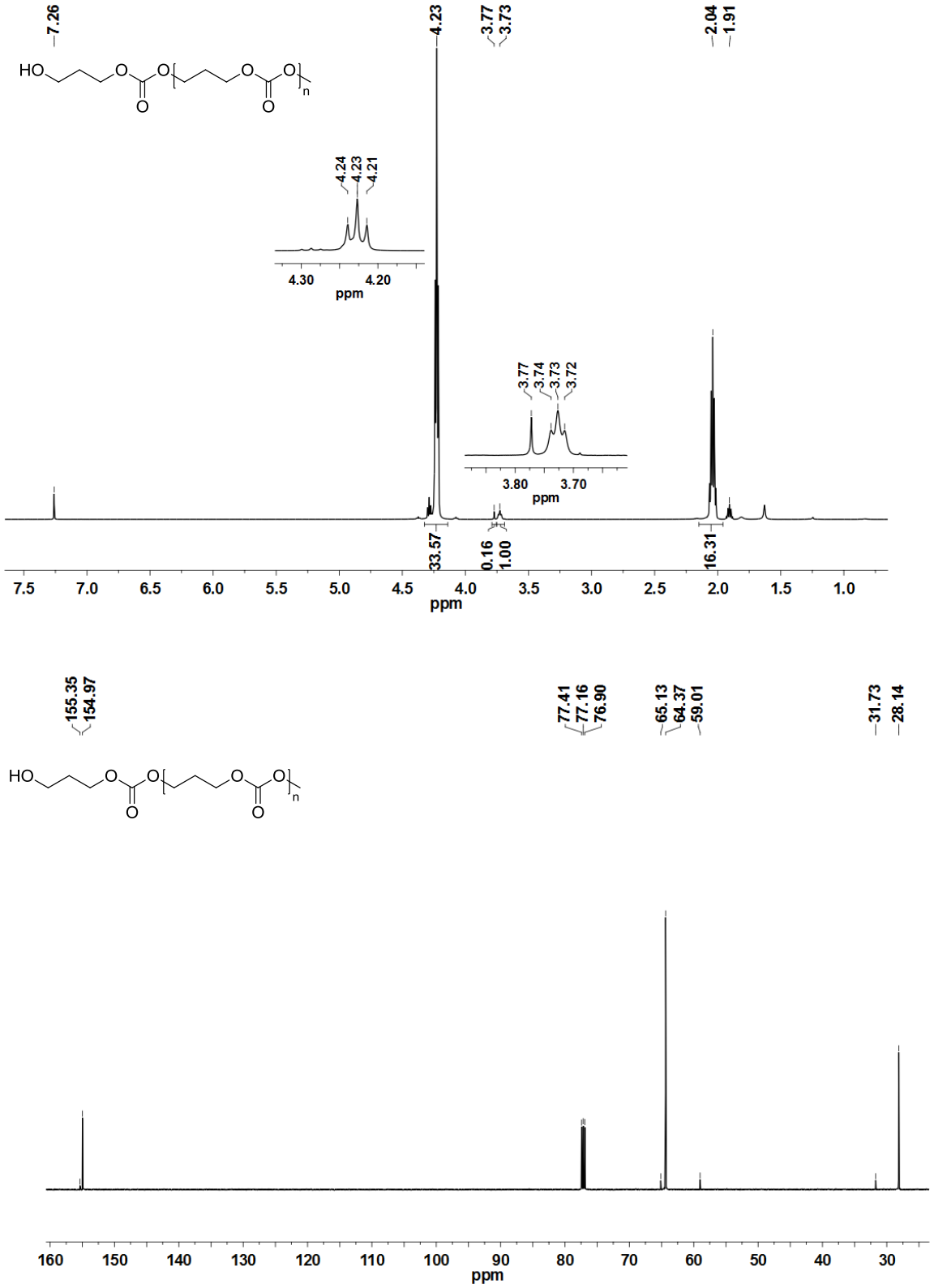

Figure SI-9. ^{1}H and ^{13}C NMR spectra of PTMC (in $CDCl_3$-*d*)

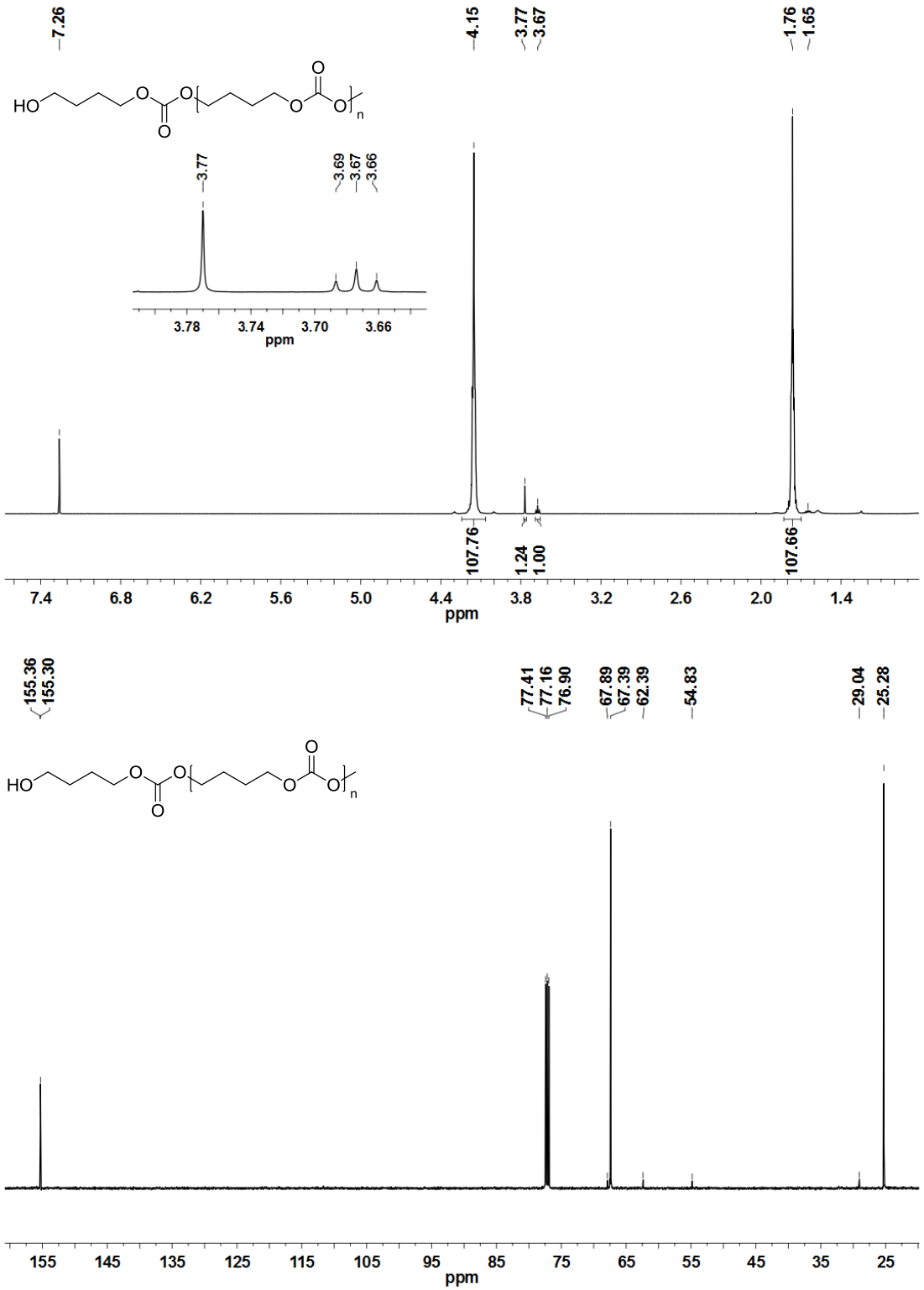

Figure SI-10. ^{1}H and ^{13}C NMR spectra of PBC (in $CDCl_3$-*d*)

