Functional Polycarbonates from Carbon Dioxide and Tailored Epoxide Building Blocks

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Jeannette Hilf geb. Geschwind

Geboren in Worms

Mainz, den 18.01.2014

Dekan: Univ.-Prof. Dr. Holger Frey

Prodekan: Univ.-Prof. Dr. Dirk Schneider

1. Berichterstatter:

2. Berichterstatter:

Hiermit versichere ich gemäß § 10 Abs. 3d der Promotionsordnung vom 24.07.2007, dass ich die als Dissertation vorgelegte Arbeit selbst angefertigt und alle benutzten Hilfsmittel (Literatur, Apparaturen, Material) in der Arbeit angegeben habe.

Die als Dissertation vorgelegte Arbeit wurde in der Zeit von Juli 2011 bis Januar 2014 am Institut für Organische Chemie der Johannes Gutenberg-Universität Mainz im Arbeitskreis von Herrn Univ.-Prof. Dr. Holger Frey angefertigt.

"Chemistry is wonderful! I feel sorry for people who don't know anything about chemistry. They are missing an important part of life, an important source of happiness, satisfying one's intellectual curiosity."

Linus Pauling (1901-1994)

Acknowledgement

An overwhelming number of supervisors, colleagues, co-workers, and friends have contributed to this thesis. It has been an honor to work for and with all of them during my research projects and I wish to express my heartfelt appreciation to every single person in this and the following sentences.

………..

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……

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Aim of this work

With regard to the growing global emission of carbon dioxide (CO_2), the efficient conversion of CO_2 into organic materials is a very interesting aim for (polymer) chemists and the chemical and energy industry, but chemically difficult. Carbon dioxide is thermodynamically extremely stable and therefore very difficult to use as a reactant. As a consequence, efficient catalysts are needed in order to activate the molecule for chemical reactions. One way to use carbon dioxide, is the production of polycarbonates by copolymerization with the epoxides.

Aliphatic polycarbonates are particularly interesting for medical purposes because of their biodegradability. One of the most active areas of current research is the development of "drug delivery" systems. However, the medical application of many currently investigated systems such as polyesters and polyglycerol, is limited because of their non-degradability or poor biocompatibility. Aliphatic polycarbonates can be degraded *in vivo* without producing toxic and acidic side products. In addition, polycarbonates generally have lower degradation rates than many biopolyesters such as polylactide. This is advantageous especially when a relatively high stability is desired for biomedical applications. Usually linear polycarbonates are used. However branched polymer structures have come into focus lately.

In contrast to linear polycarbonates branched polyester structures such as hyperbranched polycarbonates contain many functional hydroxyl groups, which provide a great range of possibilities for further chemical modifications. Such modifications enable new exciting approaches in the field of complex macromolecular architectures, such as the construction of novel nanocapsules for drug delivery, drug transportation and for bioconjugation of proteins.

The production of polycarbonates by the catalytic copolymerization of epoxides and carbon dioxide is an innovative way for their synthesis. Every year several gigatons of carbon dioxide are produced by the industry. Scarcity and rising cost for fossil resources as well as the influence of Earth's climate, are long-term consequences for our society. The efficient conversion of CO_2 into organic materials is therefore important and future-oriented. However carbon dioxide as a building block is also interesting for another reason.

Toxic educts currently used for the polycarbonate production such as phosgene, can possibly be replaced.

The first catalysts for the copolymerization of CO_2 and epoxides were already developed in 1969 by Inoue et al. and continuously improved since then. Numerous new heterogeneous and homogeneous catalyst systems have been described mainly by Darensbourg[7], Coates and Rieger. However, most catalyst systems do not tolerate any functional groups, such as hydroxyl groups or even glycidyl ethers. Therefore suitable catalyst sytems have to be found to incorporate functionalities along the polymer backbone.

The current research has mainly been driven by the search for new more efficient catalysts and only a few different epoxide monomers are used for the synthesis so far. Among them the heterogeneous zinc glutarate catalysts take a leadership position.

For the production of polycarbonates from CO_2 and epoxides, inexpensive propylene oxide (PO) and cyclohexene oxide (CHO) are widely used. Very limited literature exists concerning the synthesis of CO_2 copolymers from epoxides containing further functional groups.

By varying the epoxide functional groups, new polymer architectures can be obtained. Mainly linear homopolymers, linear random copolymers or block copolymers are described in the current literature. In general, these have only a maximum of two functional groups and thus only a limited possibility for chemical modification. Through the incorporation of functional monomers the number of end groups and functional groups can be increased and new polymer architectures can be synthesized.

It has therefore been the aim of this work to develop new pathways for the precise introduction of functionalities along the polymer backbone, either through architecture variation or through the usage of functional epoxides. Several methods have been developed. Among them the introduction of functional groups using protected glycidyl ethers as epoxide monomers and the use of multifunctional initators to from block or star-shaped polymers. Such methods should be easy to perform in order to grant broad application of the methods by other research groups or industry.

Abstract

Carbon dioxide (CO_2), an industrial waste product, is a potentially interesting C1 feedstock, as it is nontoxic, renewable, abundant and inexpensive. A promising approach for the use of CO_2 is its polymerization to polycarbonates (PC), by catalytic copolymerization of epoxides. A current drawback for many applications of the resulting materials is the low number of pendant functional groups at the PC backbone. The catalytic copolymerization of CO_2 with appropriately substituted epoxides is an ideal platform for the generation of multifunctional PCs.

This thesis aims at the development of the synthesis multifunctional polymer architectures based epoxide/carbon dioxide copolymerization. The work is motivated both by fundamental issues and application potential of the resulting materials.

Chapter 1 gives an introduction to this thesis. **Chapter 1.1** reviews the current state of the art in the synthesis of functional polycarbonates from carbon dioxide and tailored epoxide building blocks. Different monomers such as cyclohexene oxide derivatives; propylene oxide derivatives; glycidyl ethers; and cyclic anhydrides or cyclic esters are compared and discussed with respect to the incorporation of different functionalities. **Chapter 1.2** discusses catalysts and gives insights into the mechanism of the alternating copolymerization of carbon dioxide and epoxides with various substituents

Chapter 2 examines the synthesis and selected applications of different poly(propylene carbonate) architectures. In **Chapter 2.1**, blockcopolymer approach is described to synthesize CO_2-based nonionic surfactants. Copolymerization of CO_2 and propylene oxide (PO) has been employed to generate amphiphilic polycarbonate block copolymers with a hydrophilic poly(ethylene glycol) (PEG) block and an apolar poly(propylene oxide) (PPC) block. Furthermore the controlled synthesis of multi-arm star polyether-polycarbonate polyols based on propylene oxide and CO_2 is presented in **Chapter 2.2**. It has been shown that flexible multi-arm star polymers with PPC arms can be prepared using a hyperbranched poly-(propylene oxide) copolymer with glycerol branching points as a multifunctional initiator for the controlled catalytic copolymerization of carbon dioxide with propylene oxide. Notably, the post-polymerization functionalization of the hydroxyl end groups with

phenylisocyanate was shown to be highly efficient and occurred without observable backbone degradation, enabling the potential use of the multifunctional PPC polymers as flexible, non-crystalline polycarbonate polyols for polyurethanes.

Chapter 3 describes the synthesis of functional polycarbonates using glycidyl ether monomers. Glycidyl ethers are readily available and can easily be synthesized from epichlorohydrin and a desired alcohol. Functional groups that are distributed randomly at the polymer backbone can be employed to tailor the chemical properties of the materials, such as hydrophilicity/hydrophobicity, biocompatibility, and biodegradability as well as general material properties.

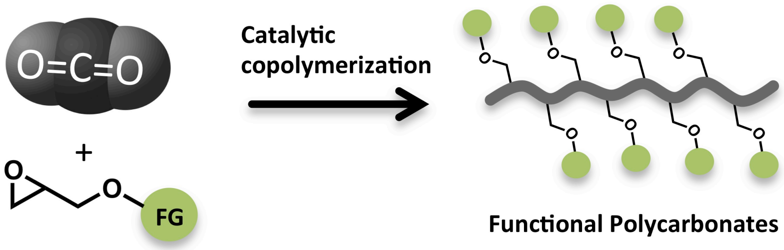
In order to prevent side reactions and catalyst poisoning, the functional groups in the monomers are usually protected prior to polymerization, and must be easy to remove after polymerization, with no or very little alteration to the polymer chains. In **Chapter 3.1** hydroxyl-functional aliphatic polycarbonates are presented, which can be prepared directly from CO_2 and glycidyl ethers with protected functionalities. 1,2-Isopropylidene glyceryl glycidyl ether as a protected diol and glycidyl methyl ether (GME) have been copolymerized with CO_2, using a readily available Zn-pyrogallol catalyst system. The resulting functional polycarbonates are promising materials, e.g., as degradable supports for catalysts, drugs or reagents.

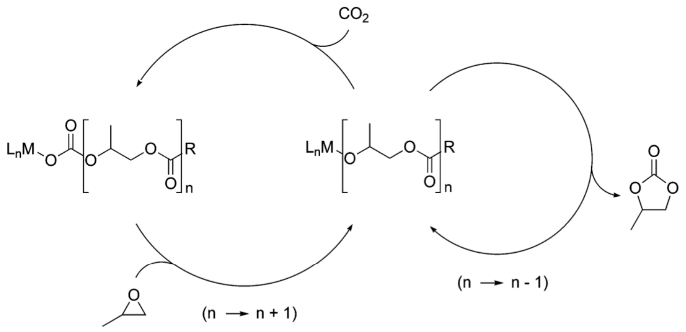
In addition, the hitherto synthetically inaccessible functional, aliphatic poly(1,2-glycerol carbonate) as a fundamental, simple polymer structure based on glycerol and CO_2 as building units is presented in **Chapter 3.2** and **Chapter 3.3**. The material was obtained by two-step procedures either from copolymerization of ethoxy ethyl glycidyl ether (EEGE) or benzyl glycidyl ether (BGE) with CO_2, followed by deprotection via acidic cleavage or hydrogenation, respectively. The removal of either protecting group was possible without backbone degradation.

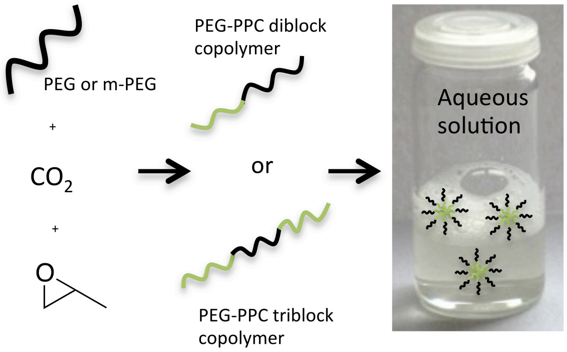
Using different easily available functional glycidyl ethers various other functionalities, e.g., triple bonds and furfuryl groups can also be introduced in polycarbonates for subsequent click-reactions (**Chapter 3.4** and **Chapter 3.5**).

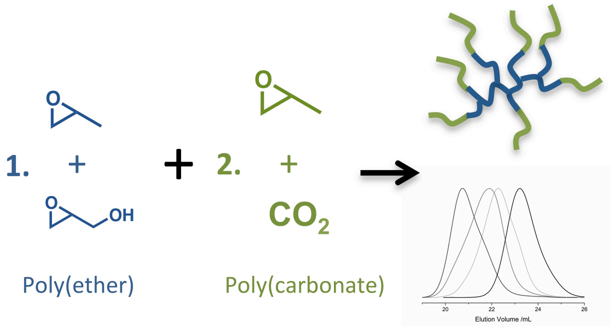
Chapter 4 describes the synthesis of functional polycarbonates with propylene oxide-based epoxide monomers. **In Chapter 4.1**, the introduction of reactive double bonds at a poly(propylene carbonate) (PPC) backbone by copolymerization of aliphatic alkene epoxides with propylene oxide and carbon dioxide is presented. The facile transformation of the double bonds was verified by a thiol-ene reaction, resulting in quantitative conversion of the double bonds. Polycarbonate derivatives with multiple functionalities have been prepared, providing suitable moieties for further grafting. To expand the scope of functional polycarbonates synthesized by the direct copolymerization of epoxides with carbon dioxide, norbornene-containing aliphatic polycarbonates from propylene oxide, 2-bicyclo[2.2.1]hept-5-ene-2-yl oxirane (BHO) and CO_2 were prepared as presented in **Chapter 4.2**. With the incorporation of pendant norbornene groups the polymer can be crosslinked, using metathesis polymerization. Depending on the concentration of the reaction mixture, long chain branched materials can be obtained.

Graphical Abstract





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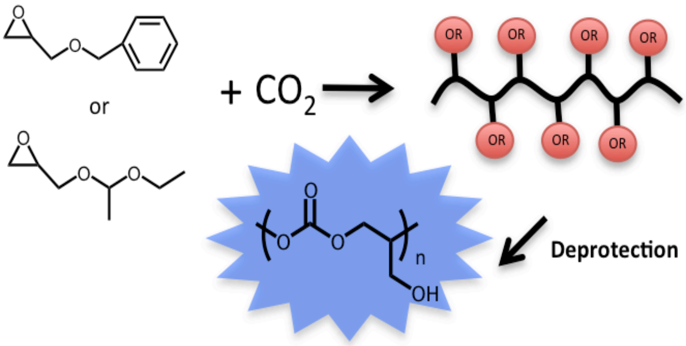
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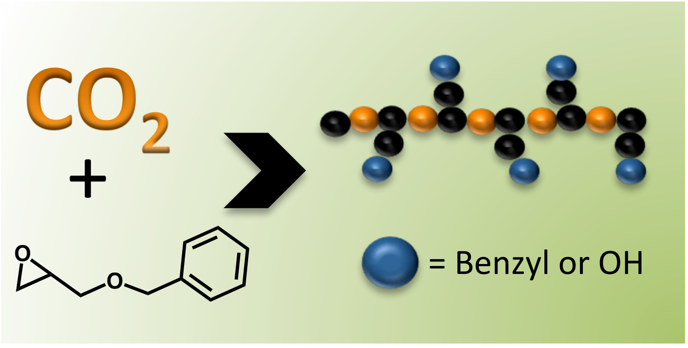
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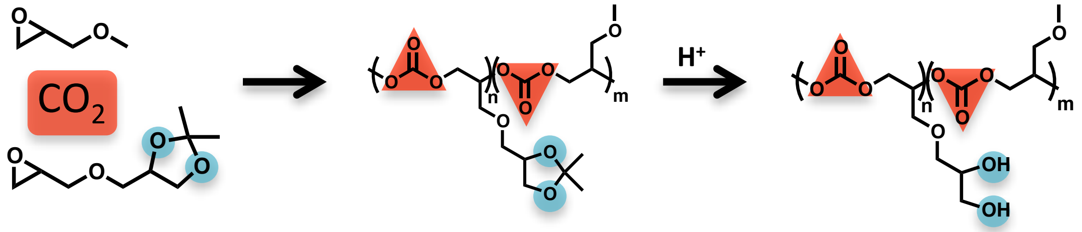
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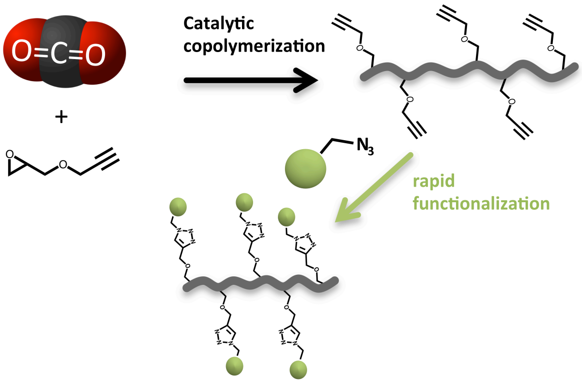
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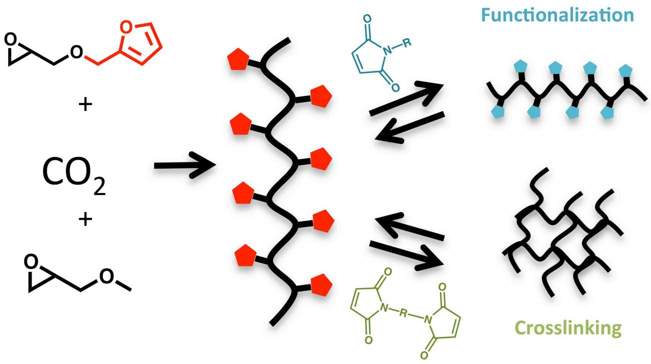
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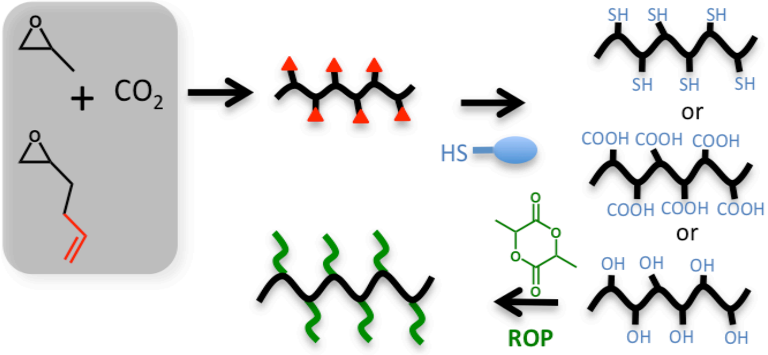
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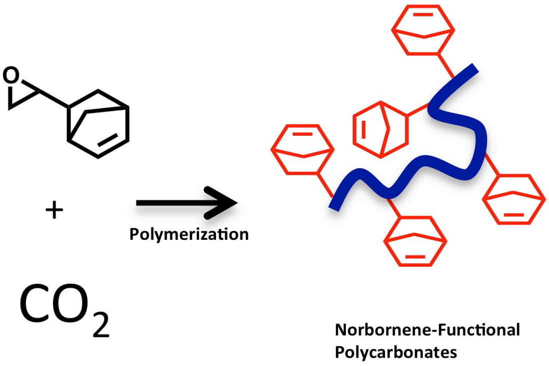
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CO_2
Polymerization
Norbornene-Functional
Polycarbonates

Chapter 1: Introduction

1.1. Functional Polycarbonates from Carbon Dioxide and Tailored Epoxide Building Blocks

Jeannette Hilf[1,2] and Holger Frey[1]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry,

Duesbergweg 10-14

Johannes Gutenberg-Universität Mainz, D-55128 Mainz

[2]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz

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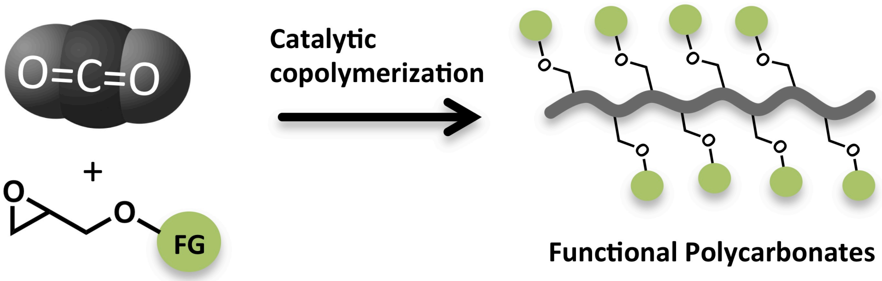

Introduction

Chemical fixation of carbon dioxide is important with respect to resource utilization and current environmental concerns. Various chemical and biological methods to capture and utilize CO_2 are under investigation. Key advantages of the incorporation of CO_2 as a C_1 building block for polymers are that it is non-toxic, cheap and readily available. The coupling of carbon dioxide (CO_2) and epoxides affording biodegradable, aliphatic polycarbonates represents a valuable transformation. Since its discovery in 1969 by Inoue et al.[1], the copolymerization of epoxides and carbon dioxide has become one of the best-studied and useful technologies for the large-scale utilization of CO_2 in chemical synthesis. In the last 40 years, a variety of catalyst systems for this copolymerization has been developed.[2] Initially, mainly heterogeneous catalysts were used[3,4] but within the last decade the use of homogeneous catalysts lead to a drastic increase in catalytic activities. Today stereoselectivity can be controlled and well-defined polymers can be synthesized. From this class, especially cobalt(III)–salen, phenoxide zinc, or β-diiminate–zinc complexes have come into focus.[5–8]

Despite intense research activities in the area of epoxide/carbon dioxide copolymerization, a profound understanding of the underlying mechanisms has not been achieved, and thus this field is under continual investigation. However, the generally accepted mechanism for the copolymerization of epoxides and carbon dioxide, as catalyzed by metal complexes is believed to occur via a coordination-insertion mechanism involving either one or two metal centers.[5] Two undesired side reactions can occur, (i) back-biting reaction leading to the formation of thermodynamically stable, five-membered cyclic carbonate or (ii) insertion of two epoxide molecules consecutively, especially for Lewis acid catalysts, leading to ether linkages (Figure 1).

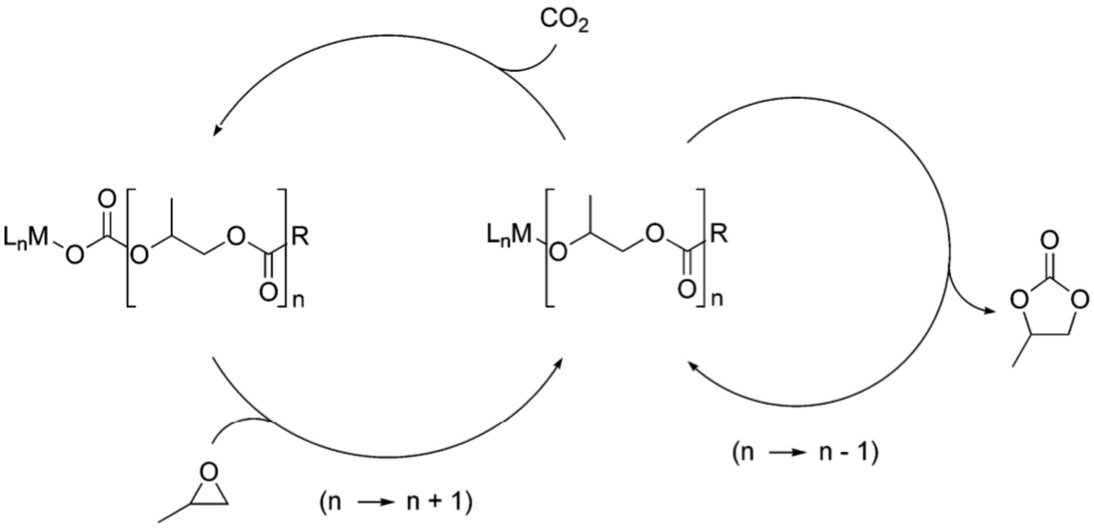

Figure 1. Alternating Copolymerization of CO_2 and PO and side-product pathway, i.e., the formation of the inert cyclic carbonate through backbiting.[9]

Unlike the expanding spectrum of catalysts, epoxides that can be copolymerized with carbon dioxide remain quite limited. However, there is an increasing interest in functional, aliphatic polycarbonates that can be prepared directly from carbon dioxide (CO_2). Functional groups distributed randomly at the polymer backbone enable tailoring of the chemical properties of the materials, such as hydrophilicity/hydrophobicity, biocompatibility, and biodegradability as well as general materials properties. Moreover, the presence of functional groups offers vast opportunities for further post-polymerization modification, including sequential binding of appropriate biomedically relevant structures, such as proteins or drugs. Furthermore, the outstanding advantage of aliphatic polycarbonates is embodied in the absence of acidic degradation products during the *in vivo* degradation.[10–12] In addition, the degradation rate of polycarbonates is slower than polyesters, which is desirable for applications that require long-term durability in the body.[13] At present the ring-opening polymerization (ROP) of six-membered cyclic carbonates is the established pathway for the synthesis of functional aliphatic PCs.[14–17] For the synthesis of poly(trimethylene carbonate) (PTMC) and poly(dimethyl trimethylene carbonate) functional polymer analogues, cyclic carbonates bearing a variety of functional groups have been developed.[18–21]

More recently, the preparation of functional aliphatic and alicyclic polycarbonates from CO_2 and epoxides with functional groups randomly distributed at the polymer backbone has been established. Suitable functional epoxide comonomers are required for this reaction. There is a very large range of commercially available and naturally occurring epoxides, from which it is possible to produce an immense variety of polycarbonate-based materials that can provide tailor-made properties.