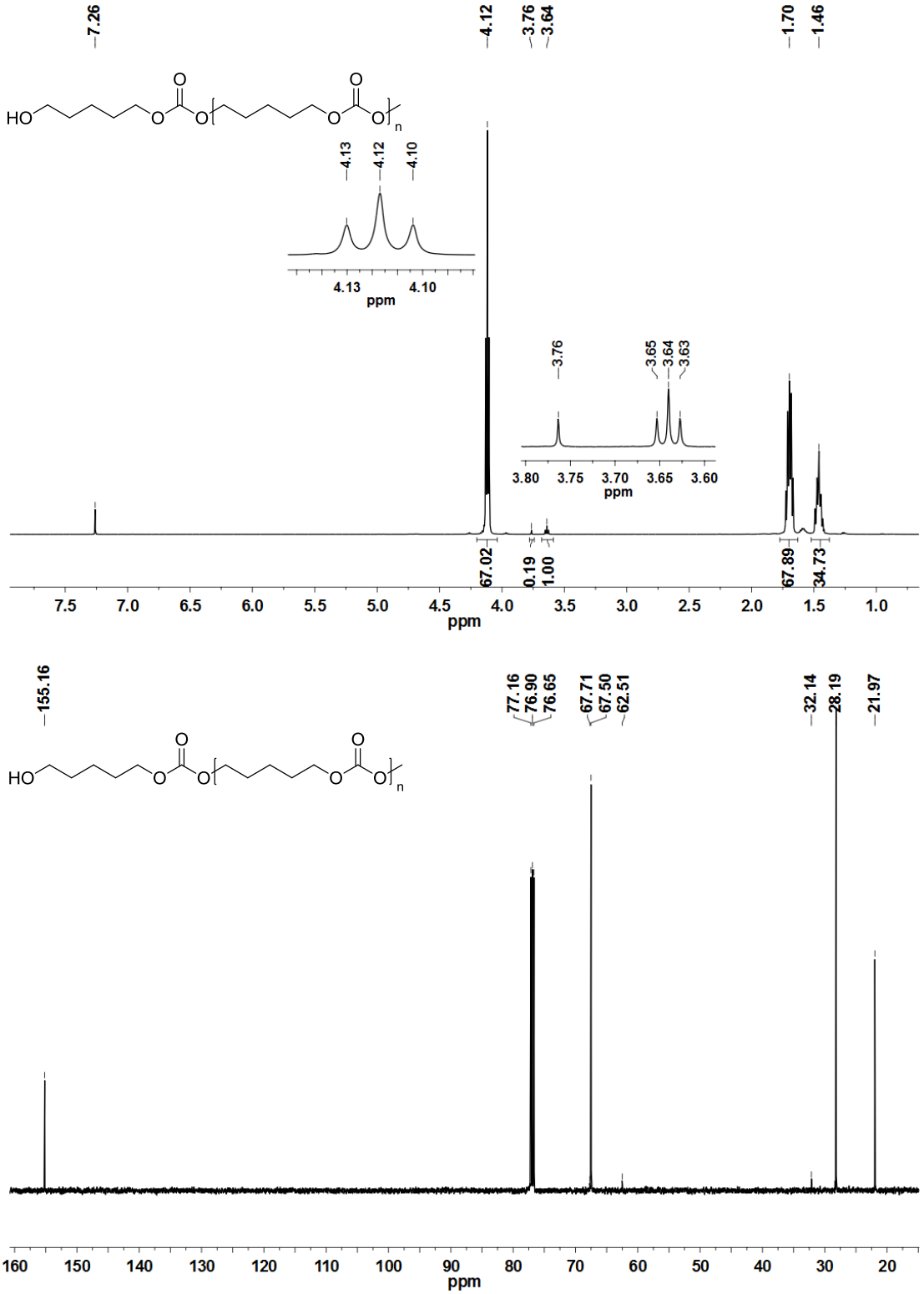

Figure SI-11. ^{1}H NMR and ^{13}C spectra of PPC (in $CDCl_3$-*d*)

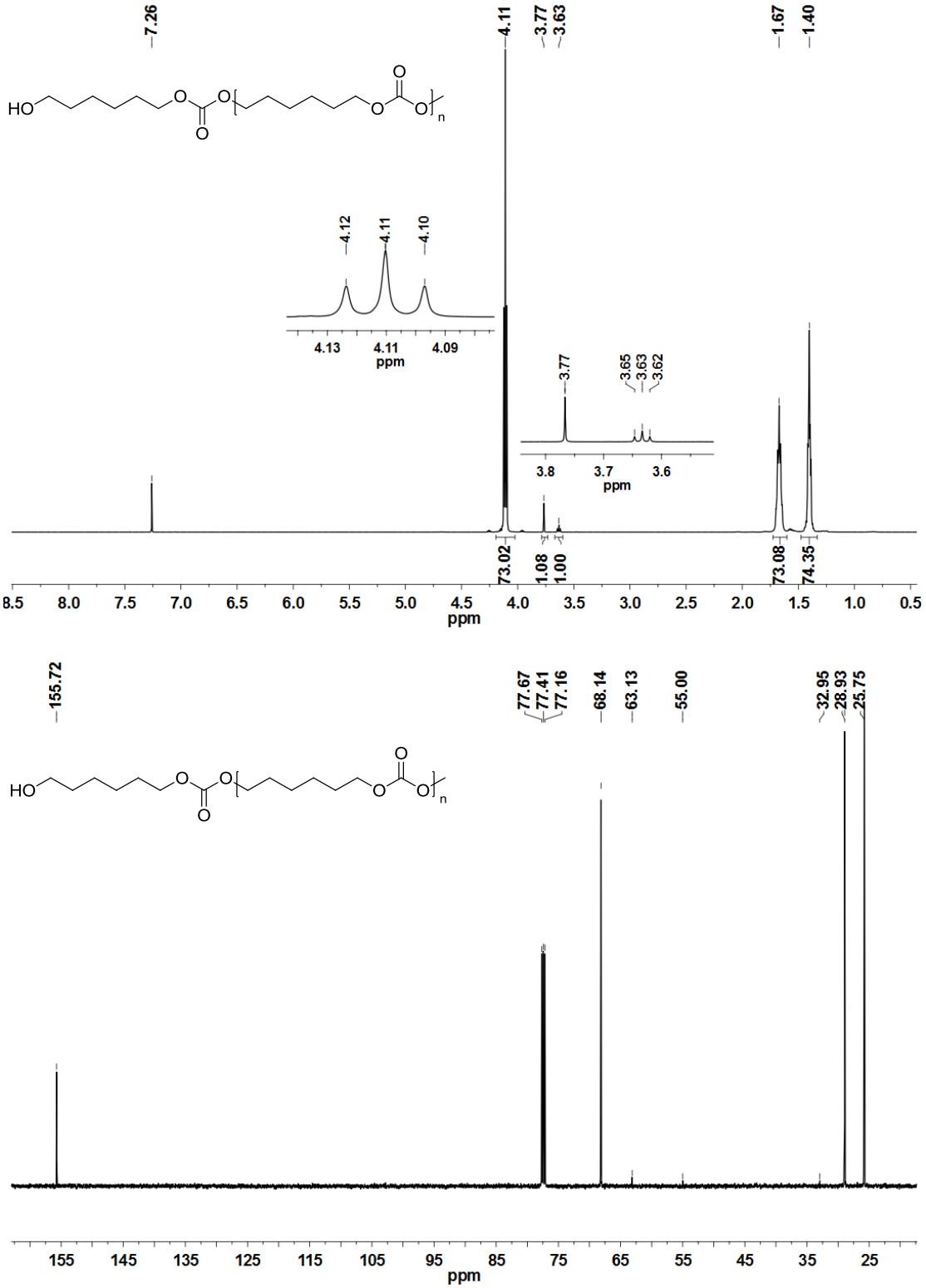

Figure SI-12. ^{1}H and ^{13}C NMR spectra of PHC (in $CDCl_3$-*d*)

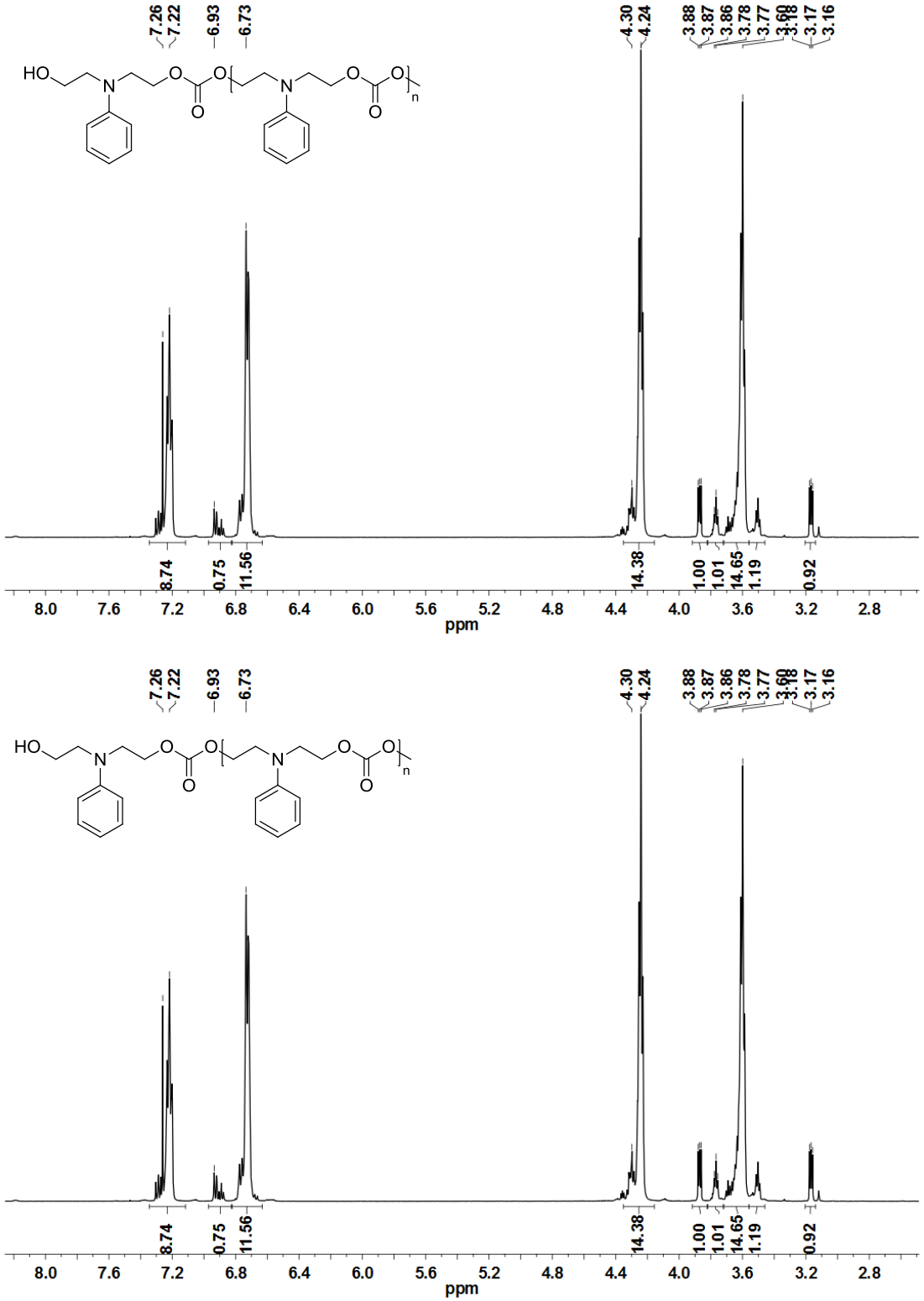

Figure SI-13. ^{1}H and ^{13}C NMR spectra of PDEAC (in $CDCl_3$-*d*)