Several types of functional monomers are employed: (i) Cyclohexene oxide derivatives; (ii) propylene oxide derivatives; (iv) glycidyl ethers; (iv) cyclic anhydrides or cyclic esters. In order to prevent side reactions, the functional groups in the monomers are usually protected prior to polymerization, and the protective groups should be conveniently removed after polymerization, with no or very little alteration to the polymer chains. Furthermore, properties and functionality of aliphatic polycarbonates can also be controlled by the polymer architecture. The chain transfer reaction including externally added alcohols can be used for the incorporation of specific initiators or the synthesis of various polymer architectures such as block- or star like copolymers.[22] Therefore epoxide/carbon dioxide copolymerization has the character of a living polymerization.

With the increasing significance of functional aliphatic polycarbonates and of epoxide/carbon dioxide copolymerization in mind, this short review summarizes the current developments concerning the design of functional polycarbonates from epoxides and carbon dioxide.

Cyclohexene Oxide-Based Epoxide Monomers

Cyclohexene oxide (CHO) is one of the most frequently used monomers for carbon dioxide/epoxide copolymerization, since its catalyst tolerance and reactivity is high and the danger of back-biting reactions is quite low. The introduction of functional groups using cyclohexene oxide derivatives still represents a limited area of research, since the respective CHO-derivatives have to be prepared in several steps. **Figure 2** and **Table 1** highlight the most important CHO-monomers that have been successfully used for copolymerization with CO_2. The incorporation of CHO-derivatives leads to polymers with glass transition temperatures above room temperature.

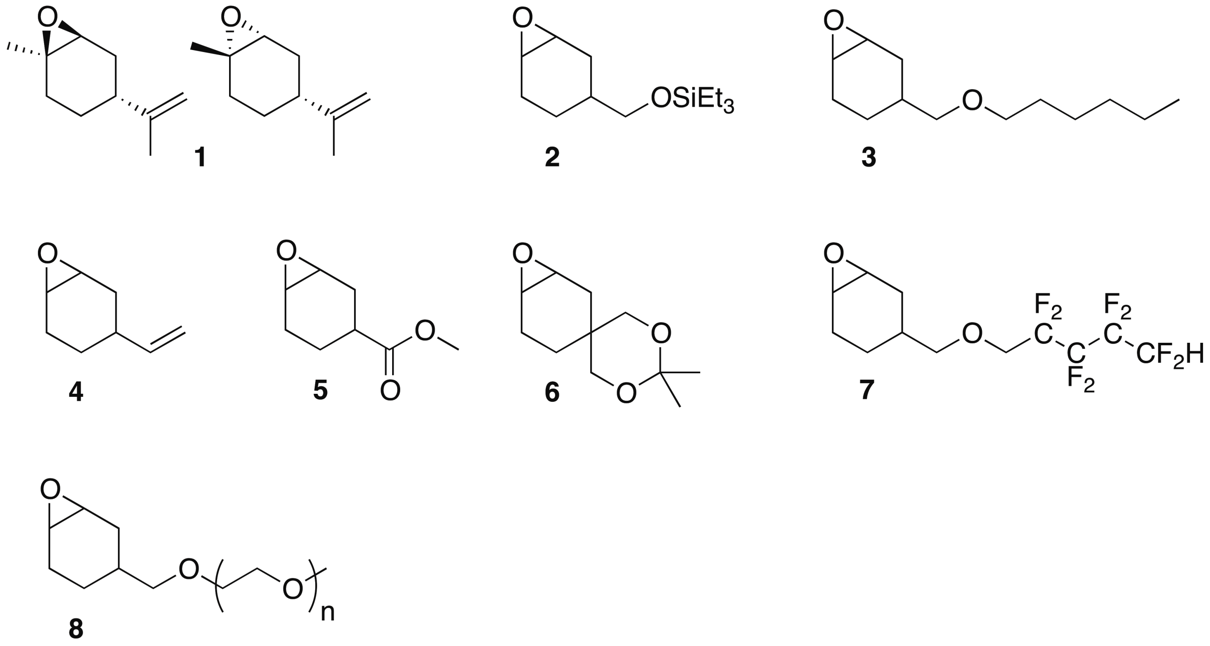

Figure 2. Selected cyclohexene oxide-based monomers used for CO_2 copolymerization (see Table 1).

Table 1. Selected copolymerization data for the monomers described in Figure 2 with CO_2.

#	Catalyst	$p(CO_2)$/bar	T/°C	%Carbonate^a	M_n^{b}	PDI^b	T_g/ °C	Ref
1	(BDI)ZnOAc	7	25	>99	10,800	1.12	111	23
2	(BDI)ZnEt	7	50	>99	24,500	1.07	-	33
3	(BDI)ZnEt	7	50	>99	30,400	1.07	-	33
4	DMC:$K_3Co(CN)_6$/ $ZnCl_2$//PTME glycol	10	80	73	10,100	2.2	-	29
5	[Et(BDI)ZnOEt]	9	50	>99	2300	4.4	53	28
6	(BDI)ZnEt	7	50	>99	16,600	1.07	-	33
7	(BDI)ZnEt	7	50	>99	18,500	1.06	-	33
8	(BDI)ZnEt	7	50	>99	18,000	1.09	-	33

^{a}Determined by 1H NMR spectroscopy; ^{b}Determined by GPC with polystyrene standards; ^{c}Glass Transition temperature determined by DSC.

First of all, limonene oxide (**1**), an epoxide derived from citrus fruits, was copolymerized with CHO and CO_2 using the BDI zinc catalysts at 25 °C and 7 atm to yield a copolymer with moderate molecular weight (10 800) and a high T_g (111 °C).[23] Furthermore, the copolymerization of carbon dioxide and indene oxide to yield poly(indene carbonate) has been achieved through the use of bifunctional cobalt(III) catalysts. These polymers have been prepared with M_ns and T_gs of up to 9700 g/mol and 138 °C, respectively. This represents the highest T_g yet observed for polycarbonates produced via coupling of CO_2 and epoxides.[24,25] The depolymerization of poly(indene carbonate) to afford primarily the cyclic carbonate, *cis*-indene carbonate, has also been investigated.[26,27] The activation energy for depolymerization of poly(indene carbonate) was found to be 189 ± 5.8 kJ mol^{-1}, which is considerably higher than that observed for a variety of other aliphatic polycarbonates.

Moreover, two ester-functionalized cyclohexene oxide monomers (3,4-cyclohexene-oxide-1-carboxylic acid methyl ester (**5**) and 3,4-cyclohexene-oxide-1-carboxylic acid phenyl ester have been copolymerized with CO_2 using the β-diketiminato zinc catalyst (EtBDI)ZnOEt (EtBDI = 2-(2,6-diethylphenyl)amido-4-(2,6-diethylphenyl)imino-2-pentene) under mild conditions.[28] MALDI-ToF-MS microstructure analyses of the formed aliphatic polycarbonates revealed the occurrence of chain transfer reactions to both monomer and polymer as a result of zinc-catalyzed transesterification reactions. As a consequence, branched and cyclic polymer structures were formed, which limited the molecular weight development and led to an increase of the polydispersity.

Several groups reported on the copolymerization of carbon dioxide with 4-vinyl-1-cyclohexene-1,2-epoxide (**4**), forming polymers bearing multiple alkenyl side chains.[29] Based on this strategy, Coates and coworkers used the pendant double bond for the formation of nanoparticles by intramolecular crosslinking via cross-metathesis reaction.[30] Fully degradable and well-defined brush copolymers were also synthesized upon transformation of the alkene groups, using thiol-ene click reactions. The resulting hydroxyl groups were used as initiators for the ring-opening polymerization of ε-caprolactone.[31]

Other cyclohexene oxide derivatives (**2,3,6-8**) can also be used for the copolymerization with carbon dioxide. Coates and coworkers described the synthesis of multiblock poly(cyclohexene carbonate)s with sequence control.[33] In this communication, the living block copolymerization of functionalized cyclohexene oxides and CO_2 is described, yielding multiblock poly(cyclohexene carbonate)s with a diverse range of functionality on the side chains and good control of block sequence and length. This concept was further used for the preparation of multisegmented polycarbonate graft copolymers by the same group. (Figure 3)[32] They synthesized norbornenyl-terminated macromonomers with variable block sequences. After subsequent ring-opening metathesis polymerization of the norbornenyl-terminated macromonomers, segmented graft copolymers were produced (Figure 3).

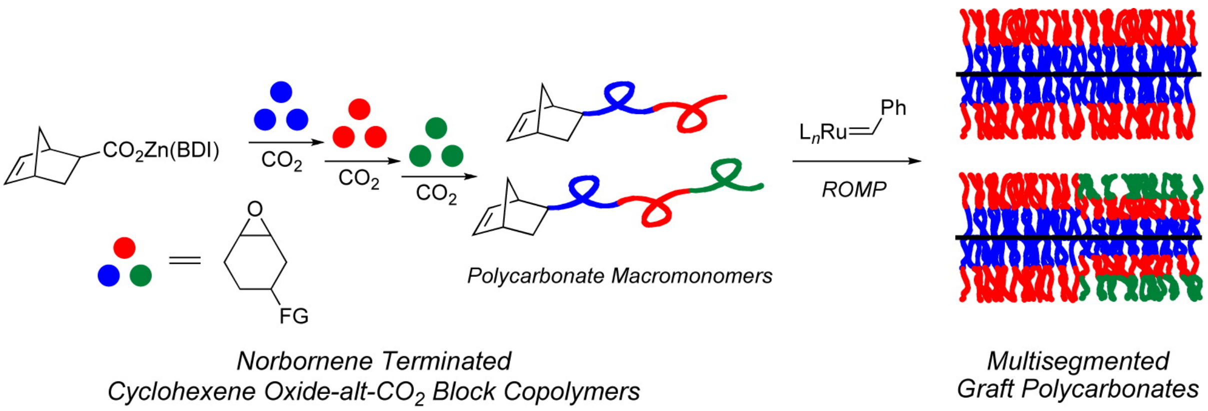

Figure 3. Synthesis of norbornenyl-terminated multiblock poly(cyclohexene carbonate)s and “grafting through” ring-opening metathesis polymerization of a norbornene-terminated multiblock copolymer "Reprinted with permission from Coates et al. *Macromolecules*, **2012**, *45 (19),* 7878–7883. Copyright 2012 American Chemical Society.[32]

Terpolymerization

Variation of the polymer properties can be also achieved by terpolymerization of cyclohexene oxide (CHO) and propylene oxide (PO) with carbon dioxide.[34] In contrast to the brittle behavior of PCHC (elongation at break of 1–2%), PPC has good flexibility (elongation at break between 600 and 1200%), but its low T_g (35–45 °C) clearly limits its use.[6] To address this problem, terpolymerizations of PO, CHO, and CO_2 have been undertaken.

However, until 2006 only limited success was achieved, mainly because of the different rates of polymerization (leading to copolymers with high degrees of compositional drift). However, a highly active, bifunctional Co(III)-Salen catalyst for the terpolymerization of CO_2 with CHO and aliphatic epoxides was described. A cobalt(III) complex of a salen ligand bearing one quaternary ammonium group at the 3-position of one aromatic ring was found to be a highly active catalyst for terpolymerization of CHO and aliphatic epoxides with CO_2 to provide selectively polycarbonates with narrow polydispersity at elevated temperatures.[35] A cobalt(III) complex of a salen-type ligand tethered by four quaternary ammonium salts was also reported for the terpolymerizations of CO_2/propylene oxide (PO)/cyclohexene oxide (CHO), CO_2/PO/1-hexene oxide (HO), and CO_2/PO/1-butene oxide (BO) without the formation of cyclic carbonates and ether linkages.[36] Furthermore, Darensbourg and coworkers described mechanistic aspects of the copolymerization of alicyclic and aliphatic epoxides with CO_2 in toluene solution and in neat epoxides in the presence of a (salan)CrCl/onium salt catalyst system.[37]

Propylene Oxide-Based and Terminal Epoxide Monomers

Compared to cyclohexene oxide, which leads to alicyclic polycarbonates with relatively high glass transition temperatures, propylene oxide (PO) leads to aliphatic copolymers with T_g values around 40 °C. Other propylene oxide derivatives can also be used for the copolymerization with carbon dioxide.

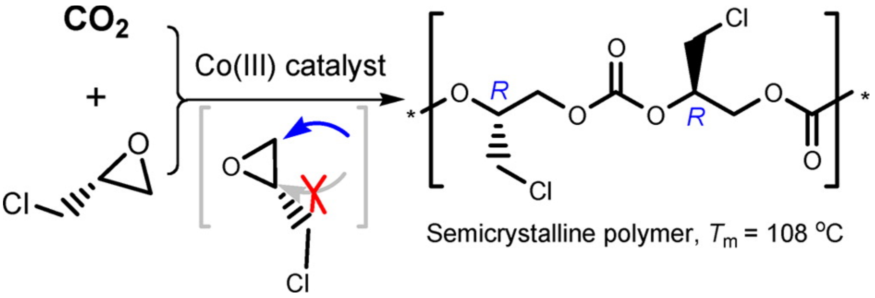

Figure 4. Copolymerization of epichlorohydrin and CO_2 "Reprinted with permission from Coates et al. *Macromolecules,* **2013**, *46 (6),* 2128–2133 Copyright 2013 American Chemical Society."[38]

Very limited literature exists concerning the synthesis of CO_2 copolymers from epoxides with electron-withdrawing groups, such as styrene oxide and epichlorohydrin (Figure 4). These polymerizations generally suffer from poor copolymer selectivity (no CO_2 is incorporated) and the concomitant production of ether linkages as well as a large amount of five-membered cyclic carbonate side products. However several groups succeeded in the copolymerization of epichlorohydrin and carbon dioxide using cobalt(III)- and aluminum-based catalyst systems. (Figure 4)[39] Darensbourg and coworkers reported the production of a CO_2/epichlorohydrin copolymer with more than 99% carbonate linkages. [38,40] Both stereospecific and therefore highly crystalline as well as stereo-irregular copolymers were obtained. Comparative kinetic studies were performed via in situ infrared measurements as a function of temperature to assess the activation barriers for the formation of cyclic carbonate versus copolymer generation.

Recently, styrene oxide was successfully copolymerized with carbon dioxide as well. Again the Darensbourg group published a detailed study on the difference in reactivity of the copolymerization reactions of styrene oxide *vs.* propylene oxide with carbon dioxide, utilizing binary (salen)cobalt(III) catalyst systems to provide perfectly alternating copolymers.[41,42] It was found that the nucleophilic ring-opening of styrene oxide occurs predominantly at the methine C_α–O bond, which leads to an inversion of configuration at the methine carbon center. This tendency results in a significantly lower reactivity in the synthesis of stereoregular poly(styrene carbonate), compared to the propylene oxide/CO_2 process.

Furthermore, the introduction of reactive double bonds at a poly(propylene carbonate) (PPC) backbone was realized by copolymerization of aliphatic alkene epoxides with propylene oxide (PO) and carbon dioxide (CO_2).[43,44] Our group prepared series of copolymers with random structure and varying comonomer content (3-22%) with molecular weights in the range of 22 000-34 000 g/mol. The resulting copolymers were characterized with respect to their microstructure and thermal properties. The facile transformation of the double bonds was verified by a thiol-ene reaction, resulting in quantitative conversion of the double bonds.[44] (Chapter 4.1)

Glycidyl Ether Monomers

Another very interesting class of epoxide monomers are glycidyl ethers. Glycidyl ethers are readily available and can conveniently be synthesized from epichlorohydrin and an alcohol. Figure 5 and Table 2 shows some of the glycidyl ethers that have been tested and the properties of the resulting copolymers, including thermal characterization. However, the thermal values should be interpreted with some caution due to their dependence on the molecular weight and the proportion of carbonate linkages in the respective copolymers.

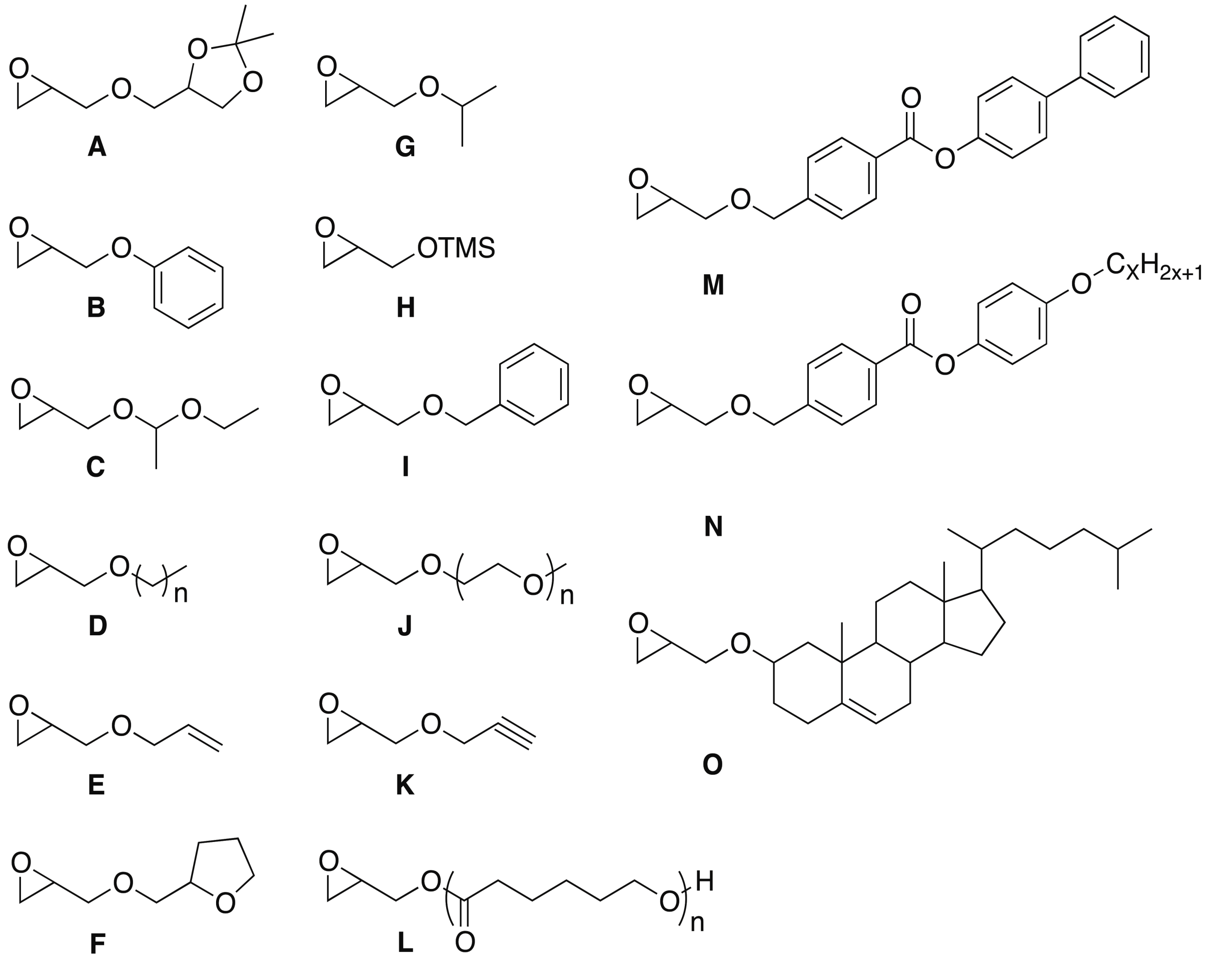

Figure 5. Glycidyl ethers used in CO_2 copolymerization reactions (copolymer data see Table 2).

As early as 1981, Inoue et al. developed a concept to introduce different groups at the polycarbonate backbone. As a method to introduce physiologically active substances into a copolymer, epoxides carrying a functional group via a hydrolysable linkage (**O**) were synthesized and copolymerized with carbon dioxide, using the diethyl zinc/water (1/0,9) system as a catalyst. The hydrolytic stability of the copolymers was also briefly investigated.[45] However no further application was described.

Recently, glycidyl ether containing alkyl ether side chains (**D**) have been used for the alternating copolymerization of carbon dioxide to prepare novel ion-conductive polymer electrolytes.[46,47] Tominaga and coworkers synthesized several types of polycarbonates incorporating glycidyl ethers (phenyl-, *tert*-butyl-, *n*-butyl-, ethyl- and isopropyl-glycidyl ether) using zinc glutarate and measured the ionic conductivity of the resulting electrolytes using LiTFSI. The polycarbonate is expected to weaken strong interaction with cations to a higher extent, compared to typical polyether electrolytes. Moreover, the respective materials possess moderately polar groups at the main chain and rather low T_g. Furthermore, phenyl glycidyl ether (**B**) and carbon dioxide were copolymerized using double metal cyanide (DMC) zinc catalysts or ionic liquid catalysts.[29,48] The latter showed good catalytic activity for the synthesis of polycarbonates with very low polydispersity (Mw/Mn =1.1 to 1.3). High carbon dioxide pressure enhanced the turnover frequency and carbonate content, which is due to the increase of carbon dioxide in the reaction solution.

Table 2. Selected epoxides-CO_2 copolymerization data for the monomers shown in Figure 5.

#	Catalyst	$p(CO_2)$/ bar	T/°C	%Carbonate[a]	M_n[b]	PDI[b]	T_g/°C[c]	Ref
A	$ZnEt_2$/pyrogallol	20	25	>99	24,800	2.5	-15	61
B	DMC:$K_3Co(CN)_6/ZnCl_2$// PTME glycol	10	80	>99	9300	3.6	-	48
C	$ZnEt_2$/pyrogallol	20	25	>99	17,000	1.5	-18	56
D	ZnGA	60	60	>99	9000	3.2	-24-45	46
E	$ZnEt_2$/pyrogallol	60	35	99	1000	-	-	49
F	$Y(CCl_3OO)_3/ZnEt_2$/glycerin	40	80	90	53,000	2.28	-	-
G	$ZnEt_2$/pyrogallol	60	35	>99	-	-	-	52
H	$ZnEt_2/H_2O$	-	-	-	-	-	-	57
I	$ZnEt_2$/pyrogallol	20	25	>99	21,000	1.24	-22	56
J	Salen(CoCl)/PPNCl	30	25	>99	3600	1.2	-	62
K	$ZnEt_2$/pyrogallol	20	25	>99	7900	2.3	-10	55
L	ZnGA	103	60	>99	10,800	1.7	-	64
M	$ZnEt_2/H_2O$	60	70	72	9300	6.2	-	45
N	$ZnEt_2/H_2O$	60	70	61	9500	2.7	-	45
O	$ZnEt_2/H_2O$	-	-	-	-	-	-	45

[a] Determined by ^1H NMR spectroscopy; [b] Determined by GPC with polystyrene standards; [c] Glass Transition temperature determined by DSC.

Functional aliphatic polycarbonates with pendant allyl groups are also widely known (**E**).[49,50] Listos and coworkers prepared carbon dioxide/allyl glycidyl ether (AGE) copolymers in the presence of a catalyst system based on $ZnEt_2$ and pyrogallol at a molar ratio of 2:1.[51] The functionality of some polycarbonates could be reduced by replacing a part of AGE with saturated glycidyl ethers, e.g. butyl glycidyl ether or isopropyl glycidyl ether (**G**).[52] Furthermore oxidation of the double bond and hydrolytic stability was tested. A few years later, an improved catalyst system was developed by Kuo and coworkers.[53] Their system consisted of $Y(C61_3CO_2)_3$, $Zn(Et)_2$, and pyrogallol dissolved in 1,3-dioxolane and was found to be highly effective for the copolymerization of allyl glycidyl ether with carbon dioxide at 60 °C and 400 psi. The resulting poly(ether carbonate) could react with 3-(trimethoxysilyl)propyl methacrylate via a free radical reaction to generate the alkoxysilane-containing copolymer precursors that were used in the subsequent sol–gel process to result in the poly(ether carbonate)–silica nanocomposite.