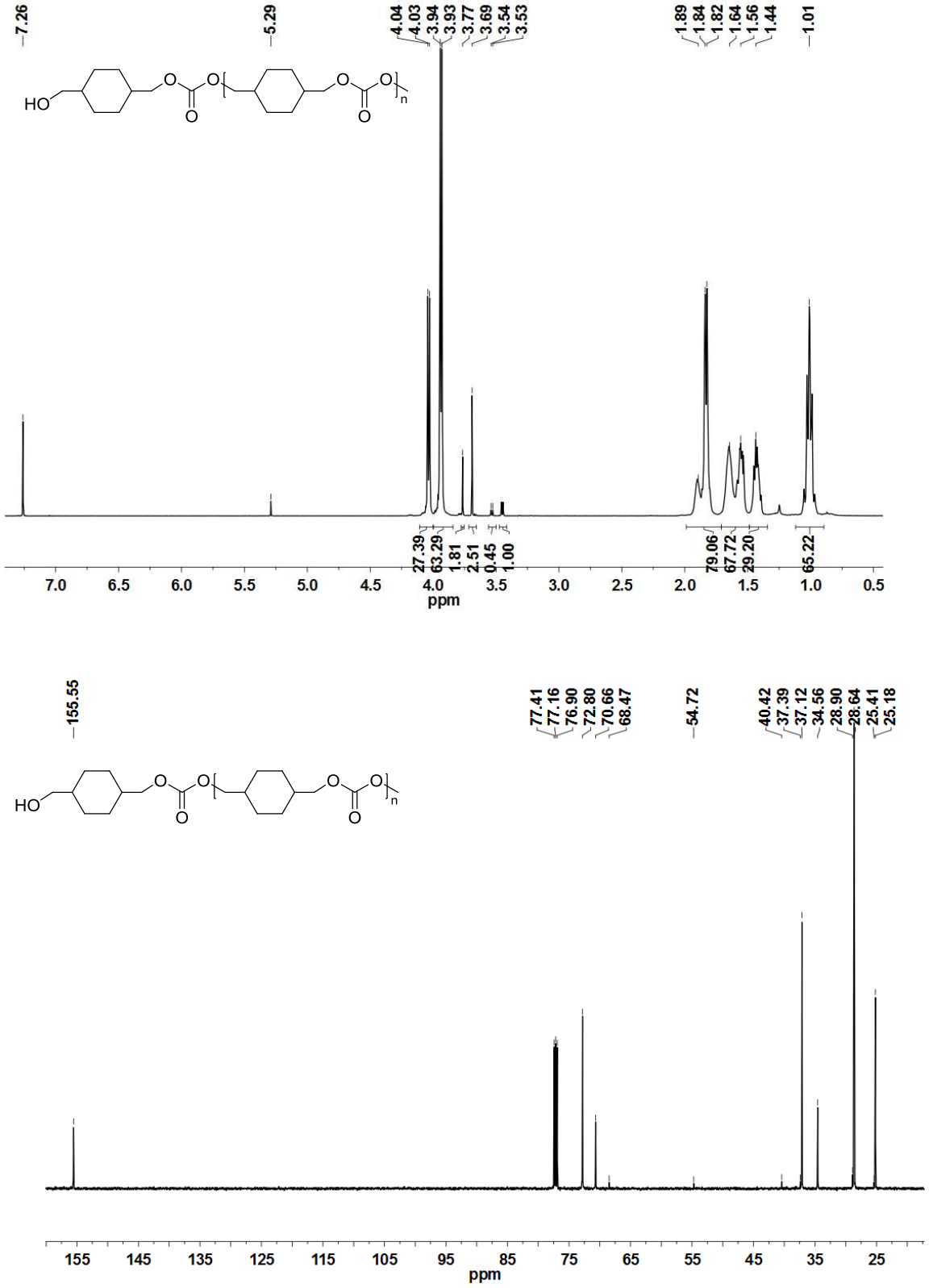

Figure SI-14. ^{1}H and ^{13}C NMR spectra of PCDMC (in $CDCl_3$-*d*)

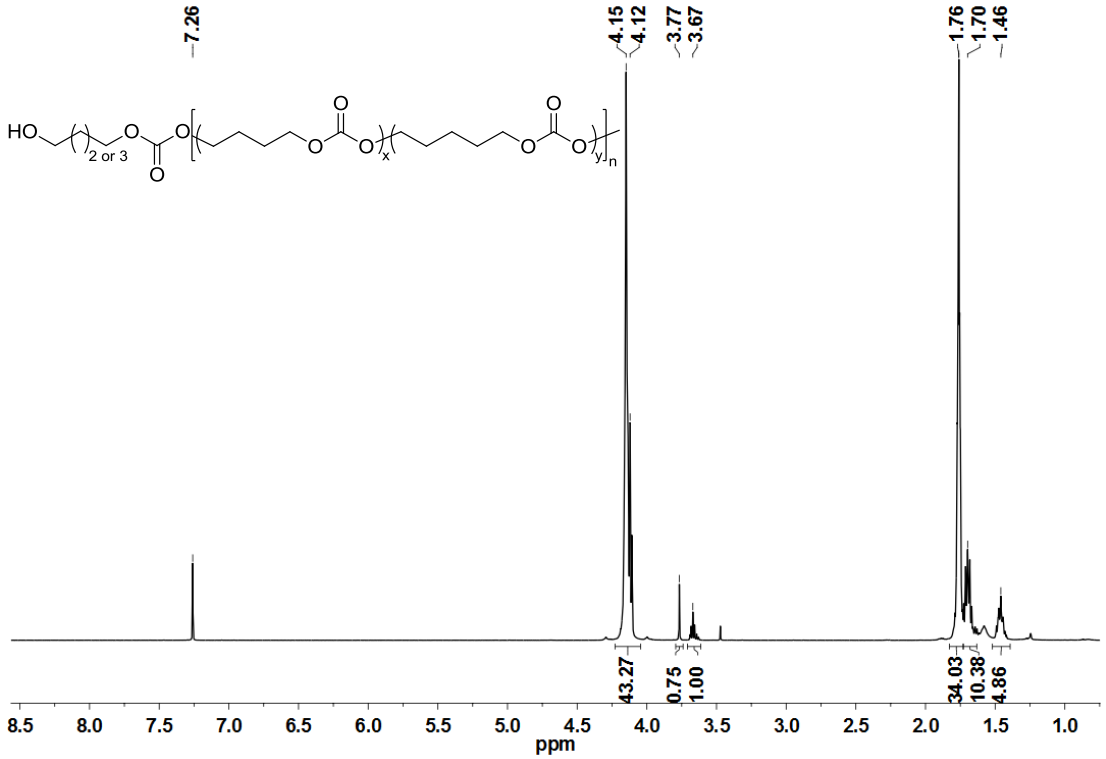

Figure SI-15. ^{1}H NMR spectrum of PBC-*co*-PPC (in $CDCl_3$-*d*)