A crosslinking strategy was used to improve the thermal and mechanical performance of poly(propylene carbonate). PPC bearing a small fraction of pendant allyl groups were synthesized by the terpolymerization of allyl glycidyl ether, propylene oxide and carbon dioxide. Once subjected to UV-radiation the polymers were crosslinked.[54] A major improvement of mechanical characteristics was observed

Moreover, the synthesis of propargyl-functional poly(carbonate)s with different content of glycidyl propargyl ether (GPE) (**K**) units was achieved via the copolymerization of propargyl glycidyl ether and carbon dioxide.[55] A new type of functional poly(carbonate) synthesized directly from CO_2 and propargyl glycidyl ether is obtained. The resulting polymers show moderate polydispersities in the range of 1.6–2.5 and molecular weights in the range of 7000–10 500 g mol^{-1}. The materials can be further functionalized by the well-known 3+2 Huisgen click-reaction.

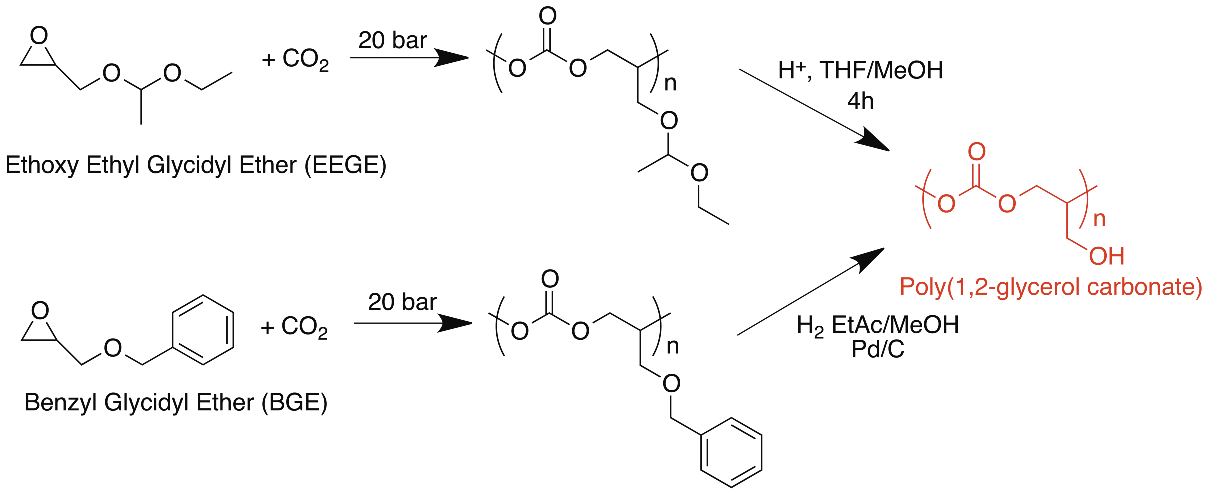

Figure 6. Synthetic Strategies for the Preparation of the hitherto elusive poly(1,2-glycerol carbonate) via Copolymerization of CO_2 and EEGE or BGE and Subsequent Deprotection. "Reprinted with permission from Geschwind et al. *Macromolecules*, **2013**, *46 (9),* 3280–3287 Copyright 2013 American Chemical Society."[56]

Already in 1979 Inoue mentioned a first attempt to synthesize a copolymer with pendant hydroxyl groups (**H**).[57] However, no characterization of the resulting copolymers was described. Very recently the introduction of hydroxyl groups at a polycarbonate backbone has found renewed interest. The hydroxyl-functional, aliphatic poly(1,2-glycerol carbonate) as a fundamental, simple polymer structure based on glycerol and CO_2 was prepared by combination of glycidyl ether monomers with carbon dioxide via two different approaches. The material was obtained by two-step procedures either from copolymerization of (i) ethoxy ethyl glycidyl ether (EEGE) (**C**) or (ii) benzyl glycidyl ether (BGE) (**I**) with CO_2, followed by removal of the protecting groups via acidic cleavage for (i) and hydrogenation for (ii). (Figure 6).[56] (Chapter 3.1 and 3.2) Independently, Grinstaff and coworkers reported an alternative catalyst system for the synthesis of poly(1,2-glycerol carbonate) and also described isotactic copolymers.[58] However, Poly(1,2-glycerol carbonate) showed a remarkable increase in degradation rate compared to poly(1,3-glycerol carbonate) with a $t_{1/2} \approx 2–3$ days. These polymers are therefore very interesting as degradable biocompatible polycarbonates. Other groups suggest the possibility of a direct copolymerization of carbon dioxide with glycidol to form branched poly(1,2-glycerol carbonate) oligomers.[59]

Furthermore, by using a non-functional comonomer, such as glycidyl methyl ether, the number of hydroxyl groups of poly(glycerol carbonate) copolymers can be varied, as shown by our group.[60] Hydroxyl groups can also be introduced by using other glycidyl ethers. For the synthesis of hydrolytically stable, hydroxyl-functional polycarbonates other epoxide monomers are required. We recently reported poly((glycidyl methyl ether)-*co*-(isopropylidene glyceryl glycidyl ether) carbonate) random copolymers with different fractions of 1,2-isopropylidene glyceryl glycidyl ether (IGG) (**A**) units.[61] After acidic hydrolysis of the acetal protecting groups a new type of functional polycarbonates obtained directly from CO_2 and glycerol is obtained, namely poly((glycidyl methyl ether)-*co*-(glyceryl glycerol) carbonate), which was shown to be stable in bulk as well as in solution. (Chapter 3.3)

In addition, biodegradable CO_2-based polycarbonates with rapid and reversible thermal response at body temperature can be prepared by one-pot terpolymerization of CO_2, propylene oxide (PO), and 2-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl)oxirane (ME_3MO) (**J**) using binary Salen Co(III)-Cl/PPNCl catalyst system. The lower critical solution temperature (LCST) was precisely controlled within a temperature range covering physiological temperature.[62,63] Another interesting copolymerization involved end-capping a polycaprolactone chain with an epoxide group (**L**), subsequently using the copolymerization with CO_2 to cross-link the copolymers to produce brush-like materials.[64]

Side chain liquid crystalline polymers possess interesting electrical and optical properties. Side-chain liquid crystalline polycarbonates have been prepared by several groups using glycidyl ethers containing mesogenic groups (**M,N**).[45] Jansen et al. synthesized side-chain liquid crystalline polycarbonates with alkoxyphenylbenzoate side groups, having a short spacer and tails ranging from 1 to 8 C-atoms.[65,66] The polymers were prepared by an organo-zinc catalyzed copolymerization of carbon dioxide and mesogenic 4-alkoxyphenyl 4-(2,3-epoxypropoxy)benzoates and they all showed smectic A structures. However, the resulting polymers had a high polydispersity and the maximum yield was about 30%.

Variation of the Polymer Architecture

Properties and functionality of aliphatic polycarbonates, i.e., solubility, amphiphilicity and materials properties in general can also be tailored by deliberate variation of the polymer architecture, i.e., by block- or segmented architectures. In an important publication, Cyriac et al. showed that the immortal copolymerization of carbon dioxide and propylene oxide can be used for the precise control of molecular weight and architecture of various block copolymers.[22,67]

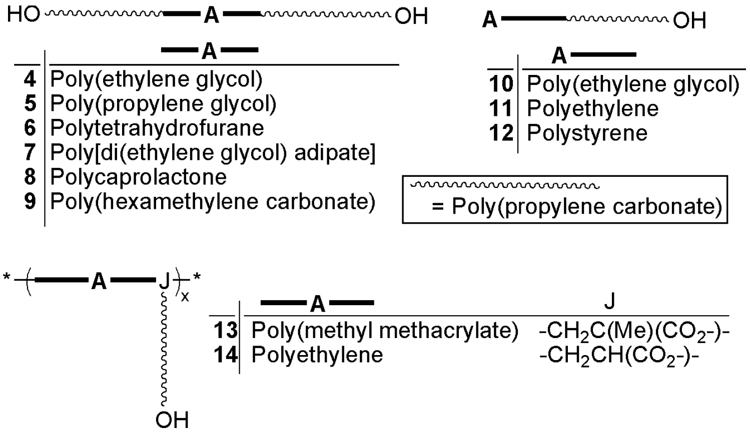

Figure 7. Structures of Block Copolymers "Reprinted with permission from Cyriac et al. *Macromolecules,* **2010***, 43 (18),* 7398–7401*;* Copyright 2013 American Chemical Society."[56]

The term "immortal polymerization" was coined by Inoue in 2000 and designates a polymerization that leads to polymers with a narrow molecular distribution in the presence of a chain transfer reaction, because of its reversibility. The transfer step leads to the "revival" of polymer chains that have become inactive.[68] As a result, the immortal polymerization can afford polymers with controlled molecular weight and chain end functionality.[68] The Lee group demonstrated that the immortal polymerization in the presence of polymer-based chain transfer agent containing -OH or -COOH group represents an excellent tool to produce well-defined polymer architectures.

The same group also described the linking of polymer chains using diepoxides in the carbon dioxide/propylene oxide copolymerization to obtain polymer networks.[69] They used both vinyl cyclohexene dioxide as well as chain transfer agents containing multiple carboxyl groups to vary the resulting polymer architectures. However, SEC revealed multi-modal distributions along with a tail at a high molecular weight fraction due to formation of the connected chains. The shape of the chain transfer agent led to variation of the chain topology, but the rheological properties were not influenced by the topology change.

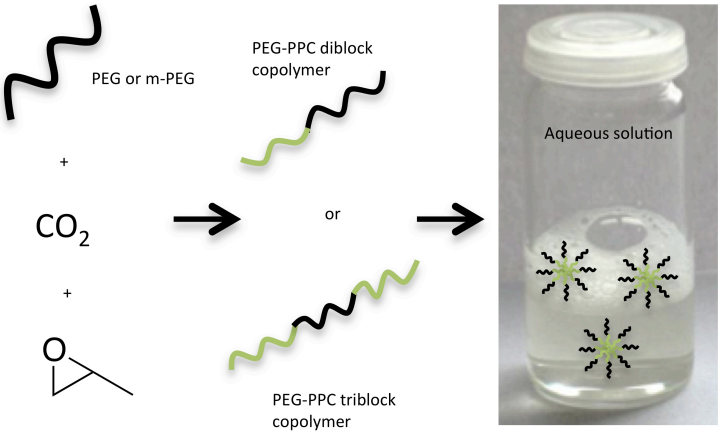

Figure 8. Synthesis of amphiphilic block copolymers from poly(ethylene glycol) and poly(propylene carbonate)"Reprinted with permission from Copyright 2013 Wiley."[56]

Recently, our group reported the synthesis of amphiphilic polycarbonate block copolymers with a hydrophilic poly(ethylene glycol) (PEG) block and a nonpolar poly(propylene carbonate) (PPC) block in a solvent-free procedure.[70] A series of poly(propylene carbonate) (PPC) di- and triblock copolymers, PPC-*b*-PEG and PPC-*b*-PEG-*b*-PPC, with narrow molecular weight distributions (PDIs in the range of 1.05–1.12) and tailored molecular weights (1500–4500 g mol^{-1}) was synthesized via an alternating CO_2/propylene oxide copolymerization, using PEG or mPEG as an initiator. (Chapter 2.1) These polycarbonate-based surfactants bear potential for a variety of applications for which currently polyether-based surfactants are employed.

Furthermore, we described the synthesis of multiarm star copolymers based on a hyperbranched poly(propylene oxide) polyether-polyol (*hb*PPO) core and poly(propylene carbonate) (PPC) arms in two steps from propylene oxide (PO), a small amount of glycidol and CO_2. The PPC arms were prepared via carbon dioxide (CO_2)/propylene oxide copolymerization, using *hb*PPO as a multifunctional macroinitiator and the (R,R)-(salcy)-$CoOBzF_5$ catalyst. Star copolymers with 14 and 28 PPC arms, respectively, and controlled molecular weights in the range of 2700-8800 g/mol have been prepared (M_w/M_n =1.23-1.61).[71] Successful conversion of the terminal hydroxyl groups with phenylisocyanate demonstrated the potential of the polycarbonate polyols for polyurethane synthesis. (Chapter 2.2)

Other block copolymers were described by Williams and Darensbourg. Williams reported the preparation of **α,ω**-hydroxy-telechelic poly(cyclohexene carbonate) with a dizinc catalyst. The telechelic polymer, was used to polymerize lactide, yielding new triblock copolymers, substantially derived from renewable resources.[72] Furthermore, Darensbourg and coworkers published the one-pot synthesis of a triblock copolymer from propylene oxide/carbon dioxide and lactide.[73]

Copolymerization with other Comonomers

Unlike the expanding spectrum of epoxide monomers, other comonomers that can be copolymerized with carbon dioxide to give functional polycarbonates or polycarbonate/polyesters remain quite limited. Introduction of a third monomer in CO2/epoxide copolymerization is a challenge in terms of the catalyst.

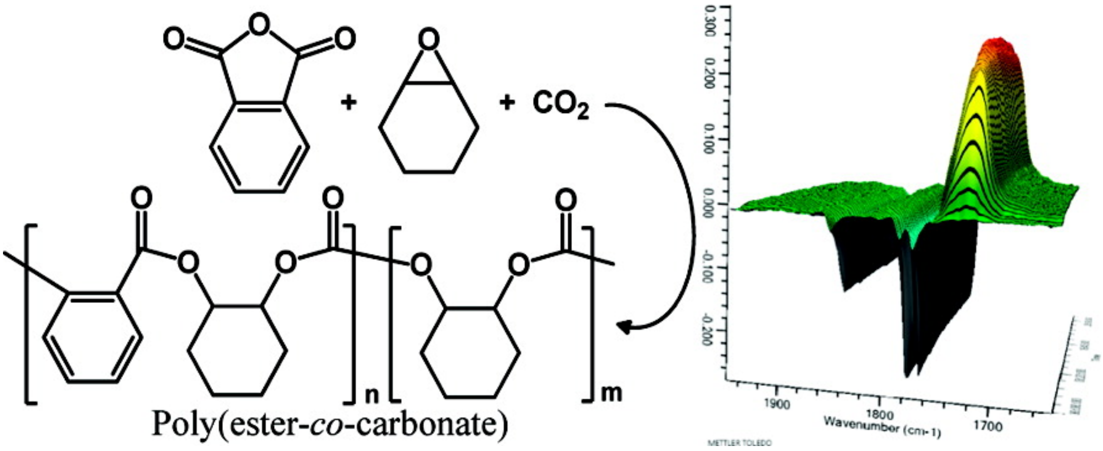

Figure 9. Copolymerization of CHO, anhydrides and carbon dioxide. "Reprinted with permission from Darensbourg et al. *Macromolecules,* **2012***, 45* (*5*), 2242–2248; Copyright 2013 American Chemical Society."[74]

Darensbourg and coworkers published a kinetic study of the terpolymerization of cyclic anhydrides and epoxides, and CO_2 catalyzed by (salen)$Cr^{III}Cl$ complexes.[74] Terpolymerization of a series of cyclic acid anhydrides with several epoxides and carbon dioxide using (salen)CrCl/onium salt catalysts afforded polyesters with high molecular weights and narrow molecular weight distributions. The (salen)CrCl catalyst in the presence of the onium salts with formula PPNX (X = Cl^-, N_3^-) for the copolymerization of the anhydrides, maleic (MA), succinic (SA), phthalic (PA), cyclohexene (CHE), and cyclohexane (CHA) with the epoxides, cyclohexene oxide (CHO), propylene oxide (PO), and styrene oxide (SO) resulted in completely alternating polyester structures.

Furthermore, Coates and coworkers developed a one step route to poly(ester-block-carbonate) diblock copolymers directly from epoxides, CO_2 and cyclic anhydrides using a β-diiminate zinc catalyst.[75] The precise block structure results from a highly selective product-determining step that is pre-rate-determining. Based on the typical reactivity of the monomers, insertion of anhydride is expected to proceed much faster than insertion of CO_2, and insertion of cyclohexene oxide is likely the rate-determining step for polyester as well as polycarbonate formation. [75]

Moreover, Huijser et al. reported ring-opening terpolymerization of epoxides with carboxylic acid anhydrides and CO_2 in the presence of chromium porphyrinato and salen catalysts to form random copolymers.[76] All experiments were performed overnight at 80 °C in toluene using 50 bar of CO_2 pressure. For the resulting polymers, the molecular weight showed a linear correlation with conversion, and the PDI was below 1.6, indicating controlled behavior of the polymerization.

Anhydride comonomers can also be used to thermally and mechanically reinforce pseudo-interpenetrating poly(propylene carbonate) networks by terpolymerization of CO_2, propylene oxide and pyromellitic dianhydride (PMDA).[77] Feng and coworkers showed that pseudo-interpenetrating poly(propylene carbonate) networks (PIPPCNs) can be easily synthesized by the terpolymerization of CO_2, propylene oxide and PMDA. PIPPCNs with a small PMDA addition of no more than 4 mol% relative to PO exhibit dramatically enhanced thermal and mechanical properties, which even exceed those of polyolefins, along with improved toughness.

Kröger et al. described the terpolymerization of carbon dioxide, cyclohexene oxide and lactide, catalyzed by a variety of zinc acetate complexes with new aminoimidoacrylate ligands.[78] The experiments were carried out with a catalyst loading of 0.25 %, using a CO_2 pressure of 4MPa without any further solvents for 16 h. Terpolymerization with *S*-lactide yielded semicrystalline copolymers with a melting point around 167 °C. The glass transition temperatures of the PCLA copolymers lay between the ones for pure PLA (ca. 50 °C, dependent on chain length) and pure PCHC (115 °C) and increase with growing PCHC content, which indicates a random distribution of lactide and polycarbonate in the polymer.

Furthermore, a heterogeneously catalyzed terpolymerization with CO_2, propylene oxide and ε-caprolactone was reported by Hwang et al. and Liu et al.[79,80] Hwang presented the zinc glutarate-catalyzed terpolymerization of CO_2 with PO and ε-caprolactone, producing aliphatic carbonate-ester terpolymers with good biodegradability. For each terpolymerization, the total yield of polymer product that was insoluble in methanol was >99%. Besides that, Huang et al. synthesized a novel aliphatic polycarbonate, poly[(propylene oxide)-*co*-(carbon dioxide)-*co*-(γ-butyrolactone)] via copolymerization of carbon dioxide, propylene oxide (PO) and γ-butyrolactone (GBL).[81]

Conclusion

The copolymerization of CO_2 and epoxides is a promising route to prepare new and often sustainable materials and has represented an emerging field in the last decade. Various innovative catalyst systems have been developed, and several reviews focusing on catalyst design have been published.[5-8] Nevertheless, to date mostly only propylene oxide and cyclohexene oxide have been used as epoxide monomers.

Although gradual advances have been achieved in the design of functional polycarbonates from CO_2, several issues still remain challenging. Currently, the preparation of the catalysts usually involves multiple steps and tailored catalysts have to be used for different epoxide monomers. In addition, precise control on the materials properties of the resulting polycarbonates, particularly with respect to molecular weight, (co)polymer composition and architecture is still a challenge.

In this review a wide range of functional epoxide monomer, suitable for the copolymerization with carbon dioxide, have been described. Derivatives of the commonly used propylene oxide and cyclohexene oxide can also be copolymerized as well as glycidyl ethers, although special catalyst systems are needed to achieve good conversion. The concept of immortal polymerization enables the possibility to produce novel functional polymer architectures. Besides that, terpolymerization with other comonomers, such as cyclic anhydrides or cyclic esters, leads to materials with tailored degradation rates.

The successful translation of aliphatic polycarbonates, especially from carbon dioxide and epoxides, for industrial uses will require further improvements in many aspects, including a deeper understanding of the polymerization mechanism. It is obvious that the full potential of functional polycarbonates from tailored epoxides and CO_2 has not been fully exploited and bears high promise for the future.

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1.2. Common Catalysts and Mechanistic Insights for the Alternating Copolymerization of CO_2 and Epoxides

Introduction

The development of methods to activate and use CO_2 for the preparation of chemicals and materials has seen a renaissance in recent years. Carbon dioxide is abundant, possesses low toxicity and is formed as a waste product in a myriad of industrial processes. Although the use of CO_2 as a chemical feedstock will never be able to compensate emission-based CO_2, its use for the preparation of polymers provides access to high-value products from a low-cost resource. Current examples of the industrial utilization of CO_2 include the large-scale production of urea, salicyclic acid and several carbonate-based materials.[1] (Figure 1)

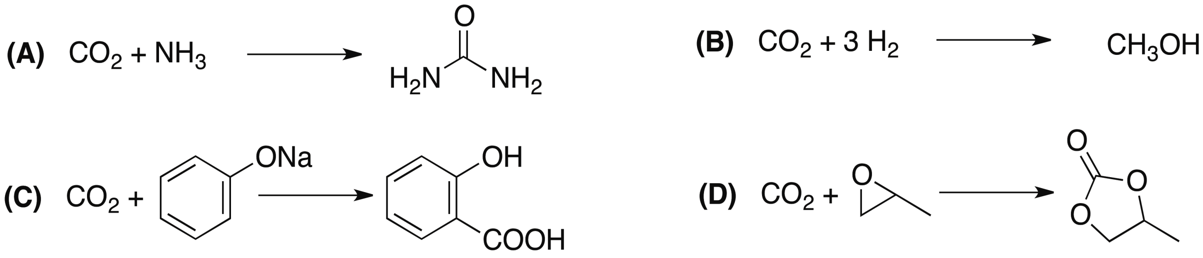


Figure 1. Utilization of carbon dioxide as a C1 feedstock for chemical reactions: (A) synthesis of urea (146 x 10^6 t/a); (B) methanol (6 x 10^6 t/a); (D) salicylic acid (0.060 x 10^6 t/a); (C) cyclic carbonate (0.040 x 10^6 t/a)[2]

Prominent among the processes that uses carbon dioxide (CO_2) as a chemical feedstock is the synthesis of biodegradable polymers.[3–7] Although, carbon dioxide is kinetically and thermodynamically stable, it reacts with highly reactive molecules, such as ring-strained heterocycles, if it is suitably activated. One of the most widely studied reactions of this kind is the copolymerization with epoxides to produce polycarbonates. The outstanding properties of aromatic polycarbonates such as strength, lightness, durability, heat resistance, easy processability, high transparency and good electrical insulation render these materials of high industrial importance with applications in the automotive, electronics, optical media, glazing and sheeting industries as well as across the medical and healthcare sectors.[8]

Although the first report on the use of ethylene oxide (EO) and carbon dioxide to generate a polycarbonate, albeit with numerous ether linkages is already contained in a patent by Stevens in 1966,[9] it was not until the seminal publication by Inoue and coworkers in 1969 that the process was shown to provide an interesting route to polycarbonates with high CO_2 content.[10] Inoue and coworkers employed a heterogeneous catalyst system derived from a 1:1 mixture of diethyl zinc and H_2O. Since these early studies, a variety of other heterogeneous and also homogeneous catalyst systems have been reported for the copolymerization of carbon dioxide and epoxides, especially propylene oxide (PO) and cyclohexene oxide (CHO), which will be described in this chapter. The complete historic development of this area has been comprehensively reviewed by several groups.[2,11–13]

Reaction Mechanism

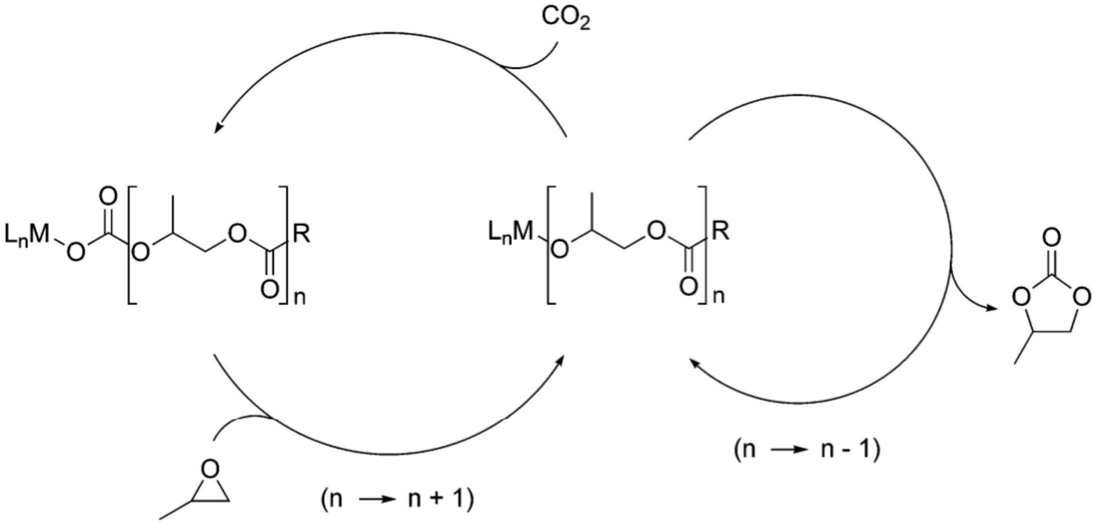


Figure 2. Alternating copolymerization of CO_2 and propylene oxide (PO) and side-product pathway, i.e., the formation of a stable cyclic carbonate through backbiting.[15]

Despite intense research activities in the area of epoxide/carbon dioxide copolymerization, a profound understanding of the underlying mechanisms is still lacking, and thus this field is under continual investigation. However, the generally accepted mechanism for the copolymerization of epoxides and carbon dioxide, as catalyzed by metal complexes is believed to occur via a coordination-insertion mechanism (Figure 2), involving either one or two metal centers.[14]

Homogeneous catalysts of the form L_nMX generally contain only one specific active-site, which can easily be tailored by modifying either the ligand framework (L_n), the catalytically active metal center (M) or the initiating group (X). The typical catalyst systems used currently will be presented below. The initiation and propagation steps involved in the coupling of epoxides and carbon dioxide are shown in Figure 3. The first step is the coordination of the epoxide oxygen to the metal center followed by insertion into the [M]-X bond. Only certain metal alkoxides are able to undergo subsequent CO_2 insertion to form a metal carbonate and hence, the range of catalysts is limited.

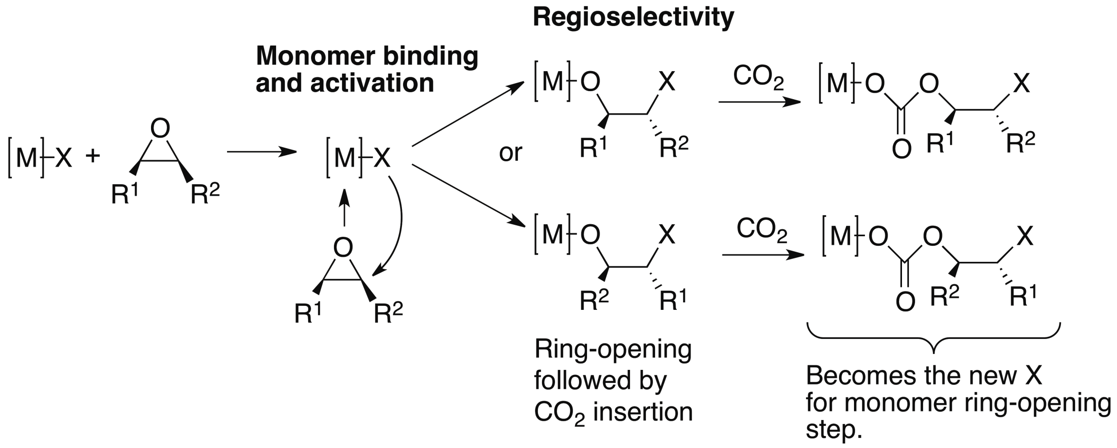


Figure 3. Initiation and propagation steps for the copolymerization of epoxides and CO_2.[16]

When $R^1 \neq R^2$, the epoxide ring-opening can occur regioselective or regioirregular. In general, for R^1 = H and R^2 = alkyl group, ring opening is favored at the least-hindered C-O bond. Stereoselectivity (head-to-head, head-to-tail or tail-to-tail connections) can be detected in the carbonate region (around 155 ppm) in ^{13}C NMR spectra. The resonance of the carbonyl carbon is slightly shifted for the different configurations. (Figure 4)

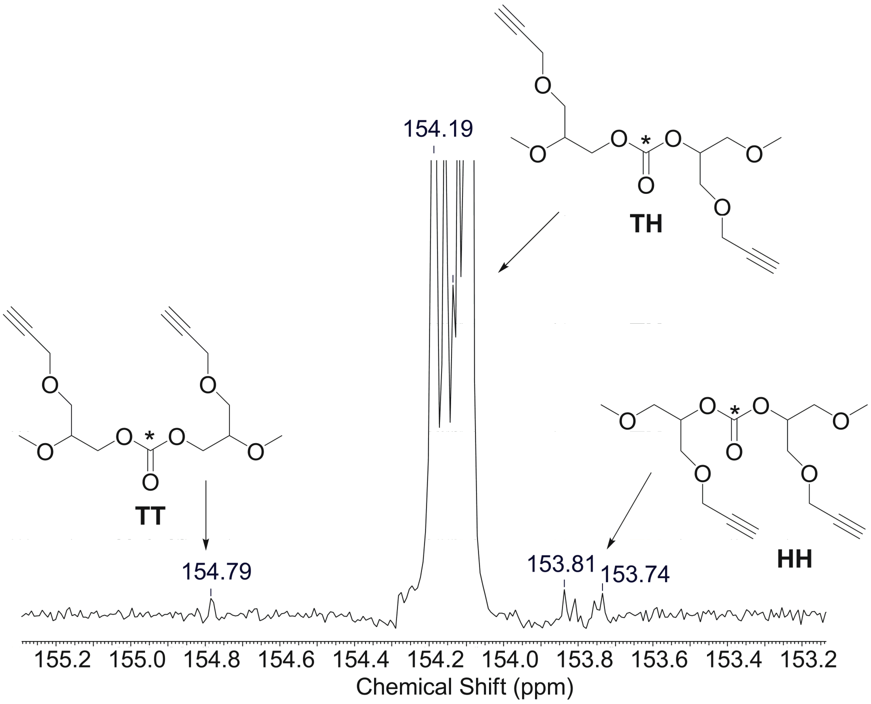


Figure 4. ^{13}C NMR spectrum of poly(glycidyl propargyl ether carbonate) in $CDCl_3$ (75 MHz). Tail-to-tail (TT), head-to-head (HH) and the desired head-to-tail (TH) linkages are shown.

The CO_2 insertion step can occur without prior coordination of carbon dioxide to the metal center.[16] However, consecutive CO_2 insertion has not been observed, as it is thermodynamically unfavored. However, consecutive insertion of two epoxide molecules can occur, especially with Lewis acid catalysts (Figure 5). This leads to the formation of ether linkages. Although these structural defects can be used to tailor the materials properties of the resulting polymer, as described by many groups,[17–20] it is undesired in many applications, and specific catalysts preventing the formation of ether linkages have been designed.

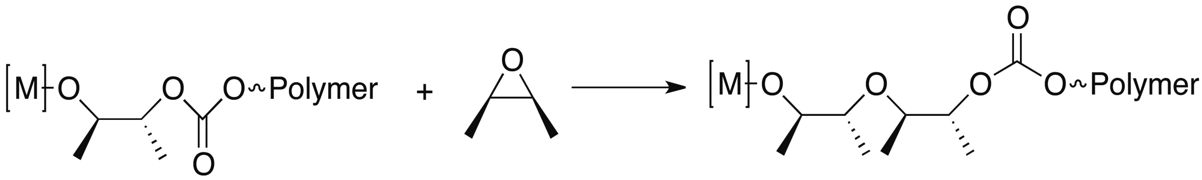


Figure 5. Formation of undesired ether linkages during the epoxide/carbon dioxide copolymerization.[16]

Furthermore, there are two possible chain transfer reactions: intramolecular back-biting and/or reaction with externally added alcohol, water or acid. The backbiting reaction occurs when the metal alkoxide chain end attacks a carbonate linkage of the copolymer chain, forming a cyclic carbonate by-product and regenerating a metal alkoxide/X species. (Figure 6) Depending on the catalyst and the epoxide monomer this process may even be favored over polymer chain growth. In general, this process is faster for aliphatic epoxides, epoxides containing electron-withdrawing groups and when the growing polymer chain dissociates from the metal center. The thermodynamically more favored stable product from epoxide/CO_2 coupling is the five-membered cyclic carbonate and increasing the reaction temperature usually leads to an increase of the stable cyclic carbonate production, for entropic reasons.

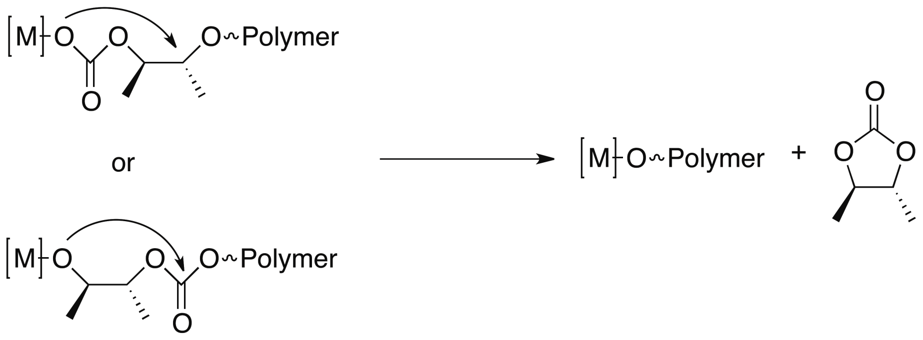


Figure 6. Two possible modes of back-biting for cyclic carbonate formation.[16]

The cyclic byproduct is clearly undesired, however special catalysts have been prepared to synthesize directly five-membered cyclic carbonates from epoxides and CO_2, which can be used as solvents or as electrolytes in batteries.[1] The chain transfer reaction including externally added alcohols on the other hand can be used for the incorporation of specific initiators or the synthesis of various polymer architectures such as linear or star like block copolymers.[21–23]

Although contrary hypotheses exist on the initiation and propagation mechanism of the alternating CO_2/epoxide copolymerization, several publications mostly consider homogeneous systems to work in a cooperative (binary or bimetallic) pathway.[15] Among the first catalysts investigated to prove the bimetallic mechanism were β-diiminate (BDI) complexes, which are most active in their dimeric state. At very low concentration, the dimerization equilibrium is shifted to the monomer state, and almost no catalytic activity is observed.[17,24,25]

An alternative source for polycarbonates synthesized directly from carbon dioxide is the oxetane/CO_2 copolymerization. Since the ring-strain of oxetanes is lower than that of epoxides (approx. 106 kJ/mol versus 114 kJ/mol), their copolymerization is thermodynamically less favored. Nevertheless, the copolymerization reaction of oxetanes and CO_2 occurs readily under similar catalytic conditions.[26] In contrast to the aforementioned five-membered cyclic carbonates, the six-membered analogues derived from oxetanes and CO_2 are thermodynamically metastable, which offers two advantages. First, compared to the copolymerization of carbon dioxide with epoxides, a lower extent of backbiting occurs and second, the resulting poly(trimethylene carbonate)s can also be synthesized from these heterocyclic compounds, following a ring-opening polymerization (ROP) mechanism. The ROP of ethylene carbonate derivatives leads to a loss of carbon dioxide and consequently the formation of ether linkages.

CO_2 copolymerization catalysts

Heterogeneous catalysts

Even though enormous progress has been made in the development of homogeneous catalysis in recent years, the traditional heterogeneous zinc-dicarboxylate systems remain industrially relevant, as they are easy to prepare and handle, non-toxic and economically viable.[10,15,27] Since the first publication on CO_2/epoxide copolymerization of Inoue and coworkers in 1969[10] a variety of new catalyst systems has been developed, and only a selection of the most relevant catalyst “highlights” will be presented here. This type of polymerization of often called immortal polymerization. Immortal polymerization can afford polymers with a controlled molecular weight, is often overlooked and leads to narrow molecular distribution, even in the presence of a chain transfer reaction.

Zinc glutarate $[Zn(O_2C(CH_2)_3CO_2]_n$ (ZnGA) is the most widely used heterogeneous catalyst for the copolymerization of epoxides, such as propylene oxide and cyclohexene oxide, and carbon dioxide due to its simple preparation, high productivity and the possibility to generate high molecular weight copolymers. There are several ways to prepare ZnGA by the introduction of different zinc sources such as $ZnEt_2$, $Zn(OH)_2$, ZnO or $Zn(OAc)_2$ and carboxylate sources (e.g. glutaric acid, glutaric anhydride or glutaronitrile).[28–30] The key parameters to control the productivity are the degree of crystallinity and the size distribution of the crystallites. Just recently Ree et al. reported new findings in the catalytic activity of ZnGA and its application in the chemical fixation of CO_2 into polycarbonates and their derivatives,[29] i.e a major improvement of the yield of poly(propylene carbonate) as well as the extension to the terpolymerization of CO_2, PO and d-valerolactone (VL). Terpolymers with high molecular weights and yields could be obtained by adjusting the PO/VL feed ratios.

Other studies have dealt with the introduction of various dicarboxylic acids derivatives of zinc glutarate and mixtures of di- and mono-acids with variable success.[31,32]

Double metal cyanides (DMC), e.g. $Zn_3[M(CN)_6]$, where M = Fe(III) or Co(III), are also a promising class of heterogeneous CO_2 copolymerization catalysts. [8,33–35] For example Ha and coworkers synthesized DMC catalysts by reacting $K_3Co(CN)_6$ with ZnX_2 (X = F, Cl, Br, I) in the presence of *tert*-butyl alcohol and poly(tetramethylene ether glycol) as complexing agents. These catalysts showed high activity for the copolymerization of epoxides and CO_2, affording aliphatic polycarbonates of low polydispersity and moderate molecular weight.

Another interesting catalytic system results from the combination of alkylmetal compounds and pyrogallol, which was described to be very active for the propylene oxide/carbon dioxide copolymerization.[36] Furthermore, several groups employed catalysts from this class for the copolymerization of CO_2 and glycidyl ethers to obtain functional polycarbonates.[5,37–39]

As Klaus et al. describe in their review, the optimal Zn–Zn distance for CO_2/epoxide copolymerization for all catalysts is assumed to lie between 3 and 5 Å. These results strongly indicate that for heterogeneous systems a very specific metal–metal distance is required for high copolymerization activities. However, the activities with such systems are restricted due to a constrained surface and diffusion limitations.[2] Despite these difficulties, the ease of synthesis and inexpensive nature of these materials makes them highly attractive.

Homogeneous catalysts

As described above, the precise nature of the active sites of heterogeneous catalysts remains unclear. The difficulty in defining the active sites made structure/activity relationships, and therefore catalyst design, very challenging. In order to obtain a solid mechanistic understanding and to overcome the high polydispersities of the copolymers produced by such systems, which resulted from inequivalent active sites and generally low CO_2 incorporation rates, well-defined homogeneous catalysts were developed.

Copolymerization catalyzed by zinc complexes

In recent years, new zinc complexes have been reported to exhibit high catalytic activity for the copolymerization of carbon dioxide and epoxide derivatives, some of which even allow the synthesis of polycarbonates with controlled molecular weights. (Figure 7)

In 1995, Darensbourg and Holtcamp reported the first discrete zinc complexes for the alternating copolymerization of carbon dioxide and epoxides.[40] Compared to heterogeneous systems, which are often linked to poor reproducibility and the production of non-uniform polymers, homogeneous systems exhibit only one highly defined active site.

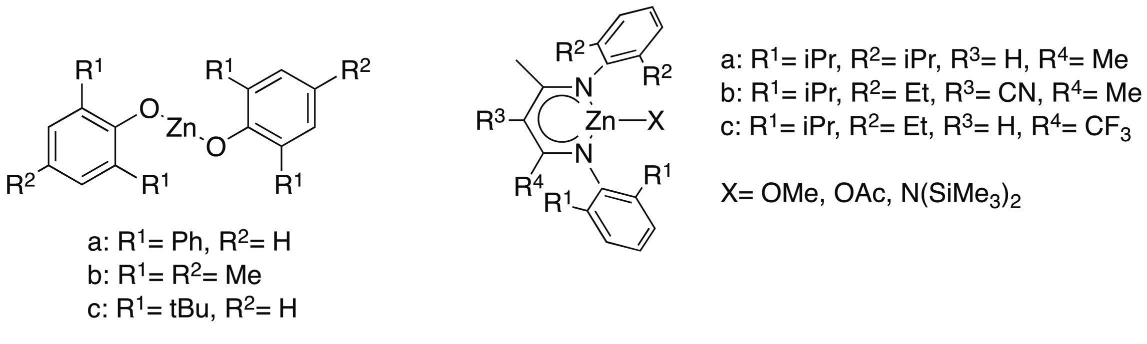


Figure 7. Zinc complexes developed for the copolymerization of epoxides and carbon dioxide. [2,12–14]

Furthermore, Darensbourg and coworkers developed distorted tetrahedral zinc phenoxide complexes, which carry two phenoxide ligands with bulky substituents in the 2 and 6 positions and two labile donor ligands, e.g. (2,6-diphenylphenoxide)$_2$-Zn(II)(THF)$_2$.[19] In a related study, Dinger and Scott reported that zinc–phenoxide cluster compounds showed activity for the alternating copolymerization of CHO and CO_2. A variety of solvent-dependent tri-, tetra-, penta-, and hexanuclear compounds were synthesized from tris(3,5-dialkyl-2-hydroxyphenyl)methane derivatives and $ZnEt_2$.[41]

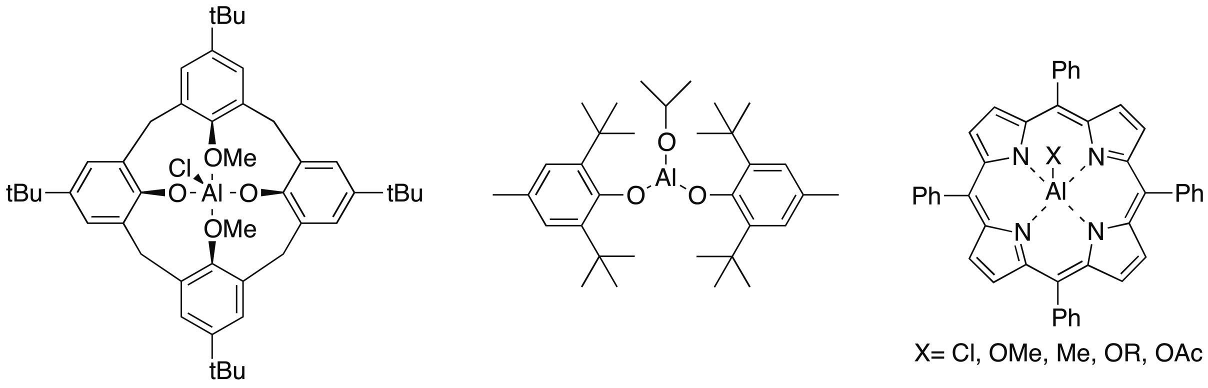
Coates and coworkers reported zinc bis(β-diiminates) to be more active than Darensbourg's zinc bis(phenoxides) for the alternating copolymerization of carbon dioxide and cyclohexene oxide. The zinc bis(β-diiminates) were dimeric in the solid state as shown by the X-ray crystallographic analysis, while the ^1H NMR data revealed monomeric solvation.[18,25,42] Several key design features, including initiating groups, steric demand of the ligands, and electronic properties, drastically altered the turn-over-frequency (TOF) of the catalysts. To model the growing polycarbonate chain, zinc–acetate, zinc–methoxide, and zinc–isopropoxide complexes were synthesized to mimic zinc carbonates and zinc alkoxides. Zinc acetate models were produced from the deprotonated (bdi)Li adducts and $Zn(OAc)_2$[18] or by addition of acetic acid to [(bdi)ZnEt] compounds.[25,43] (bdi)ZnEt was generated by the addition of $ZnEt_2$ to (bdi)H ligands.

In 2005, Lee and co-workers reported a series of zinc anilido-aldimine complexes which showed comparably high TOFs (700–3000 h^{-1}) for the production of poly(cyclohexene carbonate) with high molecular weights (90 000–280 000 g/mol).[17] Kröger et al. described the alternating copolymerization of cyclohexene oxide an CO_2 catalyzed by zinc complexes with new 3-amino-2-cyanoimidoacrylate ligands.[24,44]

Aluminum and Manganese Catalysts

In 1978, Inoue and coworkers developed the first single-site catalyst for the copolymerization of epoxides and CO_2. Their catalyst was based on a tetraphenylporphyrin (tpp) ligand framework and an aluminum metal center. Their catalyst was active for the copolymerization of both CHO or PO and CO_2 with $EtPh_3PBr$ as a co-catalyst, producing polycarbonates with molecular weights between 3500 and 6000. The polydispersity indices (PDI, = M_w/M_n) were below 1.10, albeit the reactions took 13 days to reach completion.[45,46] Recently, aluminum alkoxide complexes were also found to be active in the epoxide/CO_2

copolymerization.[47,48] Furthermore Kuran and coworkers reported an aluminum calix[4]arene, derived from 25,27-dimethoxy-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene and diethylaluminum chloride, which is active for the copolymerization.[49] Selected examples for the mentioned epoxide (co)polymerization catalysts based on aluminum are shown in Figure 8.



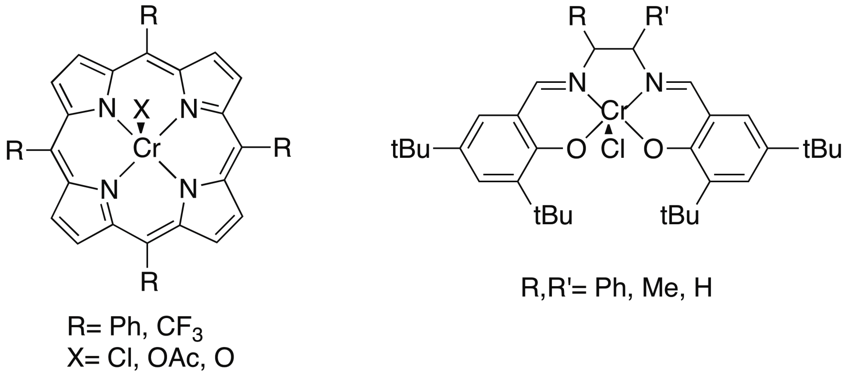
X= Cl, OMe, Me, OR, OAc

Figure 8. Aluminum complexes for the copolymerization of epoxides and carbon dioxide.

As described above, aluminum complexes are indeed active for the copolymerization of epoxides and CO_2. However, they are plagued by low activities and yield polycarbonates with high percentages of ether linkages.[47-49] It appears that without additives, current aluminum catalysts do not cleanly generate alternating copolymers.

Chromium Catalysts

The first example of a chromium complex as a catalyst for epoxide/CO_2 copolymerization was reported by Holmes and coworkers. They synthesized a fluorinated chromium porphyrin complex, which was active in presence of a DMAP cocatalyst (Figure 9). Their catalyst system showed a TOF exceeding 150 h^{-1} for cyclohexene oxide/CO_2 copolymerization, but the reaction conditions were harsh (110 °C, 222 atm CO_2).[50] Besides this complex, several other porphyrin chromium complexes are suitable for the copolymerization and cyclization of epoxides and carbon dioxide.[51] A wide range of epoxides, including PO, *trans*-2-butene oxide, epichlorohydrin, CHO, and cyclopentene oxide, were rapidly converted to the corresponding cyclic carbonates.[13]



R= Ph, CF_3
X= Cl, OAc, O

R,R'= Ph, Me, H

Figure 9. Chromium complexes for the copolymerization of epoxides and carbon dioxide.