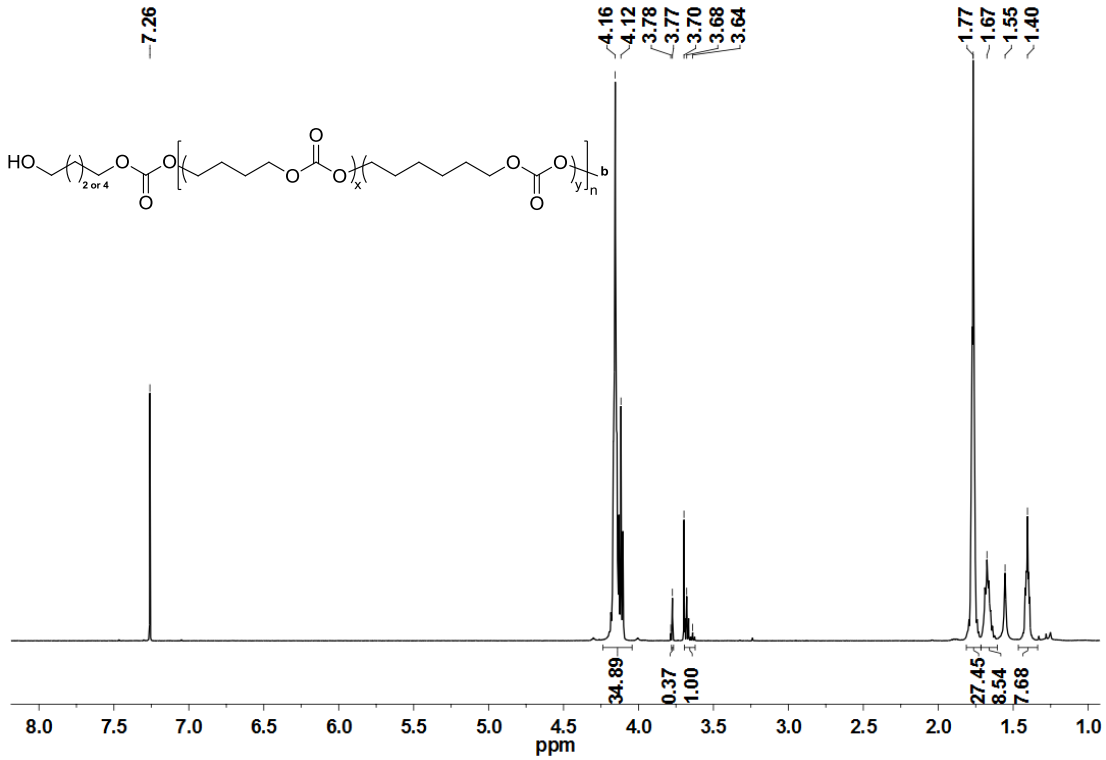

Figure SI-16. ^{1}H NMR spectrum of PBC-*co*-PHC (in $CDCl_3$-*d*)

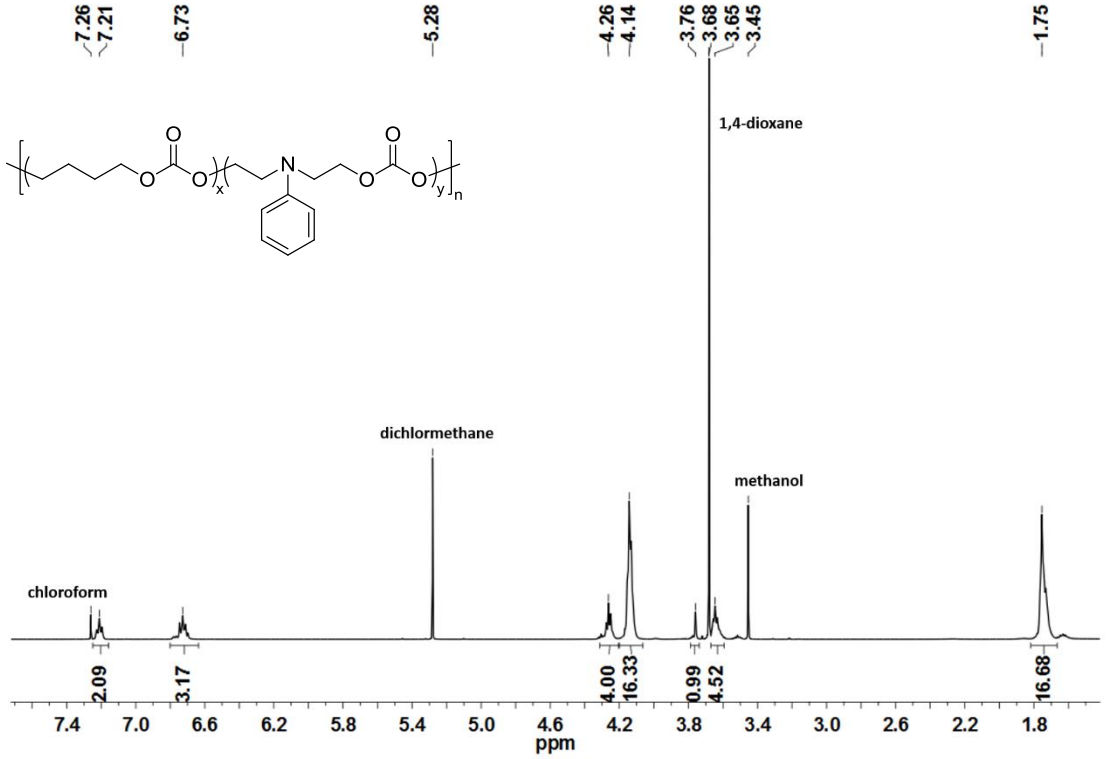

Figure SI-17. ^{1}H NMR spectrum of PBC-*co*-PDEAC (in $CDCl_3$-*d*)

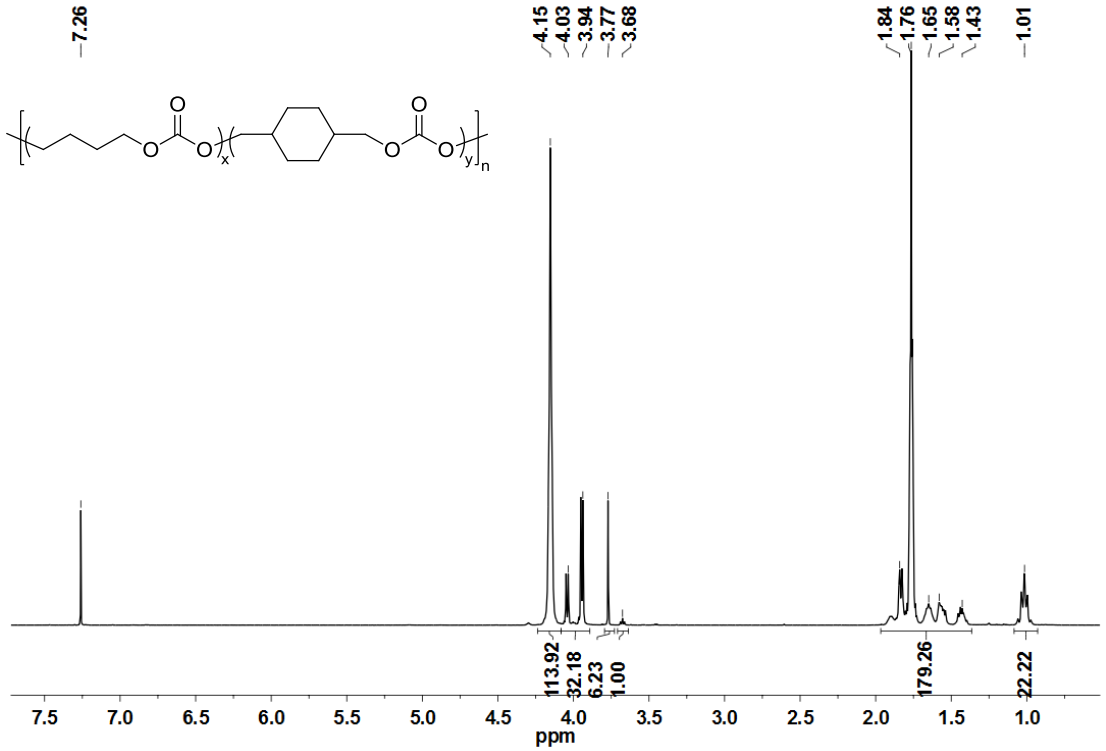

Figure SI-18. ^{1}H NMR spectrum of PBC-*co*-PCDMC (in $CDCl_3$-*d*)