Darensbourg's group employed a chromium bis(salicylidene)diamine complex. It catalyzed the alternating copolymerization of carbon dioxide and cyclohexene oxide at 80 °C at 58 atm (TOF = 10.4 h^{-1}) to afford a copolymer with a molecular weight of 8900 g/mol (PDI = 1.20). The incorporation of carbon dioxide into the copolymer was almost quantitative, but the formation of cyclic carbonate was inavoidable.[52,53]

Furthermore, Jacobsen and co-workers found [(salen)CrCl] complexes to be highly active in the asymmetric ring-opening of epoxides. This elegant work has since led to many crucial discoveries in the coupling of epoxides with CO_2; in fact the first report of (salen)chromium-mediated epoxide–CO_2 polymerization appeared in a patent in 2000 by Jacobsen and co-workers.[54–57] Several other chromium based catalyst systems have been described by Chisholm et. al,[58] Li et al.,[59] Nozaki and coworkers[60] and Rieger et al. [61] The latter prepared mono- and dinuclear salphen-type complexes. Kinetic studies indicated that the reaction occurs predominately in a bimetallic fashion in the absence of cocatalysts for both mono- and dinuclear complexes. The dinuclear system maintains its activity even under highly diluted conditions (c_{PO}/c_M = 20000) at which the mononuclear system loses its efficiency. The effect of the nature and amount of added cocatalyst on the catalytic performance was investigated as well, indicating a binary propagation mechanism both in mononuclear and dinuclear systems in the presence of cocatalysts.[61]

More recently, detailed studies have been carried out in attempt to understand the role of the cocatalyst and elucidate the reaction mechanism and have meanwhile been reviewed.[13,14]

Cobalt Catalysts

The substitution of chromium for cobalt in porphyrin and salen catalysts increased both the activity and selectivity for copolymer formation, particularly with propylene oxide. The first cobalt based catalyst system, $Co(OAc)_2$, was already reported as early as 1979 by Soga et al. with an extremely low TOF (0.06 h^{-1}).[62] Since then, numerous reports on cobalt-catalyzed coupling of epoxides and carbon dioxide have been published, especially in the last few years.[25,63–65] (Figure 10)

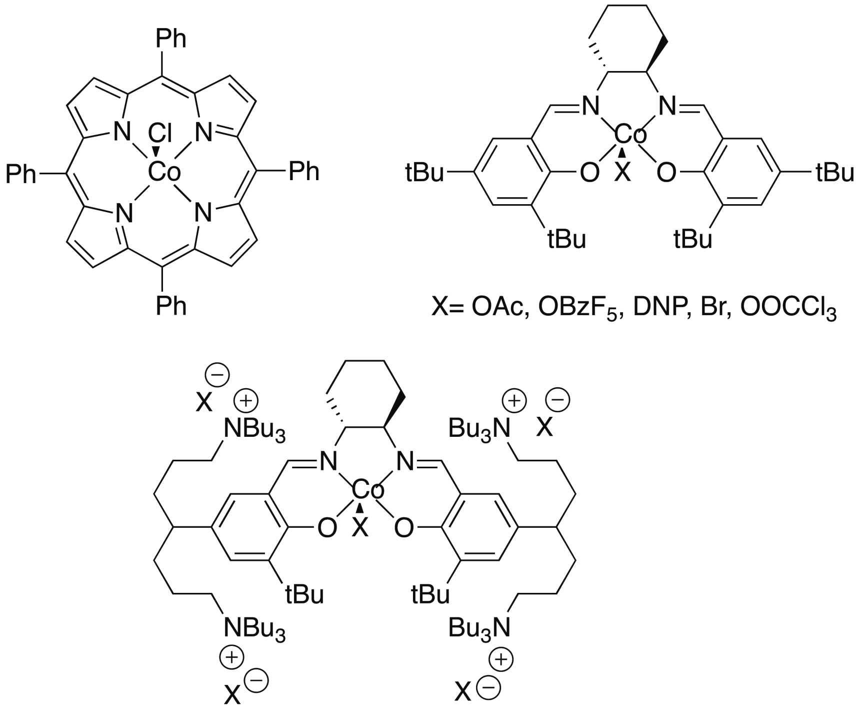


Figure 10. Cobalt complexes for the copolymerization of epoxides and carbon dioxide.

In 2003 Coates and coworkers described various studies concerning PO/CO_2 copolymerization using cobalt-salen complexes ((salcy)CoX).[25,66] The complexes (*R*,*R*)-(salcy)CoCl, (*R*,*R*)-(salcy)CoBr, (*R*,*R*)-(salcy)CoOAc, and (*R*,*R*)-(salcy)$CoOBzF_5$ were found to be highly active catalysts, yielding poly(propylene carbonate) (PPC) with no detectable byproducts. These polymerizations were regarded to be of a living nature. The PPC generated using these catalyst systems is highly regioregular and has up to 99% carbonate linkages with a narrow molecular weight distribution. Thereafter in late 2006, Lu and co-workers reported a detailed study on salenCoX complexes and PO, investigating a number of different ligand substitutions, initiating groups (such as Cl, Br, NO_3, ClO_4), and a variety of different co-catalysts. Using ionic salts, it was ascertained that the ideal ionic co-catalyst in terms of activity and selectivity was a combination of a bulky cation ($[PPN]^+ > [n\text{Hept}_4N]^+ > [n\text{Bu}_4N]^+$) and a nucleophilic anion with poor leaving group ability ($Cl^- > Br^- > I^- > ClO_4^-$).[59] To further improve the catalyst performance advanced salen-type ligands were synthesized. For example Nozaki and coworkers designed a cobalt complex with two acetate ligands and a salcyl-type ligand. The key of the catalyst design are the piperidinyl and piperidinium arms. When the two acetate ligands initiate the copolymerization, a piperidinium arm should control the nucleophilicity of the propagating species by protonating the anionic propagating species that is released from the cobalt center. The protonated propagating species is not sufficiently nucleophilic to form the corresponding cyclic carbonate through back-biting, but it can react with carbon dioxide or activated epoxide, once it is deprotonated by one of the two piperidinyl groups.[67]

Recently the Rieger group described a series of cobalt(III) chloride porphyrin complexes of the general formula 5,10,15,20-tetra(*p*-alkoxy)phenylporphyrin cobalt(III) chloride. Complexes bearing longer alkoxy-substituents revealed the highest polymerization activity and produced polycarbonates with the highest molecular weights in the range of 10.000 to 50.000 g/mol. However, all substituted catalysts display a reduced tolerance to increased temperature with respect to PPC formation. Studies of the resulting polymer microstructures showed excellent, near perfectly alternating head-to-tail epoxide incorporation at lower polymerization temperatures.[68]

Other metal centers.

Lanthanoid metal complexes, which have been widely utilized in organic syntheses since 1990s, have also been developed as catalysts for the alternating copolymerization of carbon dioxide and epoxide. Recently a rare-earth metal system comprised of yttrium tris[bis(2-ethylhexyl)phosphate], $Al\textit{i}Bu_3$, and glycerol was found to be highly active for propylene oxide/CO_2 copolymerization. The molecular weight reached was very high, exceeding 50.000 g/mol, however the product contained only up to 30% carbonate linkages.[69] This system also exhibited activity for the alternating copolymerization of CO_2 with epichlorohydrin[70] and glycidyl ethers.[71] Other rare-earth metal systems consisted of yttrium carboxylates [$Y(CO_2CF_3)_3$ or $Y(CO_2RC_6H_4)_3$, $ZnEt_2$, and glycerine. [72–74]

Iron-containing complexes have also been reported as active catalysts.[75,76] Furthermore, iron–corrole complexes were found to copolymerize epoxides with CO_2, and the first case of an iron-catalyzed propylene oxide/CO_2 copolymerization has been accomplished. Moreover, the glycidyl phenyl ether (GPE)/CO_2 copolymerization with this catalyst provided a crystalline material as a result of the isotactic poly(GPE) moiety.[78] Recently, a dinuclear iron complex[77] and a mononuclear iron complex[2] were shown to catalyze epoxide/CO_2 copolymerization, but the reported examples are still limited to cyclohexene oxide (CHO).

Summary

The investigation of the alternating copolymerization of epoxides and carbon dioxide has been a topic of interest for more than 40 years, and it still is under intense investigation. After all these years of research, several ligand/complex families have been developed and mechanistic insights have been gained. Significant advances both in activity and selectivity of the systems have been made. Homogeneous catalysts for CO_2–epoxide copolymerization offer significant increases in polymerization rates as well as selectivity compared to their heterogeneous counterparts.

Studies employing traditional phenoxide and BDI catalyst systems indicate that either a coordination-insertion mechanism or a bimetallic mechanism is probable for epoxide/CO_2 copolymerization.

The most active and selective catalyst systems at present are Cr(III) or Co(III)-salen complexes. The addition of cocatalysts to traditional porphyrin or salen complexes can considerably influence the efficiency of these systems, and also aluminum, zinc, iron or rare-earth metals complexes were successfully used for the copolymerization of epoxides and carbon dioxide.

Aliphatic polycarbonates are currently niche products, due in part to the corresponding costs but also to the limited range of materials properties. The recent development of catalysts that enable the controlled synthesis of block and random terpolymers and control of stereo and regiochemistry is of great interest, as described in Chapter 1.1.

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Chapter 2: Variation of the Polymer Architecture

2.1. CO_2-Based Nonionic Surfactants: Solvent-Free Synthesis of Poly(ethylene glycol)-*b*-Poly(propylene carbonate) Block Copolymers

Jeannette Hilf [1,†], **Patricia Schulze**[1] **and Holger Frey** [1,*]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg 10-14, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany

[†]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

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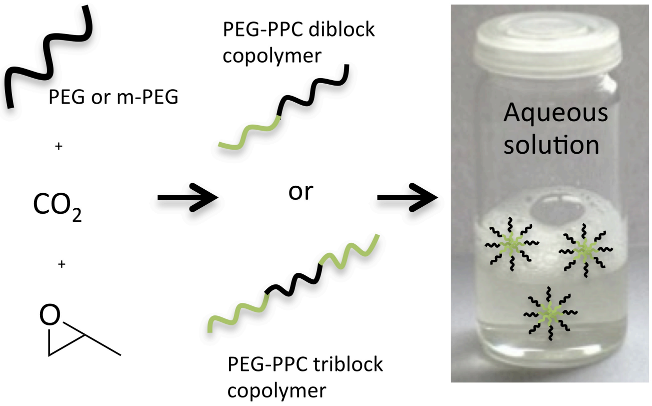


Abstract

Copolymerization of CO_2 and propylene oxide (PO) has been employed to generate amphiphilic polycarbonate block copolymers with hydrophilic poly(ethylene glycol) (PEG) block and apolar poly(propylene oxide) (PPC) block. The established (R,R)-(salcy)-$CoOBzF_5$ complex was used as a catalyst and bis(triphenylphosphine)iminium chloride (PPNCl) as an ionic cocatalyst in the solvent-free synthesis. A series of poly(propylene carbonate) (PPC) di- and triblock copolymers, PPC-*b*-PEG and PPC-*b*-PEG-*b*-PPC, respectively, with narrow molecular weight distributions (PDIs in the range of 1.05-1.12) and tailored molecular weights (1500-4500 g/mol) was synthesized via an alternating carbon dioxide (CO_2)/propylene oxide copolymerization, using PEG or mPEG as an initiator. The resulting block copolymer surfactants were characterized by NMR, GPC, IR, TGA and DSC with respect to their molecular structure and thermal properties. Critical micelle concentrations (CMC) were determined, ranging from 3-30 mg/L, depending on the degree of polymerization of the PPC and PEG blocks and the structure (AB diblock vs. ABA triblock) of the block copolymers. Nonionic poly(propylene carbonate)-based surfactants represent an alternative to established surfactants based on polyether structures.

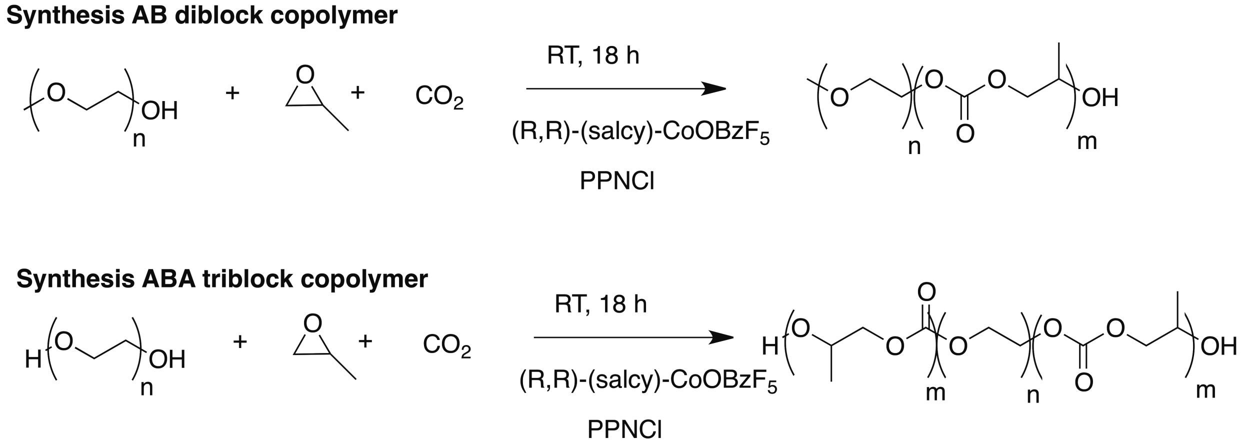
Introduction

Chemical fixation of CO_2 is an attractive topic from the viewpoint of carbon resources utilization. An effective chemical solution is to convert CO_2 into new chemical products or materials. Carbon dioxide is abundant, cheap, nontoxic and nonflammable. However, chemical transformation of carbon dioxide remains a challenge due to its thermodynamic stability. The synthesis of poly(propylene carbonate) (PPC) by alternating copolymerization of carbon dioxide (CO_2) and propylene oxide (PO) has drawn much attention in both academia and industry, and several highly efficient catalyst systems have been developed to date.[1–6] PPC exhibits favorable properties such as degradability, transparency, excellent adhesion and low permeability for oxygen and water.[7] Furthermore it burns gently in air, producing only CO_2 and water.[8] However, PPC is hydrophobic and lacks pendant functionalities for dye or drug attachment.[9] Furthermore, its mechanical properties are limited. Several strategies, such as terpolymerization with other comonomers,[10–13] crosslinking[14] or the synthesis of block copolymers have been developed in recent years to improve the properties of PPC with respect to these drawbacks.

Block copolymers are widely used in many areas, ranging from thermoplastic elastomers to drug delivery, antifouling agents, microelectronics, and optics.[15–18] However, surprisingly few reports have been published on block copolymers based on polycarbonate blocks synthesized from CO_2. Triblock copolymers from lactide and telechelic poly(cyclohexene carbonate) were prepared by Williams et. al.[19]. In a key work, Lee and coworkers demonstrated in 2010 the use of the immortal CO_2/propylene oxide copolymerization for the precise control of molecular weight and architecture of a variety of block copolymers[9]. Furthermore, Coates et al. employed living block copolymerization for the synthesis of multiblock poly(cyclohexene carbonate)s with sequence control.[20] In addition, several groups developed one step-routes for the synthesis of diblock copolymers from epoxides, cyclic anhydrides and carbon dioxide.[21–24]

Amphiphilic block copolymers (AB or ABA-type) with large solubility differences between hydrophilic and hydrophobic segments can form a variety of supramolecular structures and are often used as polymer surfactants.[25,26] Amphiphilic block copolymers based on the biocompatible poly(ethylene glycol) (PEG) and a biodegradable hydrophobic block, such as poly(lactide) showed no toxicity and led to prolonged blood circulation time for drugs in vivo due to the stealth effect of PEG. Sustained release of drug molecules was observed, owing to the controlled degradation of the biodegradable polyester block.[27,28]

PEG based poly(carbonate) block copolymers that rely on the long established ring-opening polymerization of cyclic carbonate monomers can be found in literature.[29,30] However, to the best of our knowledge, nonionic polymer surfactants composed of PEG as the hydrophilic block combined with a hydrophobic poly(propylene carbonate) (PPC) block, prepared directly from CO_2 and propylene oxide (PO) have not been reported to date. In the present work, we describe the synthesis of amphiphilic AB- and ABA di- and triblock copolymers consisting of PEG and poly(propylene carbonate) (PPC) blocks, using commercially available PEGs as chain transfer agents (Scheme 1).


Synthesis AB diblock copolymer

Synthesis ABA triblock copolymer

Scheme 1: Solvent-free synthesis of PEG/PPC di- and triblock copolymers

Our work is based on the abovementioned results by Lee and coworkers, who described a variety of PPC block or graft copolymers with precise control of chain length and topology.[9,31,32] In this work, among numerous other polymer structures the authors also demonstrated block copolymer synthesis using mono- and difunctional PEG. They relied on the concept of "immortal polymerization" introduced by Inoue long ago,[33] using commercially available polymers as initiators, yet not elaborating on surfactant properties of the materials.

In our approach, we aimed at a considerably simplified synthesis protocol that is easily amenable for scale-up: In contrast to the strategy reported by Lee, who used a catalyst that has to be prepared in a multi-step synthesis,[34] we employed the established (R,R)-(salcy)-$CoOBzF_5$ complex and bis(triphenylphosphine)iminium chloride (PPNCl) as an ionic cocatalyst.[3] In addition, we have developed a solvent-free and air-tolerating synthesis procedure, which is of crucial importance for real-world applications of the resulting PPC-based surfactants. A series of di- and triblock copolymers with systematically varied molecular weights of both blocks has been prepared. The materials have been fully characterized in terms of composition and molecular structure. Furthermore, the surfactant properties in aqueous solution have also been characterized.

Experimental Section

Materials and Instrumentation.

Propylene oxide (PO, 98%, Aldrich) was distilled over CaH_2 under reduced pressure prior to use. Poly(ethylene glycol) (PEG) and poly(ethylene glycol monomethyl ether) (mPEG) (Sigma Aldrich) were dried in vacuum before use. Carbon dioxide (>99.99%) was used as received. All other reagents were purchased from Aldrich or Acros and used as received.

NMR characterization.

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer, operated at 300 and 75.4 MHz respectively, at 21°C and the chemical shifts are given in parts per million (ppm). All spectra were referenced to the residual solvent signal.

Gel permeation Chromatography.

For SEC measurements in DMF (containing 0.25 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column ($10^6/10^5/10^4$ g mol^{-1}), a UV (275 nm) and a RI detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service.

Differential Scanning Calorimetry.

DSC curves were recorded with a Perkin-Elmer DSC 7 CLN2 in the temperature range from – 100 to 150 °C at heating rates of 10 K min^{-1} under nitrogen.

Thermogravimetric Analysis.

TGA measurements were obtained with a TGA Perkin-Elmer Pyris 6 in a temperature range from 30-600 °C at heating rates of 20 K min^{-1} under nitrogen.

IR-Spectroscopy.

FT-IR spectra were recorded using a Thermo Scientific iS10 FT-IR spectrometer, equipped with a diamond ATR unit.

Critical Micelle Concentration.

Surface tension measurements to determine the critical micelle concentrations (CMC) were performed with a Dataphysics DCAT 11 EC tensiometer, equipped with a TV 70 temperature control unit, a LDU 1/1 liquid dosing and refill unit, as well as a RG 11 Du Nouy ring. Surface tension data was processed with SCAT v3.3.2.93 software. All solutions for surface tension measurements were stirred for 180 s at a stirring rate of 60%. After a relaxation period of 180 s, three surface tension values were measured. The mean values of the three measurements were plotted against the logarithm of the concentration. The slopes of the traces at high concentrations as well as in the low concentration range were determined by linear regression. The concentration at the fits' intersection was the CMC. The Du Nouy ring was rinsed thoroughly with water and annealed in a butane flame prior to measurements.

Synthesis of (R,R)-(salcy)-$CoOBzF_5$.

(R,R)-(salcy)$CoOBzF_5$ was prepared as described by Coates et. al.[3] Recrystallized (R,R)-(salcy)-Co^{II} and pentafluorobenzoic acid (0.42 g, 2 mmol) were added to a 50 mL round-bottomed flask charged with a Teflon stir bar. Toluene (20 mL) was added to the reaction mixture, and it was stirred open to air at 22 °C for 12 h. The solvent was removed by rotary evaporation at 22 °C, and the solid was suspended in 200 mL of pentane and filtered. The dark green material was dried in vacuo and collected in quantitative yield (1.5 g). ^1H NMR (DMSO-d_6, 400 MHz): δ 1.30 (s, 18H), 1.59 (m, 2H), 1.74 (s, 18H), 1.90 (m, 2H), 2.00 (m, 2H), 3.07 (m, 2H), 3.60 (m, 2H), 7.44 (d, 4H) 2.5 Hz, 2H), 7.47 (d, 4H) 3.0 Hz, 2H), 7.81 (s, 2H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 24.39, 29.61, 30.13, 30.42, 31.55, 33.57, 35.83, 69.38, 118.59, 128.78, 129.29, 135.86, 141.83, 162.21, 164.66. Carbons on the phenyl group of pentafluorobenzoate were not assigned in the ^{13}C NMR spectrum owing to complex carbon fluorine splitting patterns.

Synthesis of PEG/PPC di- and triblock copolymers (exemplified for sample 9).

A 100 mL Roth autoclave was dried under vacuum at 40 °C. (R,R)-(salcy)-CoOBzF5 (11.7 mg, 0.0143 mmol), the cocatalyst (PPN)Cl (8.2 mg, 0.014 mmol), PO (1.6 mL, 24 mmol) and 1g (0.5mmol) dried mPEG 2000 g/mol were placed in a glass tube with a Teflon stir bar inside the autoclave. The autoclave was pressurized to 50 bar CO2, and the solution was stirred at 30 °C for 18 h. The reactor was vented, the polymerization mixture was dissolved in chloroform (5 mL), quenched with 5% HCl solution in methanol (0.2 mL) and then precipitated in ice-cold pentane. The polymer was collected and dried in vacuo. Yield 98 % 1H NMR (CDCl3-d1, 300 MHz): δ (ppm) = 4.99 (methine CH backbone), 4.17 (methylene CH2), 3.50 (PEG backbone), 3.37 (-OCH_3 mPEG) and 1.30 (CH_3).

Results and Discussion

Synthesis and Molecular Characterization

Amphiphilic PPC/PEG block copolymers have been prepared by copolymerization of CO_2 and propylene oxide, systematically varying molecular weights of both blocks. Precise control of the chain length and architecture of block and graft copolymers can be achieved in CO_2/PO copolymerization, using the concept of immortal polymerization by the addition of various chain transfer agents.[9] In the current work, poly(ethylene glycol) containing two hydroxyl end groups and poly(ethylene glycol) mono-methyl ether containing one hydroxyl group were used as chain transfer agents, i.e., as initiators for the poly(propylene carbonate) synthesis (cf. Scheme 1). All polymerizations were carried out under identical reaction conditions, i.e., room temperature and 50 bar CO_2 pressure with a (R,R)-(salcy)$CoOBzF_5$ catalyst and bis(triphenylphosphine(iminium chloride) (PPNCl) as a cocatalyst. It should be emphasized that no solvent was used for all polymerizations, since PEG as well as mPEG are soluble in neat propylene oxide and – with respect to the hydrophilic-hydrophobic balance - the targeted molecular weights of the nonionic, PPC-based surfactants were moderate, thereby keeping viscosity low. Conversion of propylene oxide to the desired poly(propylene carbonate) block copolymer was quantitative. The catalyst and cocatalyst were efficiently removed from the polymer solution after polymerization via precipitation in ice cold pentane, as demonstrated by NMR.

Based on a given mPEG or PEG chain length, systematically varied degrees of polymerization for the PPC block were obtained by adjusting the monomer/initiator ratio, as shown in Table 1, which summarizes the results with respect to molecular weights, polydispersities as well as thermal properties.

Table 1. Characterization data for all PEG-*b*-PPC copolymer samples prepared

#	**Sample^a**	**M_n g/mol (NMR)**	**M_n^{b} g/mol (SEC)**	**PDI (SEC)**	**T_g^{d} °C**	**T_m^{d} °C**	**CMC mg/L**
1	$mPEG_{25}$	1100	1100	1.06		38.7	-
2	$mPEG_{25}$-*b*-PPC_{10}	2100	1500	1.07	-42.6	26.5	16
3	$mPEG_{25}$-*b*-PPC_{18}	3000	2200	1.17	-40.8	-	6
4	$mPEG_{25}$-*b*-PPC_{37}	4900	2600	1.11	-19.3	-	5
5	$mPEG_{45}$	2000	2000	1.05		54.9	-
6	$mPEG_{45}$-*b*-PPC_{2}	2200	2500	1.12	-44.9	51.4	-
7	$mPEG_{45}$-*b*-PPC_{16}	3600	3100	1.06	-43.0	41.3	17
8	$mPEG_{45}$-*b*-PPC_{27}	4700	3800	1.06	-39.8	30.7	13
9	$mPEG_{45}$-*b*-PPC_{45}	6600	4500	1.08	-33.1	29.7	8
10	PEG_{45}	2000	2000	1.05		54.8	-
11	PPC_{9}-*b*-PEG_{45}-*b*-PPC_{9}	3800	2700	1.12	-43.4	23.3	30
12	PPC_{18}-*b*-PEG_{45}-*b*-PPC_{18}	5700	3300	1.12	-38.8	-	20
13	PPC_{25}-*b*-PEG_{45}-*b*-PPC_{25}	7100	4200	1.09	-36.7	-	n.s.$^{e)}$

Reaction conditions: 50 bar CO_2, 18h, RT $^{a)}$Block lengths determined by ^{1}H NMR spectroscopy, $^{b)}$Determined by SEC calibrated with a PEG standard in DMF at 40 °C, $^{d)}$Glass transition and melting temperature obtained from DSC; $^{e)}$insoluble in aqueous solution.

Cyclic carbonate side products were not formed according to the IR spectra of the crude reaction mixture (Figure S2). Incorporation of carbon dioxide into the polymer and formation of the poly(propylene carbonate) blocks was confirmed by IR- as well as NMR spectroscopy. Only one carbonate band at 1755 cm $^{-1}$ is detected, which can be clearly assigned to the carbonyl group of the linear carbonate. Importantly, no bands for a cyclic carbonate, which appear at around 1790 cm^{-1}, were observed in the IR spectra of the copolymers.

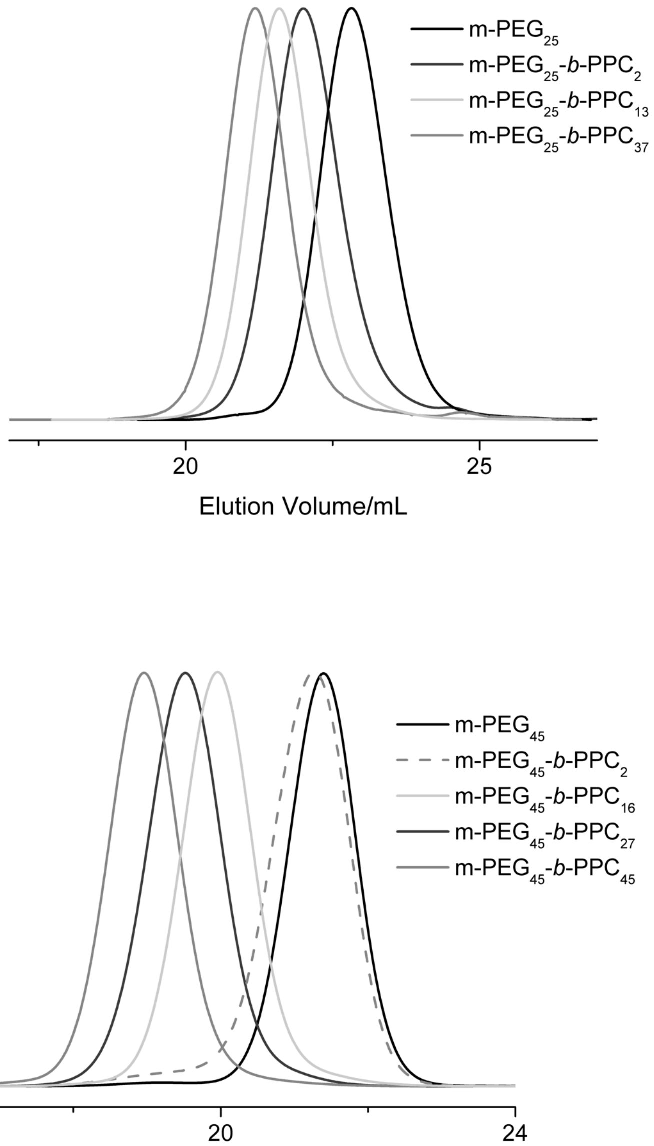


Figure 1. SEC diagrams for all PEG-*b*-PPC AB-diblock copolymer surfactants prepared.

Size exclusion chromatography (SEC, PEG standards) resulted in molecular weights between 1500 and 4500 g/mol and low PDI (M_w/M_n) values between 1.06 and 1.12. All molecular weight distributions were monomodal, indicating complete conversion of the mPEG or PEG initiator polymer and no formation of poly(propylene carbonate) homopolymer. The SEC results for all diblock copolymers are shown in Figure 1, demonstrating the narrow and monomodal distribution of the block copolymers and the absence of PPC homopolymer, despite the simplified, solvent-free synthesis procedure. The monomodal SEC diagrams for the ABA triblock copolymers are given in the Supporting Information (Figure S1).

In general, a systematic deviation of the molecular weights determined by SEC and the values calculated from NMR measurements was found. This effect was ascribed to the different hydrodynamic radii of the amphiphilic PPC/PEG block copolymers and the linear PEG standards of comparable molecular weight.

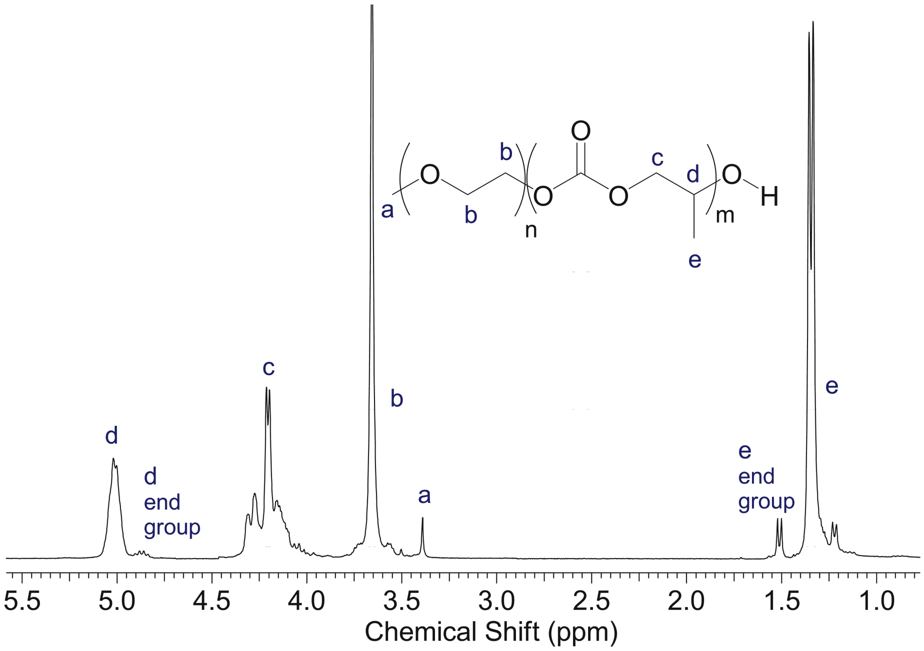


Figure 2. ^1H NMR spectrum of mPEG$_{45}$-*b*-PPC$_{27}$ (Table 1, entry **8**) (300MHz, $CDCl_3$)

The resulting copolymers were further characterized by ^1H NMR-, ^{13}C NMR- as well as 2D NMR- (COSY and HSQC) spectroscopy with respect to their composition and structure. The alternating polycarbonate structure of the PPC block was confirmed, since no poly(propylene oxide) signals were detected. In Figure 2, a typical ^{1}H NMR spectrum of mPEG$_{45}$-*b*-PPC$_{27}$ (Table 1, entry 8) is shown. In addition to the PEG-backbone signal (3.63 ppm) and the PEG methyl end group (3.37ppm), the resonances for the PPC block at 1.33 (methyl), 4.19 (methylene) and 4.99 (methine) ppm can be discerned. Using the signals of the methoxy group of the PEG block, the molecular weights of both blocks can be calculated from the NMR spectra.

For the triblock copolymers no methyl end group was available for the determination of the molecular weights via NMR. Therefore the end group signals of the PPC blocks were used for the calculation of M$_n$, resulting in similar results. All results are summarized in Table 1.

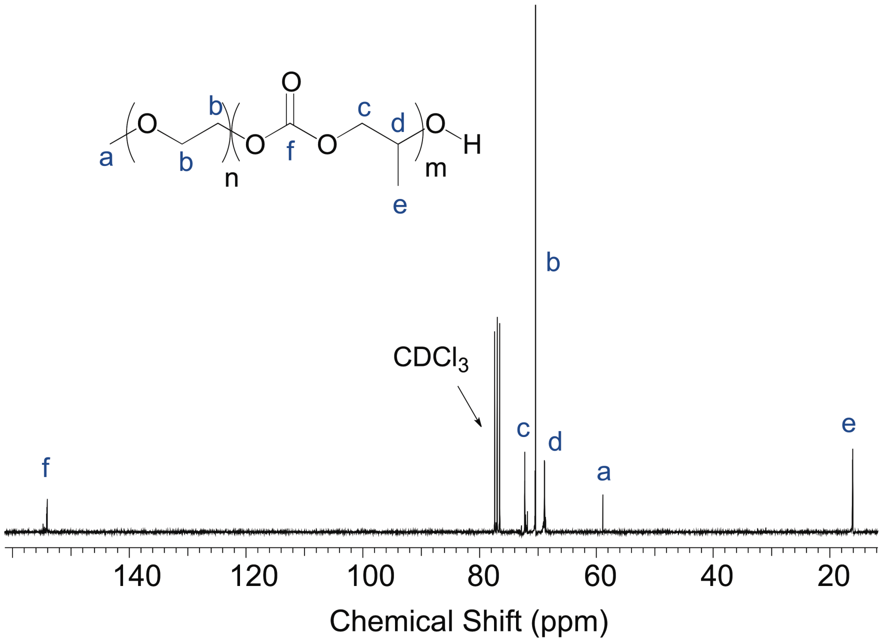


Figure 3. ^{13}C NMR spectrum of mPEG$_{45}$-*b*-PPC$_{27}$ (Table 1, entry 8).(75.4 MHz, CDCl$_3$)

The ^{13}C NMR spectrum of sample mPEG$_{45}$-*b*-PPC$_{27}$ (Table 1, entry 8) is exemplarily shown in Figure 3. The resonances at 154.33 ppm (signal f), 72.43 ppm (signal c), 69.05 ppm (signal d) and 16.25 ppm (signal e) can be assigned to the poly(propylene carbonate) backbone, whereas signal b (70.59 ppm) and signal a (59.07 ppm) is due to the PEG block. 2D NMR spectra (HSQC, COSY) of the block copolymers are given in the Supporting Information (Figures S4-S5).

Thermal Properties

The thermal stability of PPC was studied using thermogravimetric analysis (TGA). It is well known that the main low energy thermal decomposition pathway of PPC commencing at temperatures of about 150-180°C is backbiting or unzipping.[35,36] The main product is cyclic propylene carbonate (cPC), which has an atmospheric boiling point of 240 °C.[37] cPC is very compatible with PPC and is only released from it slowly. Therefore TGA measurements of decomposition temperatures are not very sensitive for the study of the decomposition of PPC below 200°C. In fact, a loss of mass at temperatures above 200°C may represent the physical desorption of the cyclic carbonate from the already decomposed PPC polymer. However, since we are dealing with PPC/PEG block copolymers, two decomposition temperatures, one for each block, are expected. This assumption is confirmed by the experimental results. A complete overview is given in Figure S6 (diblocks) and in the Supporting Information (Figure S7 triblocks). The first block to decompose is the poly(propylene carbonate). Its degradation is assigned to the step at around 180-220°C, the second step originates from the decomposition of the poly(ethylene glycol) block at around 380-420°C. Since it depends on the block length, and therefore the mass ratio of the blocks, the relative weight loss is different. For example for $mPEG_{45}$-*b*-PPC_{27} (Table 1, entry 8), with almost equal molecular weight of both blocks the relative weight loss of both blocks is similar, whereas the first step of $mPEG_{45}$-*b*-PPC_{27} (Table 1, entry 6), consisting of a much smaller PPC than PEG block, is considerably smaller than the weight loss for the PEG block upon degradation.

Besides the composition determined by TGA also other thermal characteristics, such as T_g and T_m have been studied with differential scanning calorimetry (DSC) and are also given in Table 1 (Figure 4). The poly(propylene carbonate) homopolymer is an amorphous material with a glass transition temperature (T_g) at about 40 °C, whereas the poly(ethylene glycol) homopolymer exhibits a T_g at around -60 °C and a melting temperature (T_m) of about 60°C, depending on the molecular weight. For all samples prepared no glass transition temperatures of the PEG or PPC homopolymers were detected. These results confirm again that PEG/PPC copolymers and not homopolymer mixtures were obtained.

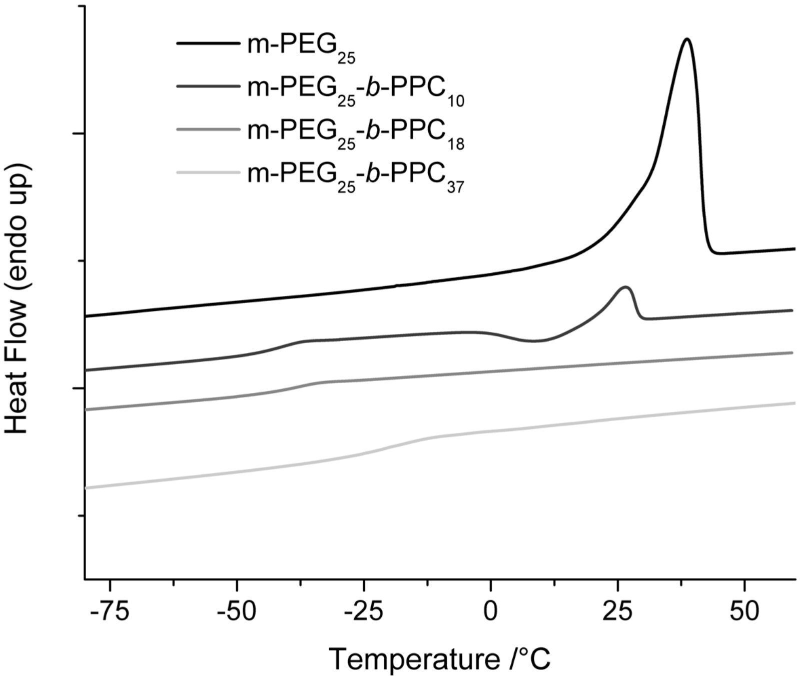


Figure 4. DSC results for all PEG_{25}-*b*-PPC copolymers (Table 1, entries **1**-**4**)

All diblock copolymer samples show a clear trend with respect to their thermal behavior. The glass transition temperatures increased with increasing length of the PPC block, whereas the melting point of the PEG block and also the degree of crystallization decreased with increasing length of the PPC block. This is explained by the fact that the PPC block is amorphous and in addition impedes crystallization of the PEG block. Concerning the glass transition and melting temperatures, similar trends were found for the triblock copolymer samples. However, only for PPC_9-*b*-PEG_{45}-*b*-PPC_9 a PEG-melting point can be detected, whereas for the other two samples no PEG melting point was found. The overall PEG content in those samples is lower, and the PPC chains are attached to both ends of the PEG block, suppressing efficient PEG crystallization.

Surfactant Behavior

The combination of hydrophilic PEG blocks with PPC chains leads to polymer surfactants. All block polymers synthesized in this work are water soluble, except for PPC_{25}-*b*-PEG_{45}-*b*-PPC_{25} (sample **13**, Table 1). It is well-known that amphiphilic block copolymers consisting of a hydrophilic PEG block and a hydrophobic polyester segment, such as poly(e-caprolactone) or poly(lactide) form micelles in aqueous solution.[38–40] The same behavior can be found for the PEG/PPC block copolymers prepared in this work. In an aqueous system, the hydrophobic blocks aggregate to form the micellar core, and the hydrophilic blocks constitute the outer shell to minimize the free energy. The onset of micelle formation characterized by the critical micelle concentration (CMC) is an important surfactant characteristic. We evaluated the influence of the relative and absolute lengths of the two blocks on micellization of the amphiphilic block copolymers. The CMCs of the PEG/PPC di- and triblock copolymers were determined from the surface tension of the aqueous polymer solutions with varied surfactant concentration, employing the Du Nouy ring method. As an example, Figure 5 shows the development of the surface tension of an aqueous solution of mPEG$_{45}$-*b*-PPC$_{16}$ diblock copolymer (Table 1, sample 7) vs. logarithmic concentration. Below the CMC, the surface tension shows a pronounced decrease with increasing polymer concentration, and above a certain concentration the surface tension is essentially constant, indicating the formation of micelles. The CMC was taken as the intersection of the tangents of the curve in these two parts. All CMC values are listed in Table 1.

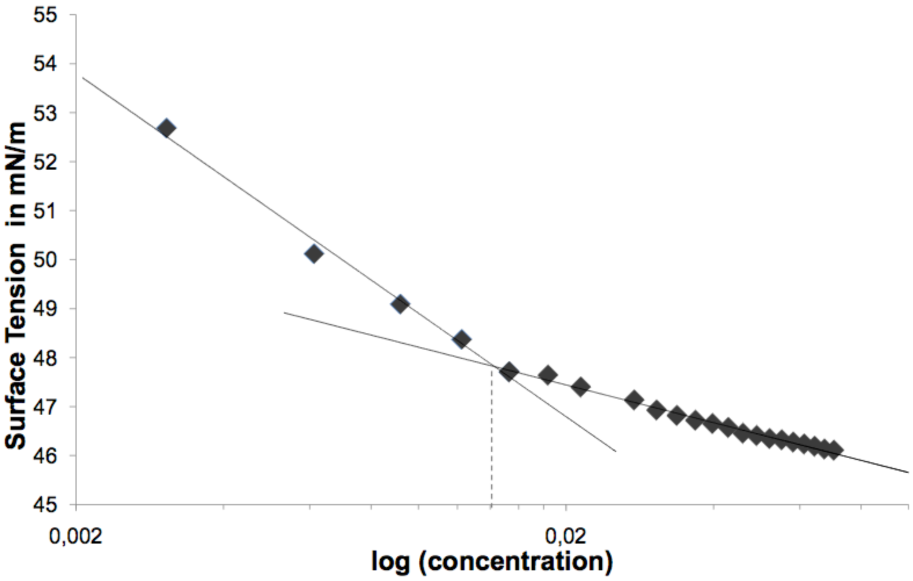


Figure 5. Surface tension measurements of an aqueous solution of sample **8** (mPEG$_{45}$-*b*-PPC$_{27}$) for the determination of the CMC.

With the three series of block copolymers obtained, it is possible to evaluate the influence of the length of the PEG and PPC blocks on the surfactant behavior and to compare diblock and triblock copolymer structures.

From the CMC measurements, clear trends emerge: An increase in the molecular weight of the hydrophobic block generally decreases the CMC, so for a given PEG length, the CMC of the copolymer decreases with increasing PPC content. For the triblock copolymers, with increasing DP_n of the apolar PPC blocks, lowering of the CMC values is observed. This is in line with expectation, because the compounds become less soluble in aqueous solution.[41,42] Comparing different PEG block lengths, the CMC values were found to be very similar in this work. However, if the hydrophobic block is very short, as for example in mPEG$_{45}$-*b*-PPC$_2$ (Table 1, sample **6**) no critical micelle concentration was detected, and a high PPC/PEG ratio also leads to the absence of a CMC, because the polymer is not water soluble any more (PPC$_{25}$-*b*-PEG$_{45}$-*b*-PPC$_{25}$, sample **13**).

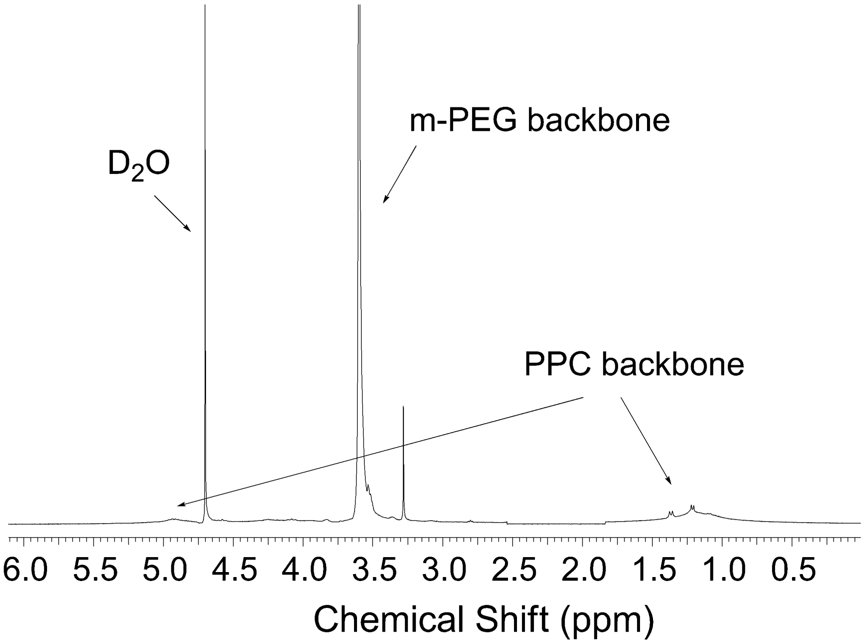


Figure 6. ^{1}H NMR spectrum of mPEG$_{25}$-*b*-PPC$_{18}$(Table 1, entry **8**)

Compared with other poly(ethylene glycol) /poly(carbonate) or poly(ethylene glycol)/polyester systems, the obtained values are in the same order of magnitude. For instance, for PEG/polylactide (PLA) di- and triblock copolymers the CMC values were determined to be 10-145 mg/L, depending on the degree of polymerization of PLA and PEG blocks and the structure of the block copolymers.[41] Also for amphiphilic PEG/poly(trimethyl carbonate) block copolymers obtained by ring-opening polymerization the values were comparable to the data obtained in the current work.[43]

The formation of micelles can also be detected by NMR spectroscopy. Using a solvent in which both blocks are soluble, such as chloroform, the resonances of both blocks can clearly be discerned in the NMR spectra (Figure 2). However, when using a solvent in which only one block is soluble, e.g., water as a non-solvent for the PPC block, only the outer shell of the micelles can be detected. Figure 6 shows the ^1H NMR spectrum of mPEG$_{25}$-*b*-PPC$_{18}$ (Table 1, entry 8) in D_2O. Only the poly(ethylene glycol) backbone signal (3.63 ppm) and the methyl end group signal (3.37ppm) are visible. The PPC signals (1.33, 4.19 and 4.99ppm) have vanished, indicating the formation of micelles, wherein the water-insoluble PPC chains are located in the core.

Conclusions

Nonionic surfactants with degradable PPC segments have been prepared in one synthetic step directly from PEG, CO_2 and propylene oxide, simplifying a synthetic protocol reported by Lee et al. recently.[9] A series of PEG-*b*-PPC di- and triblock copolymers has been synthesized by immortal alternating copolymerization of CO_2 and propylene oxide onto PEG and mPEG as macro-transfer agents/initiators. Systematic series of diblock and triblock copolymer surfactants were synthesized with tailored molecular weight and narrow molecular weight distributions (M_w/M_n = 1.05-1.12) in close to quantitative yields. The synthetic strategy did not require the addition of solvents, which makes it conveniently amenable to scale-up and large scale preparation. The block structure of the di- and triblock PEG-*b*-PPC structures was confirmed by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy and SEC. Glass transitions and melting behavior of the PEG domain were influenced by the relative length of the PPC block and the architecture of the polymer.

CMC values of the resulting non-ionic polymer surfactants were determined to be 3-30 mg/L by surface tension measurements, depending on the molecular weight of the PPC and PEG blocks. The novel surfactants bear promise for a variety of applications, e.g., in micellar catalysis and for pharmaceutical, cosmetic and medical purposes. Compared with the well-known amphiphilic block copolymers consisting of a PEG block and hydrophobic polyesters, such as poly(ε-caprolactone) or poly(lactide) blocks, the PPC-PEG block copolymers exhibit an intrinsic advantage especially in the field of biomedical applications, such as drug encapsulation and transport: eventual hydrolysis of ester bonds in PLA gives rise to the generation of carboxylic acid, which causes undesired tissue responses and inflammation,[44] while hydrolysis of carbonate bonds only generates the neutral alcohol and carbon dioxide. Further work in this direction is in progress.