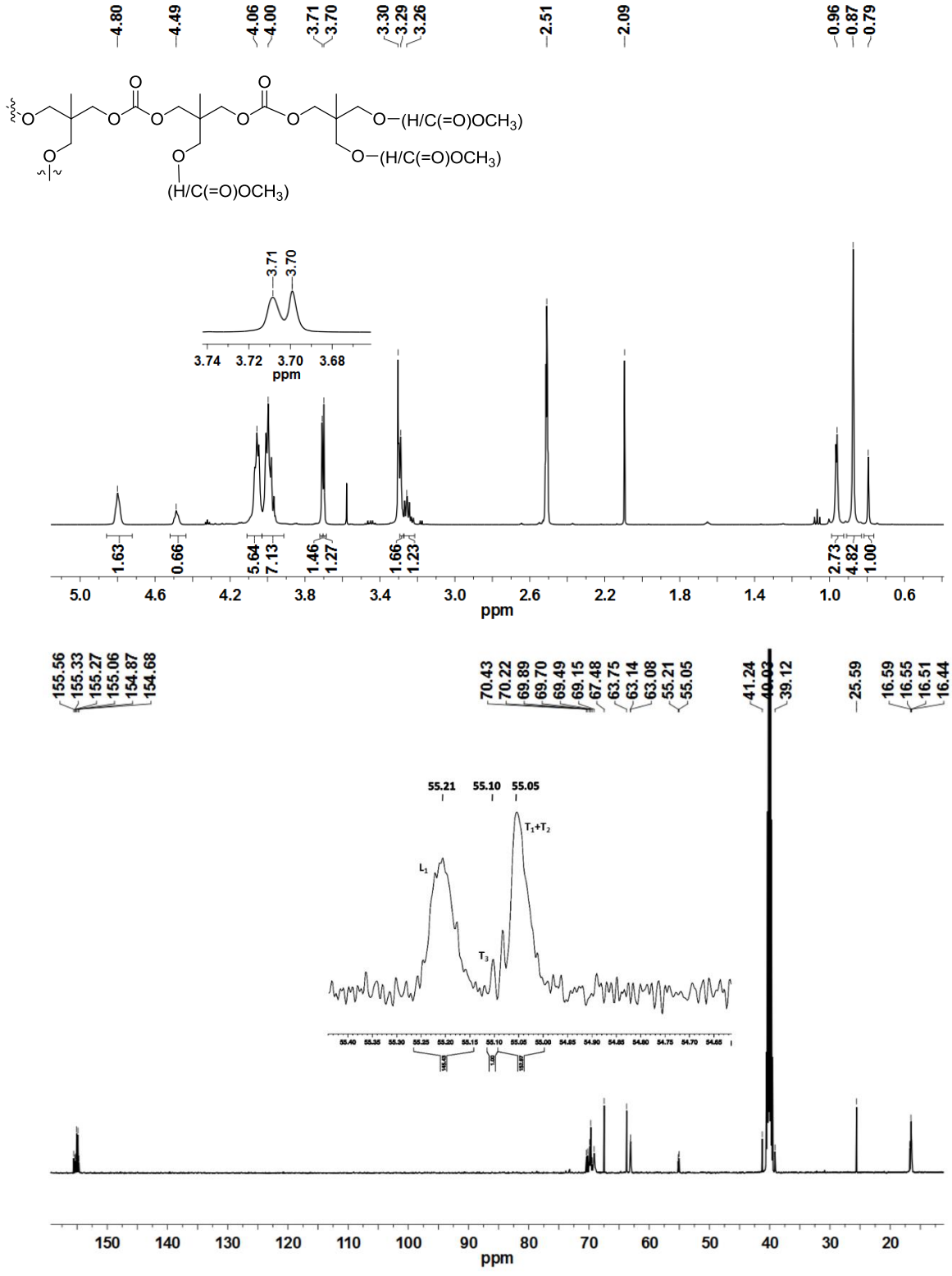

Figure SI-19. ^{1}H and ^{13}C NMR spectrum of PTHEC (in DMSO-d_6)

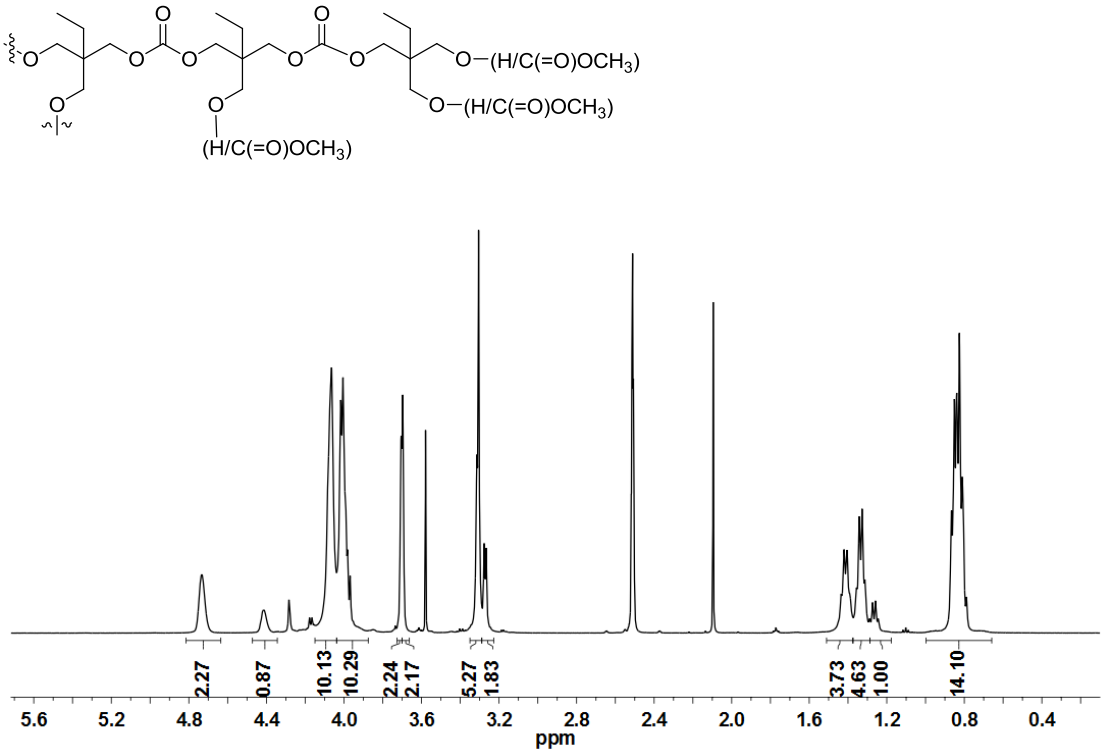

Figure SI-20. ^{1}H NMR spectrum of PTHPC (in DMSO-d_6)