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Supporting Information for: CO_2-Based Nonionic Surfactants: Solvent-Free Synthesis of Poly(ethylene glycol)-*b*-Poly(propylene carbonate) Block Copolymers

Jeannette Hilf [1,†], Patricia Schulze[1] and Holger Frey [1,*]

SEC Results for all triblock copolymers

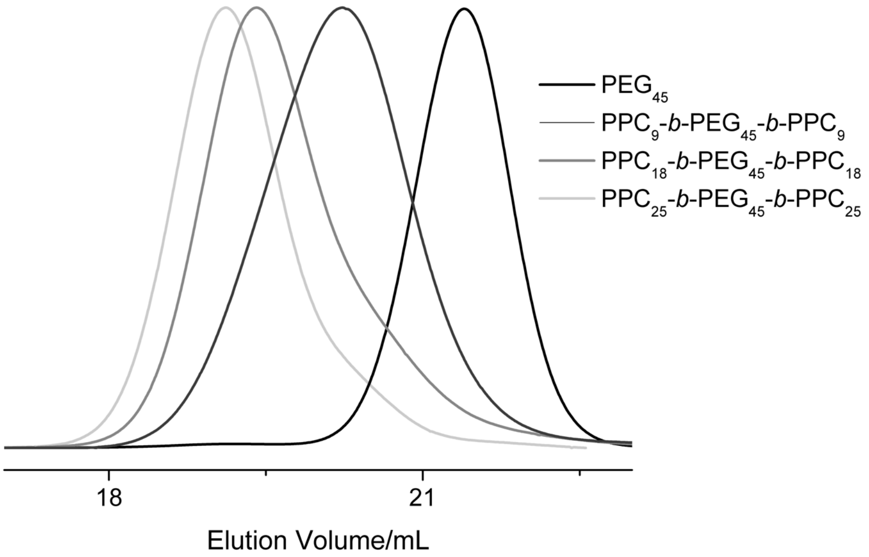

Figure S1. SEC results for all triblock copolymer samples (Table 1, entries 10-13).

FT-IR Results

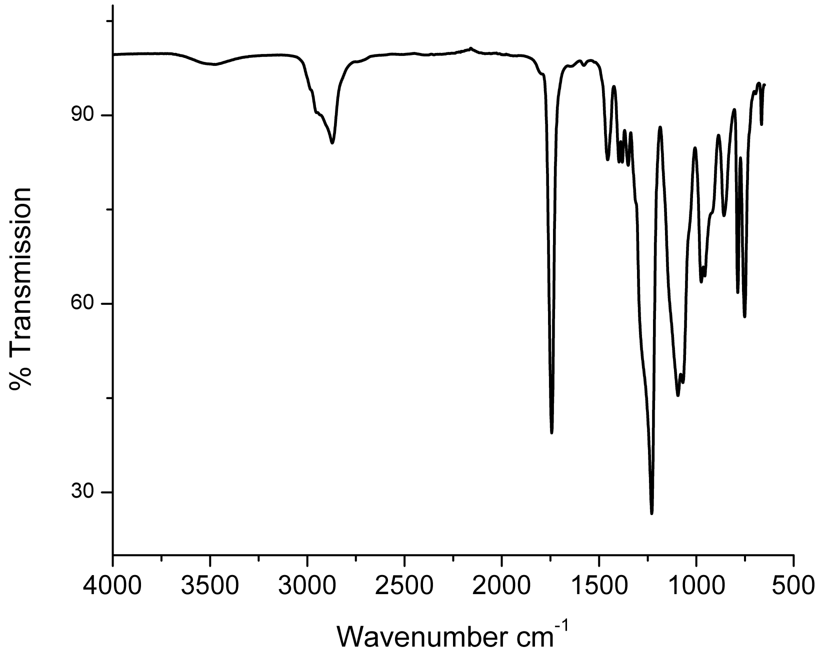

Figure S2. FT-IR spectrum of mPEG$_{45}$-*b*-PPC$_{27}$ (Table 1, entry 8).

Representative ^{1}H, ^{13}C NMR and 2 D NMR spectra of the PEG/PPC surfactants

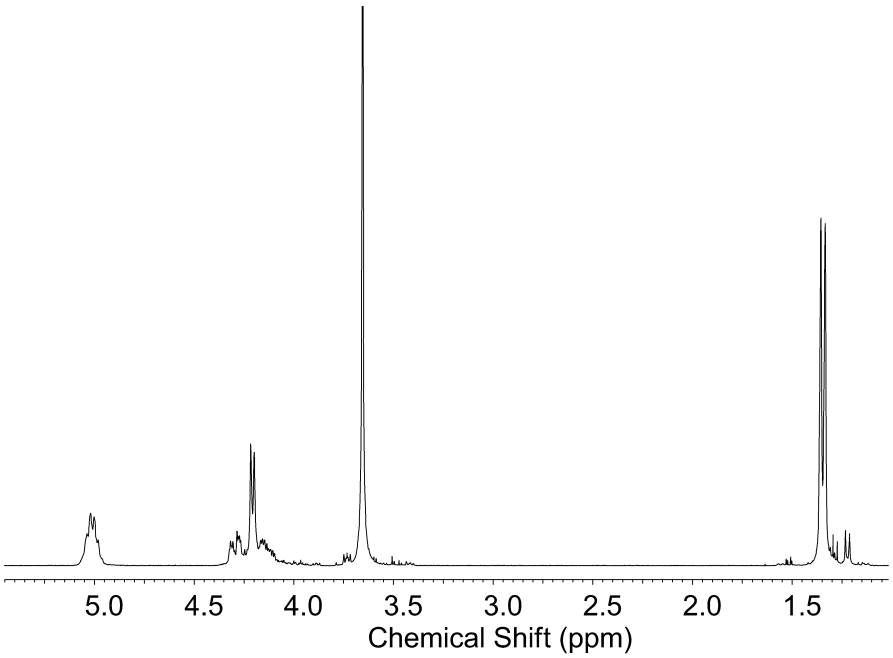

Figure S3. ^{1}H NMR spectrum of PPC$_{18}$-*b*-PEG$_{45}$-*b*-PPC$_{18}$ (Table 1, entry 12)

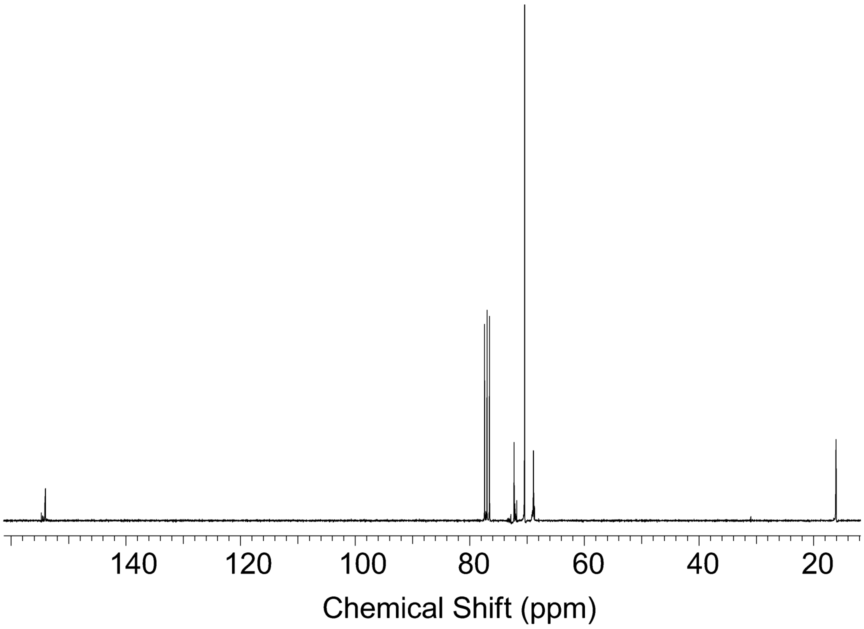

Figure S4. ^{1}H NMR spectrum of PPC_{18}-*b*-PEG_{45}-*b*-PPC_{18} (Table 1, entry 12)

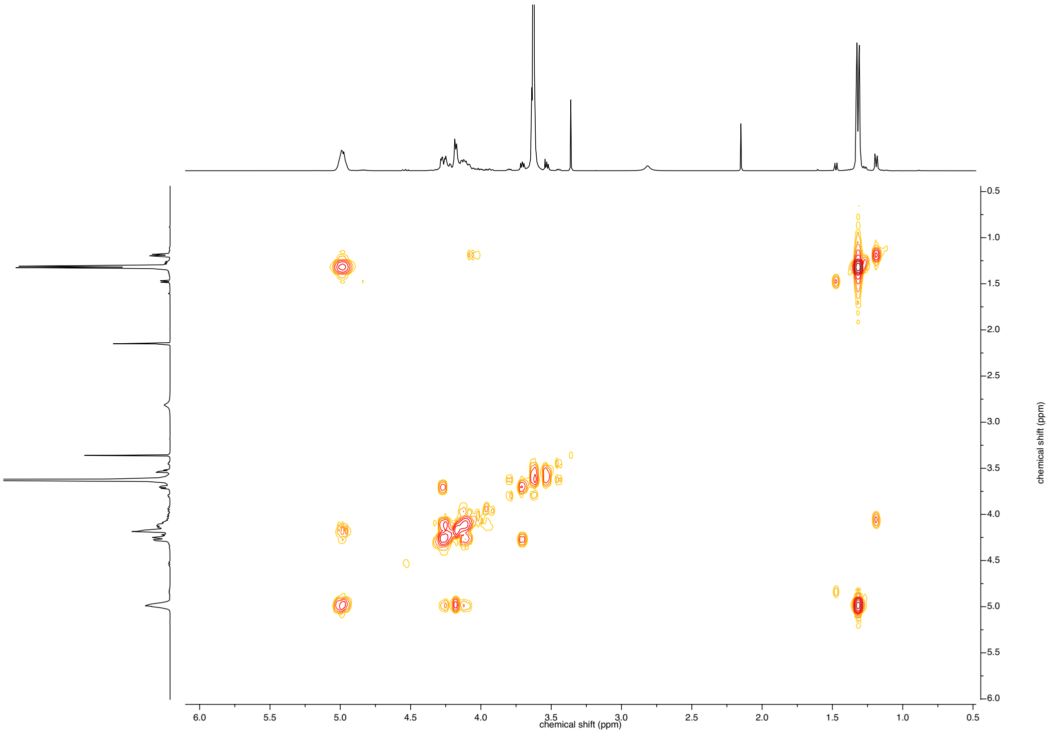

Figure S5. COSY spectrum of $mPEG_{45}$-*b*-PPC_{27} (Table 1, entry 8)

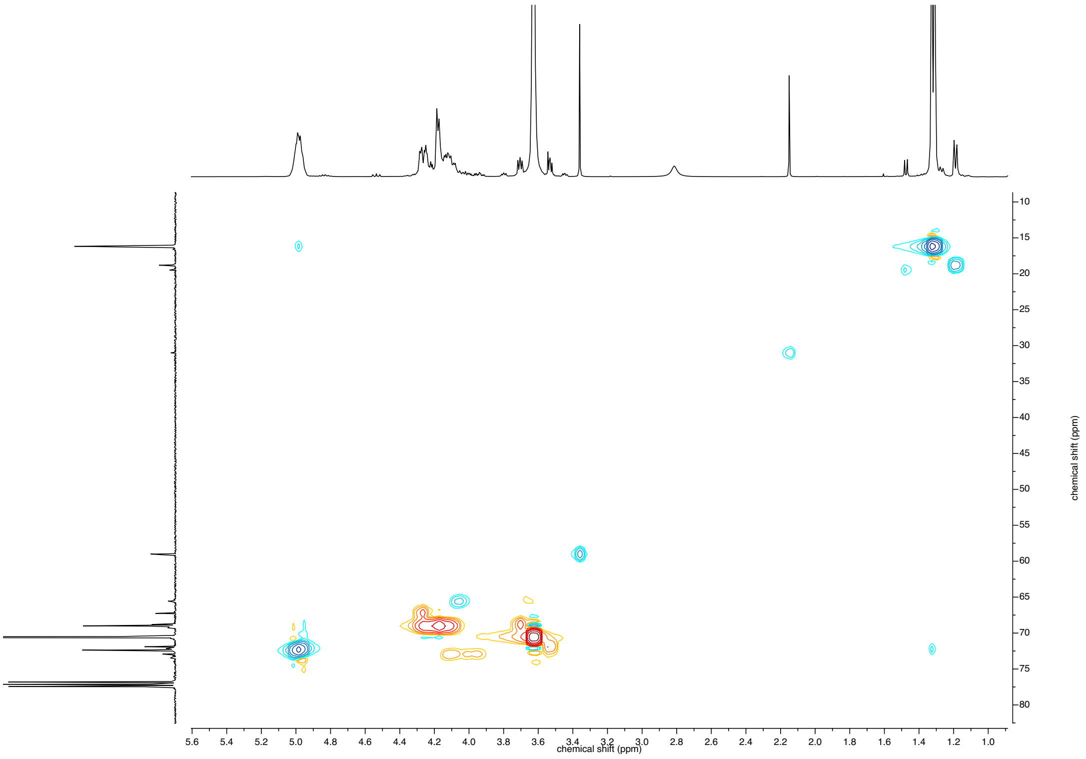

Figure S6. HSQC spectrum of mPEG$_{45}$-*b*-PPC$_{27}$

Thermogravimetric (TGA) Results

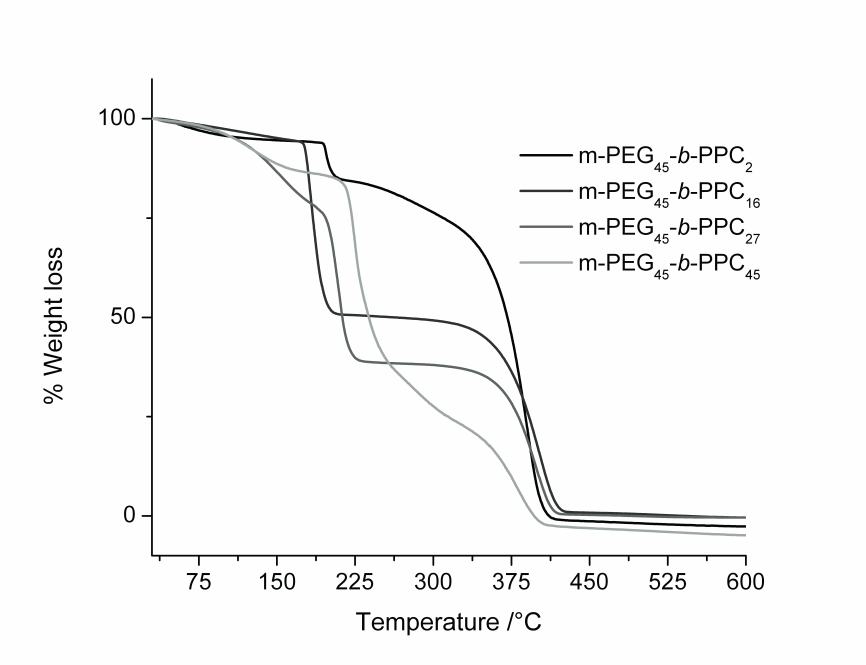

Figure S7. TGA results for all PEG$_{45}$/PPC copolymers (Table 1, entries 6-9)

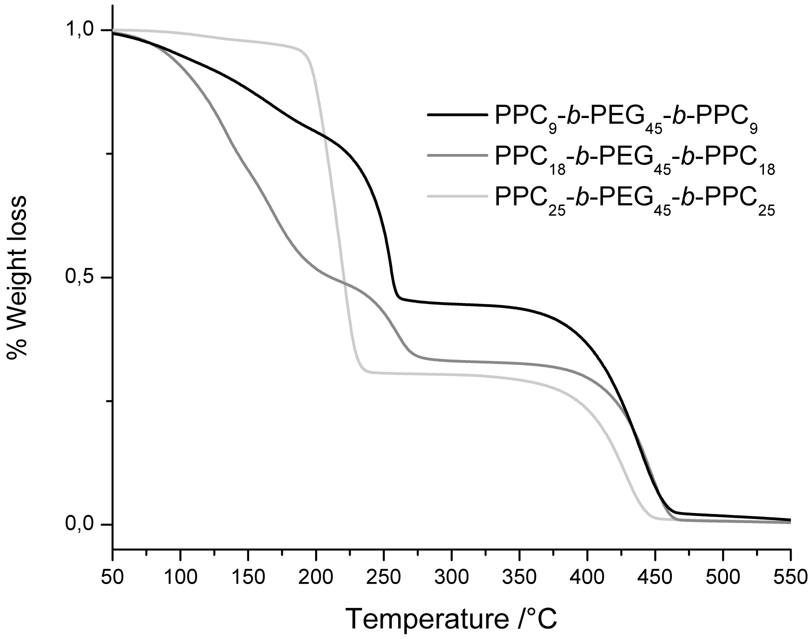

Figure S8. TGA results for all triblock copolymer samples (Table 1, entries 11-13).

DSC Results

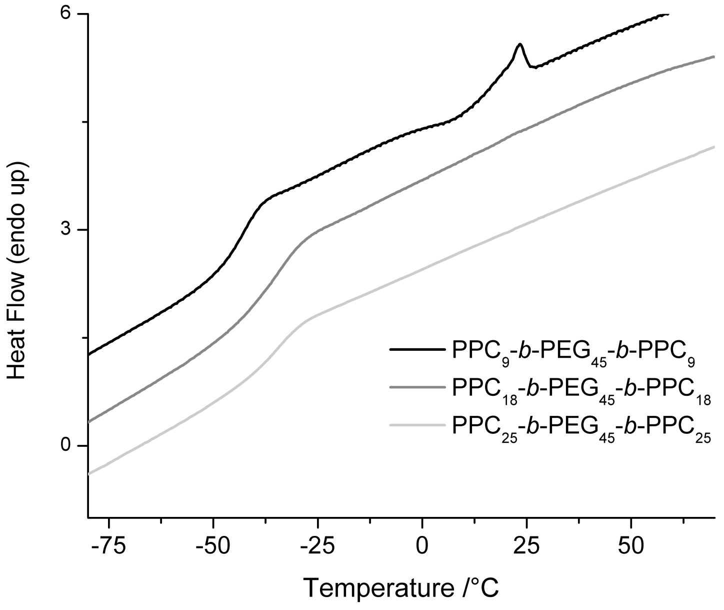

Figure S9. DSC results for all triblock copolymer samples (Table 1, entries 11-13).

2.2. Controlled Synthesis of Multi-Arm Star Polyether-Polycarbonate Polyols Based on Propylene Oxide and CO_2

Jeannette Hilf[1,†], Patricia Schulze,[1] Jan Seiwert[1] and Holger Frey[*1]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg 10-14, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany

[†]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

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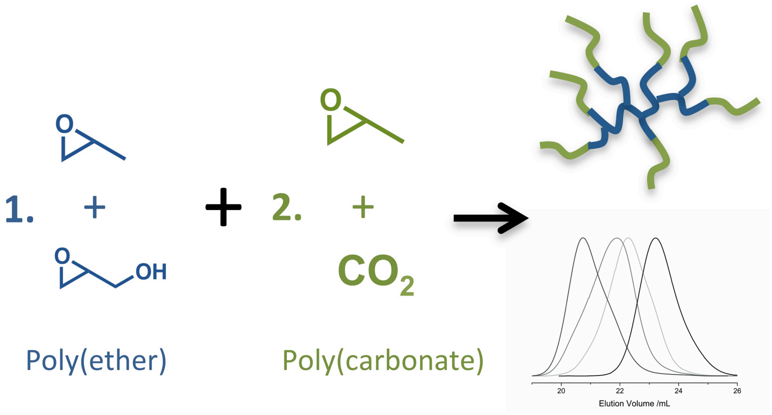


Abstract

Multiarm star copolymers based on a hyperbranched poly(propylene oxide) polyether-polyol (*hb*PPO) as a core and poly(propylene carbonate) (PPC) arms have been synthesized in two steps from propylene oxide (PO), a small amount of glycidol and CO_2. The PPC arms were prepared via carbon dioxide (CO_2)/propylene oxide copolymerization, using *hb*PPO as a multifunctional macroinitiator and the (R,R)-(salcy)-$CoOBzF_5$ catalyst. Star copolymers with 14 and 28 PPC arms, respectively, and controlled molecular weights in the range of 2700-8800 g/mol have been prepared (M_w/M_n =1.23-1.61). Thermal analysis revealed lowered glass transition temperatures in the range of -8 to 10°C for the poly(propylene carbonate) star polymers compared to linear PPC, which is due to the influence of the flexible polyether core. Successful conversion of the terminal hydroxyl groups with phenylisocyanate demonstrates the potential of the polycarbonate polyols for polyurethane synthesis.

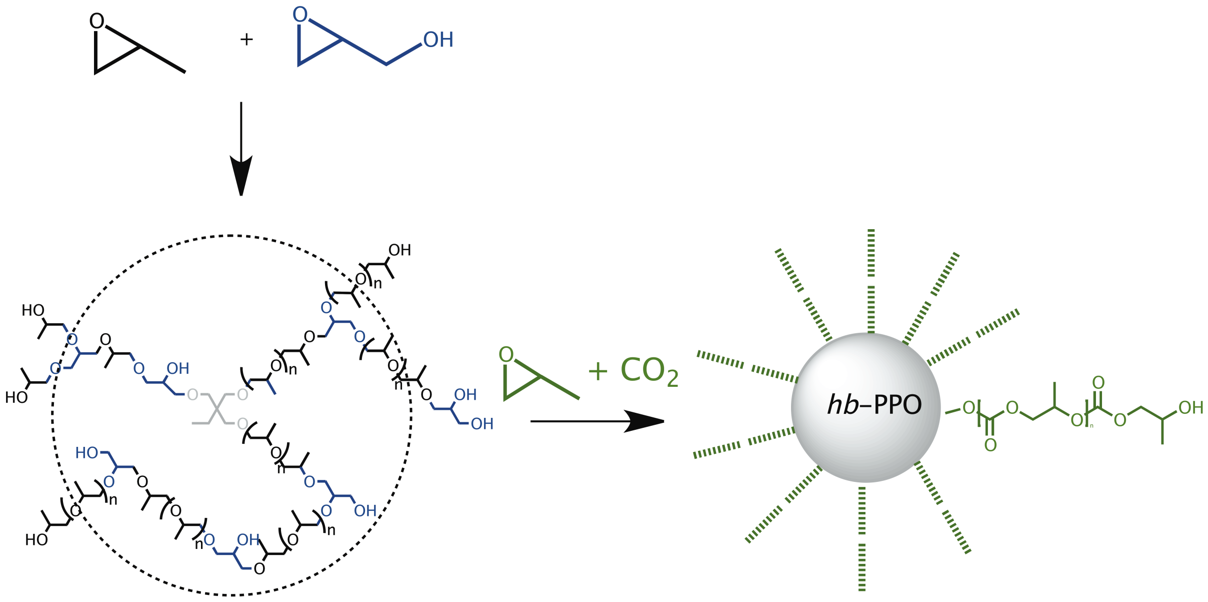
Introduction

Carbon dioxide (CO_2), an industrial waste product, is a potentially interesting C1 feedstock, as it is nontoxic, renewable, abundant and inexpensive. The growing recent interest of organic and bio-organic chemists in CO_2 has led to the development of a variety of synthetic reactions using carbon dioxide directly as a raw material, especially in the field of polymer chemistry. [1–7] Since the seminal discovery of the copolymerization of CO_2 and epoxide monomers by Inoue et al in 1969,[8,9] numerous works on different heterogeneous and homogeneous catalyst systems have been reported, and mostly propylene oxide and cyclohexene oxide have been polymerized to poly(propylene carbonate) (PPC) and poly(cyclohexene carbonate) (PCHO).[10–16] The commercialization of PPC has recently reached a modest volume of approximately 1000 t/year and is gaining increasing attention.[5] The main reason for the interest in PPC is its smooth biological degradation characteristics.[5] Current challenges for PPC include the diversification of its properties, especially with respect to broadening the scope of applications beyond the use as a thermoplastic material. Mostly linear poly(propylene carbonate) homopolymers have been studied to date.[13,17–19] Only few works aimed at the synthesis of block copolymers or branched PPC architectures. Since it is well-known that in the synthesis of PPC molecular weights can be controlled, using various catalyst systems in an immortal polymerization, and in elegant works Lee et al.

demonstrated the general feasibility of linear PPC block copolymers[8,9,14,20–23], tailoring of macromolecular parameters such as molecular weight, polydispersity, and chain-ends for PPC-based complex polymer structures is emerging as a current focus of research.