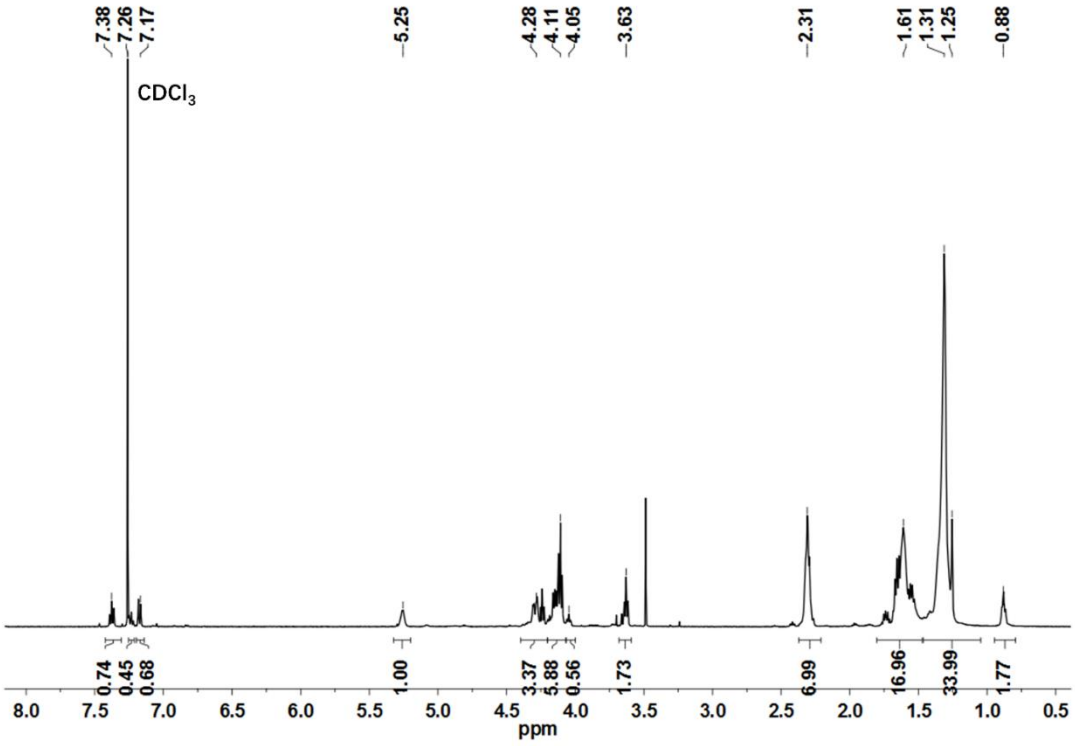

Figure SI-21. ^{1}H NMR spectrum of HBPC from TriOL (in $CDCl_3$-d)

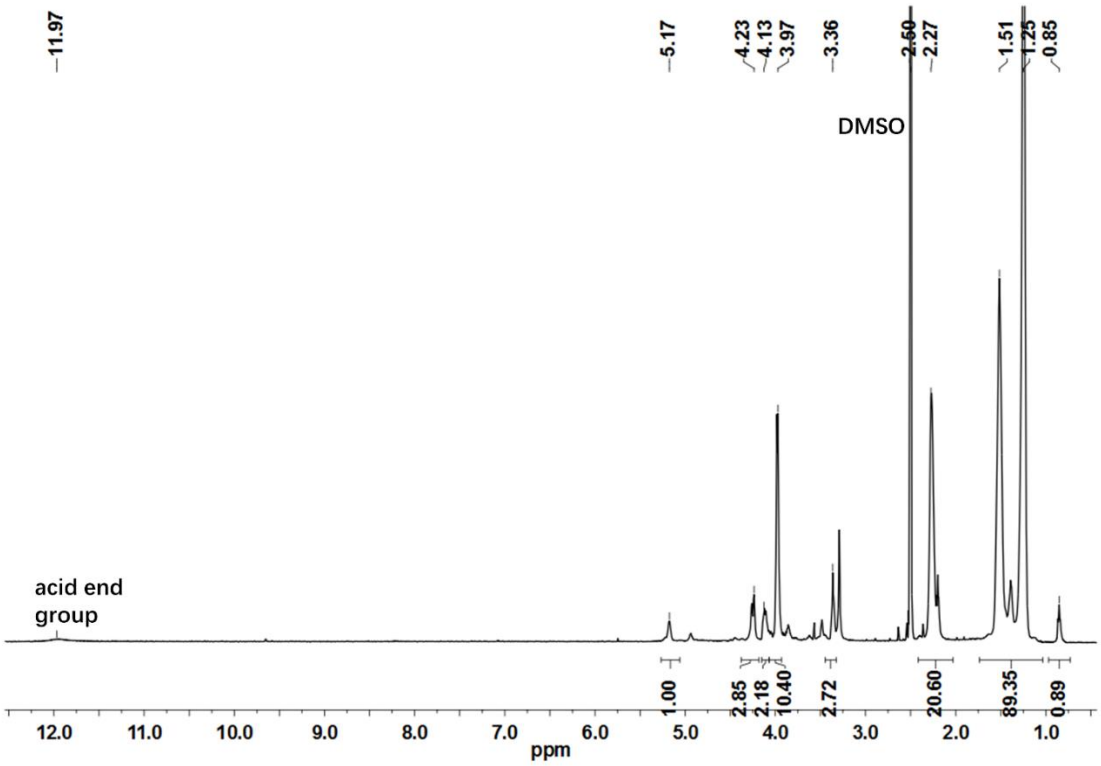

Figure SI-22. ^{1}H NMR spectrum of HBPE from TriOL (in DMSO-d_6)

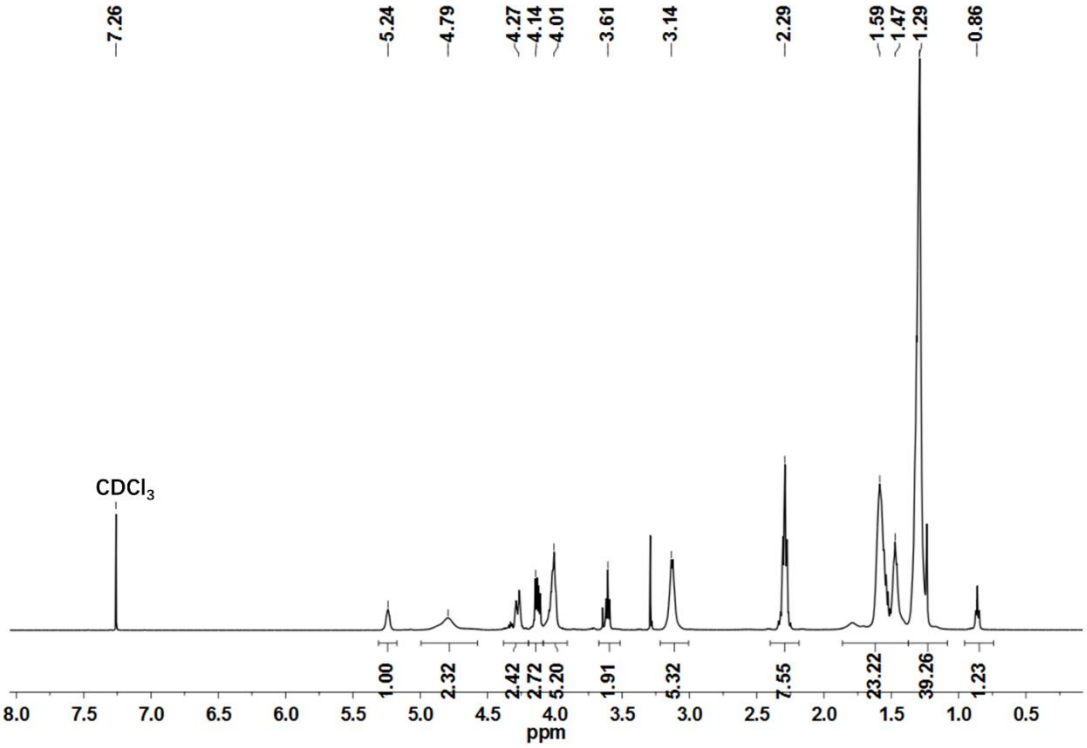

Figure SI-23. ^{1}H NMR spectrum of HBPU from TriOL (in $CDCl_3$-d)

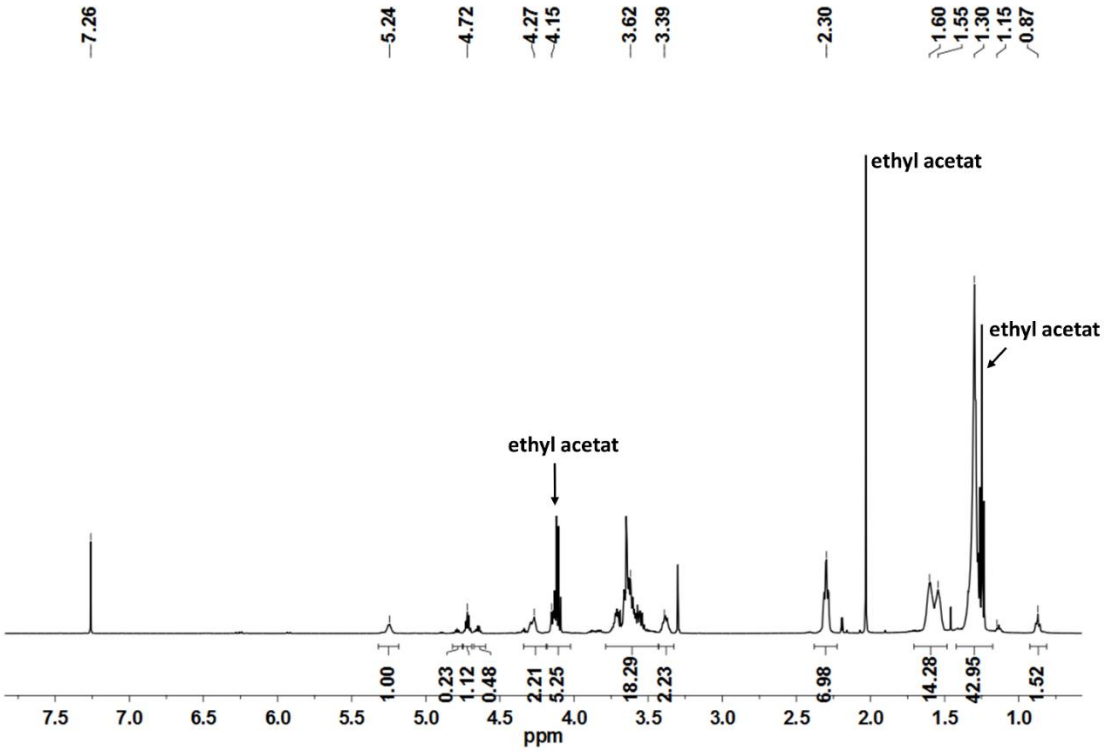

Figure SI-24. ^{1}H NMR spectrum of HBPA from TriOL (in $CDCl_3$-*d*)

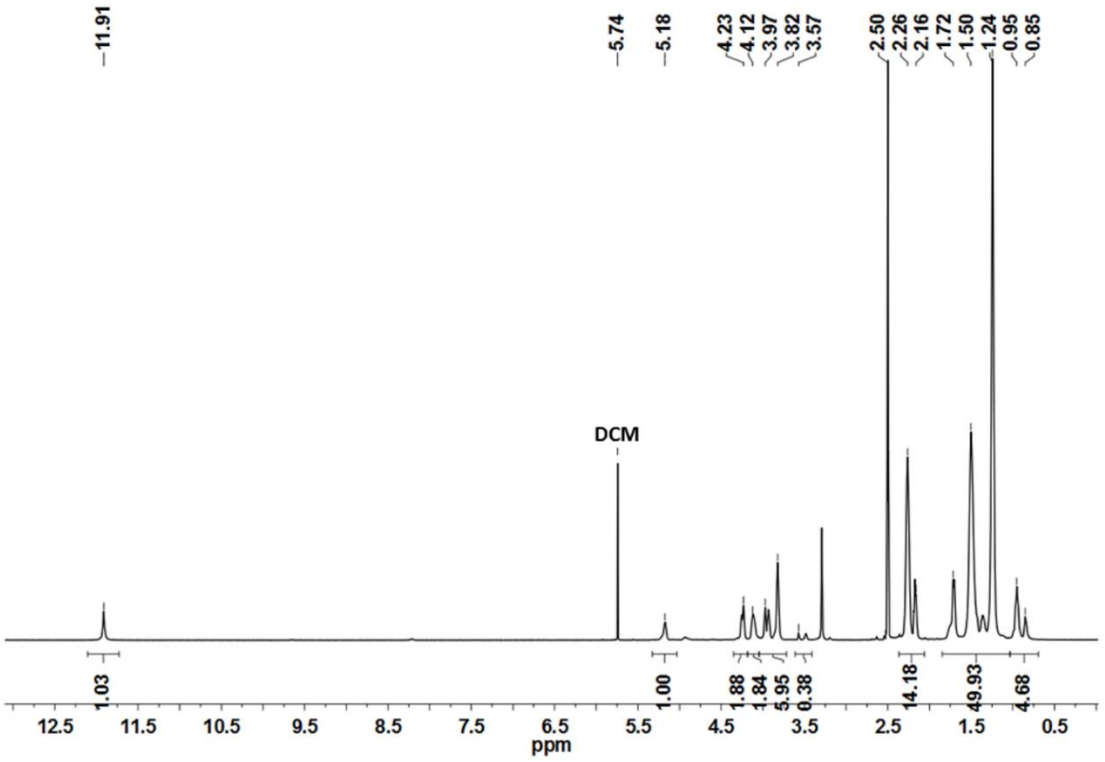

Figure SI-25. ^{1}H NMR spectrum of HBPE-AC from TriAC (in DMSO-d_6)

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