Here we present a rapid two-step approach to flexible multi-arm star polymers with PPC arms. In multi-arm star polymers a large number of linear arms is connected to a central branched core. Such materials show unusual mechanical, rheological, and biomedical properties that differ from the corresponding linear polymers.[24–28] Furthermore they are particularly interesting because of their large number of functional end groups compared to linear polymers of similar molecular weight as well as their improved solubility profile.[24,29,30] To date, multifunctional polycarbonate polymer architectures have been exclusively prepared by the ring-opening polymerization of six-membered cyclic carbonate monomers.[31,32,33] Aliphatic polycarbonate polyols have already been suggested for a wide range of potential applications.[34–38] The additional free hydroxyl groups in polycarbonate polyols provide sites for the attachment of dyes, flame retardants, bioactive molecules, or cross-linking of materials. In addition, polycarbonate polyols have been introduced for the manufacture of polyurethanes for high-performance coating applications.[39] However, the respective cyclic carbonate monomers have to be prepared in multistep reactions, which represents a drawback for actual application.

In this work we describe a synthetic route for flexible multiarm star block copolymers, using a hyperbranched poly-(propylene oxide) copolymer with glycerol branching points[40] as a multifunctional initiator for the controlled catalytic copolymerization of carbon dioxide with propylene oxide (Scheme 1). This approach results in PPC multi-arm star copolymers with flexible polyether core. The resulting multifunctional PPC copolymers have been investigated with respect to molecular weight control, PPC chain length per arm, thermal properties as well as the possibility to use the terminal hydroxyl groups for derivatization reactions with isocyanates.



Scheme 1: Two-step synthesis of hyperbranched PPC multiarm star copolymers from PO and CO_2 with *hb*-PG-*co*-PPO core (left); branching points are generated from glycidol in the first step.

Experimental Section

Instrumentation as well as synthesis and characterization of the hyperbranched PPO core structures[40] and the preparation of the catalyst employed for the PO/CO_2 copolymerization are described in the Supporting Information.

Synthesis of *hb*-PG-*co*-PPO/PPC star copolymers (Table 1, sample 3).

A 100 mL Roth autoclave was dried under vacuum at 40 °C. (R,R)-(salcy)-$CoOBzF_5$ (11.7 mg, 0.0143 mmol), the cocatalyst (PPN)Cl (8.2 mg, 0.014 mmol), PO (1.9 mL, 26 mmol) and dried 200 mg ***hb*-$PG_{0.17}$-*co*-$PPO_{0.83}$** (Table 1, sample 1) were placed in a glass tube with a Teflon stir bar inside the autoclave. The autoclave was pressurized at 50 bar CO_2 and was left to stir at 30 °C for 18 h. The reactor was vented, the polymerization mixture was dissolved in chloroform (5 mL), quenched with 5% HCl solution in methanol (0.2 mL) and then precipitated in ice-cold pentane. The polymer (sample 3) was collected and dried *in vacuo*. Yield 95 % ^1H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) = 5.00 (methane CH backbone), 4.19 (methylene CH_2), 3.55 (hyperbranched core), 1.33 (CH_3) and 1.18 (CH_3 core).

Transformation with Phenylisocyanate.

150 mg *hb*-($PG_{0.39}$-*co*-$PPO_{0.61}$)-*g*-PPC_{38} and 2mL phenylisocyanate were mixed and stirred under Argon for 4 h. The solution was precipitated once in methanol and twice in pentane to remove the excess of phenylisocyanate. The resulting product was dried at 60°C in vacuum for 24 h. Yield 90 % ^{1}H NMR ($CDCl_3$-*d₁*, 300 MHz): δ (ppm) = 7.40-7.08 (aromatic protons and $CDCl_3$-*d₁)*, 5.00 (methane CH backbone), 4.19 (methylene CH_2), 3.55 (hyperbranched core), 1.33 (CH_3) and 1.18 (CH_3 core).

Results and Discussion

Multifunctional, hyperbranched PPO copolymers with varied glycerol content and consequently varied number of glycerol branching points and end groups[40] have been used to synthesize PPC multi-arm star copolymers. The polyether-polyol samples were prepared by one-pot synthesis via random copolymerization of propylene oxide and glycidol (anionic ring-opening multibranching polymerization), using partially deprotonated trimethylolpropane as a trifunctional initiator according to a recently published procedure.[40]As listed in Table 1, two different hyperbranched PPO copolymers, namely *hb*-$PG_{0.17}$-*co*-$PPO_{0.83}$ and *hb*-$PG_{0.39}$-*co*-$PPO_{0.61}$ (listed as samples **1** and **5** in Table 1) have been prepared and used as multifunctional initiators, containing 17 and 39 mol% glycerol units, respectively. The fraction of glycerol units incorporated in the polymer was calculated by referencing to the methyl group of the initiator (0.78 ppm) and comparing this value with the integral of the methyl group of the propylene oxide units (0.99-1.05 ppm) and the methylene and methine groups of the polymer backbone (3.1-3.9 ppm). In addition, the total number of glycidol units of each macromolecule corresponds to the total number of hydroxyl groups (4.4-4.7 ppm) minus the number of hydroxyl groups introduced by the initiator moiety (assuming that the core is fully incorporated into all polymer molecules of the distribution). In the case of a trimethylolpropane core, n(OH) core equals a value of 3. The other five protons of each glycerol unit as well as three propylene oxide protons generate a broad resonance between 3.1 and 3.8 ppm. Hence, the ratio between propylene oxide and glycerol repeat units can be directly calculated. For sample 1 and 5 the average number of hydroxyl groups was determined to be 14 and 28, respectively. Depending on the amount of hydroxyl functionalities, the number of arms can be varied in the *grafting-from* strategy applied. Characterization data for the core molecules can be found in the Supporting Information.

Table 1. Characterization data of all copolymer samples prepared

#	**Sample**[a]	**M_n (g/mol)** [b]	**M_n (g/mol) (NMR)**	**PDI**[b]	**# PPC Arms**[c]	**DB**[d]	**T_g (°C)**[e]
1	*hb*-$PG_{0.17}$-*co*-$PPO_{0.83}$	1800	4300	1.45	-	0.28	-59
2	*hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_9	2700	17 100	1.23	14	0.28	-8
3	*hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{19}	5800	31 400	1.41	14	0.28	2
4	*hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{27}	8800	42 800	1.38	14	0.28	7
5	*hb*-$PG_{0.39}$-*co*-$PPO_{0.61}$	1400	3500	1.61	-	0.55	- 48
6	*hb*-($PG_{0.39}$-*co*-$PPO_{0.61}$)-g-PPC_{22}	3500	66 300	1.62	28	0.55	-5
7	*hb*-($PG_{0.39}$-*co*-$PPO_{0.61}$)-g-PPC_{38}	5300	112 000	1.53	28	0.55	1
8	*hb*-($PG_{0.39}$-*co*-$PPO_{0.61}$)-g-PPC_{46}	6800	134 800	1.58	28	0.55	10

Reaction conditions: 50 bar CO_2, 2h, RT; *a)*block lengths determined by ^{1}H NMR spectroscopy, *b)*SEC calibrated with PEG standards in DMF at 40 °C, *c)* determined by ^{1}H NMR spectroscopy *d)*Degree of branching of the polyether core determined by Inverse-Gated ^{13}C NMR spectroscopy *e)*Glass transition obtained from DSC.

In a solvent-free synthesis procedure, different poly(propylene carbonate) arm lengths were obtained by varying the PO/CO_2 monomer to hydroxyl group concentration of the multifunctional macroinitiator (Figure 1). The synthesis of the copolymers was achieved via a *grafting-from* approach, performing the copolymerization of propylene oxide (PO) and carbon dioxide (CO_2) in the presence of the multifunctional polyether as a macro-transfer agent, i.e., as a multifunctional initiator. It is imperative for the approach described in this work that the hyperbranched PPO macroinitiator is soluble in propylene oxide under pressure. In a series of solubility experiments it was established that the macroinitiator forms a homogeneous solution in the PO/CO_2 monomer mixture. Due to the solubility of the hyperbranched PPO macroinitiator in neat propylene oxide no additional solvent was used. All PO/CO_2 polymerizations were carried out under identical reaction conditions, i.e., argon atmosphere, room temperature and 50 bar CO_2 pressure with a (R,R)-(salcy)$CoBzF_5$ catalyst and bis(triphenylphosphine(iminium chloride) (PPNCl) as a cocatalyst for 2 hours. The catalyst and cocatalyst were efficiently removed from the final product via precipitation in cold pentane (0°C). The resulting star polymers have been characterized by NMR- and IR-spectroscopy, size exclusion chromatography (SEC) and differential scanning calorimetry (DSC). All data are summarized in Table 1.

In Figure 1 the ^{1}H NMR spectrum of *hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{27} (Table 1, sample 4) in $CDCl_3$ is shown as a typical example for the multi-arm star copolymers. In this case, the average degree of polymerization of each PPC-arm is 27. In addition to the hyperbranched PPO core signal (d = 3.50 and 1.12 ppm), the typical resonances for poly(propylene carbonate) can be discerned (d = 5.00, 4.19 and 1.33 ppm). The average PPC side chain length and also the molecular weight were determined by comparison of the integration values of the PPC chain end-group resonances (d = 4.86 ppm) with the poly(propylene carbonate) methine resonances (d = 5.00 ppm). The number of PPC chains attached can be calculated as described below. Detailed characterization of the hyperbranched core molecules was performed as described in the Supporting Information. From these studies the number of protons in the macroinitiator-core is known. With this information the number of PPC end groups can be determined, and thus the number of PPC side chains can be calculated. For the star copolymers prepared in this study, the number of PPC side chains is in good agreement with the number of hydroxyl groups from the macro initiator. ^{13}C NMR spectroscopy also confirmed the structure of the copolymers, and the typical carbonate resonance of the PPC arms at δ = 154.26 ppm can clearly be detected. Furthermore the typical signals of the polyether core molecules are clearly visible at δ = 77.16, 65.68 and 17.35 ppm (**Figure S6**).

In addition to the NMR data, the incorporation of CO_2 into the polymer was confirmed by IR spectroscopy (Figure S5). Only one carbonate band at around 1740 cm^{-1} was detected, which can be assigned to the C=O group of the linear carbonate. No bands for a cyclic carbonate, which appear at around 1790 cm^{-1}, were observed in the IR (or NMR) spectra of the non-purified copolymers.

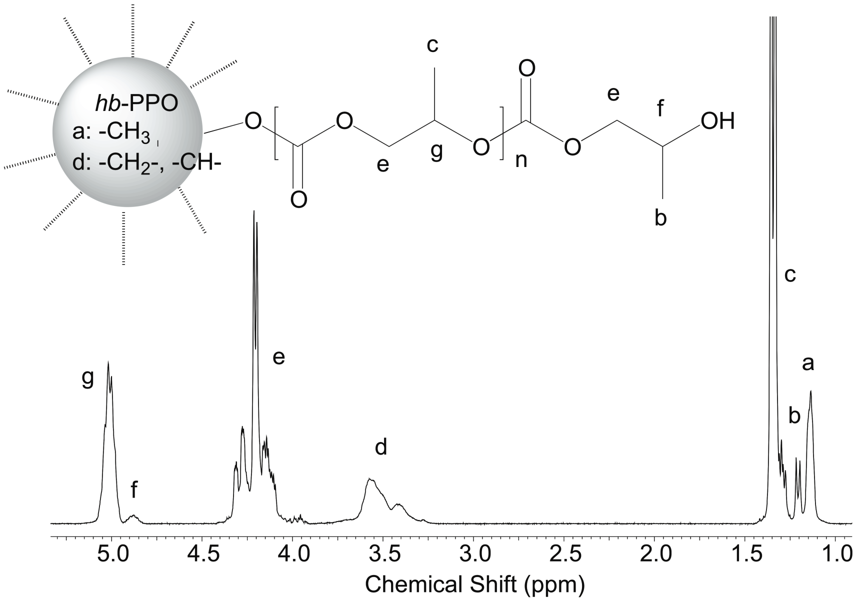


Figure 1. ^{1}H NMR spectrum of *hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{27} (Table 1, sample 4) (300 MHz, $CDCl_3$)

Size exclusion chromatography (SEC) revealed apparent molecular weights between 2700 and 8800 g/mol, monomodal distributions and low to moderate PDI values between 1.23-1.61. The molecular weights (M_n) of all synthesized copolymers were significantly higher than for the starting core copolymers, and the molecular weight distributions were monomodal, indicating complete conversion of the *hb*-PPO-*co*-PG core molecule (Figure 2). In general, a strong deviation of the molecular weights determined by SEC and the calculated values based on the NMR results was observed (Table 1). The underestimation of M_n is particularly noticeable for samples 6-8 with the highest DB of the core molecule and can be ascribed to the highly branched architecture. It is well-known that the hydrodynamic radius, which determines the elution volume of the polymer, does not increase linearly with the increase in mass.[41,42] Generally star-shaped or hyperbranched copolymers show lower hydrodynamic volume in solution compared to linear analogues of similar molar mass. This explains why the most significant underestimation of molecular weight is found for the higher branched systems with the longest side chains.

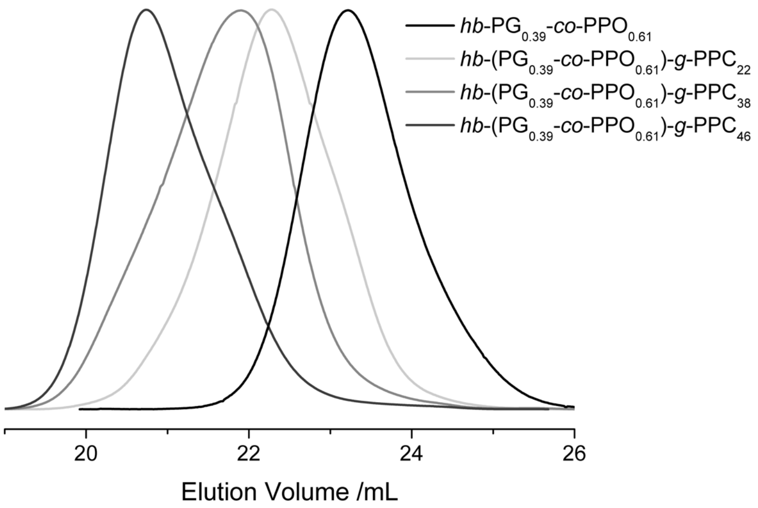


Figure 2. SEC results for some of the (PG-*co*-PO)-*g*-PPC star copolymers in chloroform (samples 5-8, Table 1).

Thermal and Solution Properties

The thermal behavior of the PPC multi-arm copolymers has been studied by differential scanning calorimetry (DSC). No melting points were detected, as expected due to the atatic nature of the PPC chains and the hyperbranched core. For all samples no separate glass transition temperatures for the *hb*PPO or PPC homopolymer constituents were detected. These results lend additional support to the conclusion, that *hb*PPO/PPC star copolymers without homopolymer contaminants were obtained, as also confirmed by the SEC data. In general, the glass transition temperatures of the star copolymer structures are in the range of -8°C to 10°C and increase with increasing degree of polymerization of the PPC chains attached. However, compared to the linear PPC homopolymer (T_g around 40°C) the glass transition temperatures are still considerably lowered for the star copolymers, which is attributed to the flexibilizing effect of the polyether core. On the other hand, polymerization of poly(propylene carbonate) onto the hyperbranched core molecule leads to an increase of the T_g by about 50 °C compared to the highly flexible polyether core polymers. With increasing degree of polymerization of the PPC block from 9 to 46 units the glass transition temperature increases from -8°C to 7 °C and from -5°C to 10°C, respectively, which demonstrates the increasing impact of the PPC chains with their length. No significant difference can be found for the different types of stars, and also no significant effect of the number of PPC arms on T_g is visible. In summary, rather flexible polycarbonate-polyols can be realized by employing the mobile polyether core structure.

The intrinsic viscosity of samples 1-4 was determined using a Ubbelohde viscometer at 25°C in chloroform (for details see Supporting Information). The lowest intrinsic viscosity (5.9 cm^3/g) was obtained for the hyperbranched core molecules (sample 1), which agrees with expectation, since it is a hyperbranched structure with low molecular weight. The star copolymers revealed values from 9.1 (sample 2) and 11.6 (sample 3) to 12.6 cm^3/g (sample 4). Depending on the degree of polymerization of the PPC side chains the intrinsic viscosity increased, which again is in agreement with expectation. However the overall intrinsic viscosities are low in comparison to linear PPC[44] and reflect the star shaped structure of the synthesized copolymers.

Functionalization

Polycarbonate polyols with 2-3 hydroxyl end groups have been introduced as components for polyurethane elastomers, foams and coatings, in analogy to the polyether polyols that are highly established in these fields. Polycarbonate polyols are prepared by reacting polyol components such as 1,4-butanediol, 1,6-hexanedediol or 2-methyl-1,8-octanediol with an organic carbonate, such as dimethylcarbonate. However, most of these polyols available at present are solids at room temperature. Therefore additional solvents or heating is required in order to form polyurethanes. Therefore, non-crystalline and flexible polycarbonate polyols are desirable. Compared to linear polyether-polycarbonate polyols, the number of hydroxyl groups is strongly increased for the star shaped polycarbonate polyols reported in this work, and as shown above they are not crystalline. The hyperbranched polyether core provides flexibility, and the amorphous PPC arms prevent crystallization.

For a proof of principle study phenylisocyanate has been used as a model compound for the reaction with the newly synthesized star shaped polyols to form urethanes. To this end, the polymers were mixed with an excess of phenylisocyanate and stirred for 4 hours. Subsequently the polymers were precipitated in cold pentane and dried in high vacuum to remove the excess of isocyanate. Figure S10 shows the ^1H NMR spectrum of *hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{19} (Table 1, sample 3) in $CDCl_3$ after reaction with phenylisocyanate. The aromatic signals of the phenyl group can clearly be seen in the region from d = 7.45 to 7.00 ppm, and the integral fits with the number of PPC side chains. SEC confirmed transformation of the hydroxyl end groups (Figure S9), evident from a strong UV-signal. Thus, these hyperbranched polyether-polycarbonate stars are promising polyols for polyurethane formation. Further work in this area is in progress.

Conclusions

To the best of our knowledge this work is the first account of the combination of anionic multibranching polymerization and the immortal polymerization of epoxides and CO_2. Multi-arm star shaped poly(propylene carbonate) polyols have been synthesized directly from CO_2 and propylene oxide, based on a flexible, hyperbranched poly(propylene oxide) core. Importantly, this core molecule is fully soluble in liquid PO, which is a crucial precondition for the solvent-free synthesis strategy described. The average degree of polymerization of the poly(propylene carbonate) arms is adjustable by the monomer/initiator ratio. For the full structure elucidation of the resulting polymers SEC, NMR spectroscopy, DSC and FT-IR spectroscopy have been employed. A systematically varied series of polycarbonate stars with apparent molecular weights between 1400-8800 g/mol was obtained. The polydispersity was moderate for all materials, and the polydispersity index was in the range of 1.23 to 1.62 for all polymers. The materials exhibited low viscosity in solution, as is typical for multi-arm star polymers. It should be emphasized that a solvent-free procedure was used for the PPC star polymer synthesis, which renders the approach interesting for large scale.

Depending on the degree of polymerization of the PPC arms the glass transitions decreased in comparison to the linear poly(propylene carbonate). Notably, the post-polymerization functionalization of the hydroxyl end groups with phenylisocyanate was shown to be highly efficient and occurred without observable backbone degradation, enabling the potential use of the multifunctional PPC polymers as flexible, non-crystalline polycarbonate polyols for polyurethanes.

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Supporting Information for: Controlled Synthesis of Multi-Arm Star Polyether-Polycarbonate Polyols Based on Propylene Oxide and CO_2

Jeannette Hilf[1,†], Patricia Schulze[1], Jan Seiwert[1] and Holger Frey[*1]

Materials and Instrumentation.

Propylene oxide (PO, 98%, Aldrich) was distilled over CaH_2 under reduced pressure prior to use. Carbon dioxide (>99.99%) was used as received. All other reagents were used as received.

NMR experiments.

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer, operated at 300 and 75.4 MHz and the chemical shifts are given in parts per million (ppm).

Gel permeation Chromatography.

Size exclusion chromatography (SEC) measurements were carried out in $CHCl_3$ on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P 100 pump, a set of three PSS SDV columns (104/500/50 Å), RI- and UV-detectors (absorption wavelength: 254 nm or 500 nm). All SEC diagrams show the RI detector signal, unless otherwise stated, and the molecular weights refer to linear polystyrene (PS) standards provided by Polymer Standards Service (PSS).

Differential Scanning Calorimetry.

DSC curves were recorded with a Perkin-Elmer DSC 7 CLN2 in the temperature range from – 100 to 150 °C at heating rates of 10 K min^{-1} under nitrogen.

IR-Spectroscopy.

FT-IR spectra were recorded on a Thermo Scientific iS10 FT-IR spectrometer, equipped with a diamond ATR unit.

Ubbelohde Viscometer.

Viscosity measurements to determine the intrinsic viscosity were performed with a LAUDA S5 and LAUDA PVS 1 Ubbelohde viscometer, equipped with a Metrohm liquid dosing unit. An 0c capillary with k=0.003 and 290 mm length was used. All measurement were performed at 25 °C. For each sample four different concentration were measured. For each concentration, after a relaxation period of 10 s, five flow times were measured. The mean values of the five measurements were used to calculate the reduced viscosity. The intrinsic viscosity was then obtained by plotting the reduced viscosity against concentration and extrapolating against c=0.

$$[\eta] = \lim_{c \to 0} \eta_{red}$$

Synthesis

Synthesis of hyperbranched PPO-*co*-PG copolymers (as described by Schömer et al.[1])

Typical procedure for the preparation of hyperbranched random copolymers of propylene oxide and glycidol: An exemplary synthetic protocol is described for $hbPPO_{0.80}$-co-$PG_{0.20}$: A two-necked flask equipped with a septum, teflon seal and a magnetic stirrer was connected to a vacuum line. 45 mg (0.33 mmol) of 1,1,1-tris(hydroxymethyl)propane (TMP) was deprotonated with 0.3 eq. potassium tert-butoxide in methanol and dried azeotropically with benzene to remove the methanol together with formed tert-butanol and other volatiles. 2.32 g (40 mmol) propylene oxide (PO) was transferred to an ampoule and subsequently to the reaction flask in vacuo.

The flask was sealed and 740 mg (10 mmol) freshly distilled glycidol was introduced through the septum via cannula. The reaction mixture was then immediately heated to 120°C and stirred for 18 h. After addition of an excess of methanol to quench the polymerization the solution of the copolymer was precipitated in a mixture of hexanes and isopropanol to afford the hyperbranched $PPO_{0.80}$-co-$PG_{0.20}$ in ca. 80-90% yield.

Synthesis of (R,R)-(salcy)-CoOBzF$_5$.

(R,R)-(salcy)CoOBzF$_5$ was prepared as described by Coates et. al.[43] Recrystallized (R,R)-(salcy)-Co^{II} and pentafluorobenzoic acid (0.42 g, 2 mmol) were added to a 50 mL round-bottom flask charged with a Teflon stir bar. Toluene (20 mL) was added to the reaction mixture, and it was stirred open to air at 22 °C for 12 h. The solvent was removed by rotary evaporation at 22 °C, and the solid was suspended in 200 mL of pentane and filtered. The dark green material was dried *in vacuo* and collected in quantitative yield (1.5 g). ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 1.30 (s, 18H), 1.59 (m, 2H), 1.74 (s, 18H), 1.90 (m, 2H), 2.00 (m, 2H), 3.07 (m, 2H), 3.60 (m, 2H), 7.44 (d, 4J) 2.5 Hz, 2H), 7.47 (d, 4J) 3.0 Hz, 2H), 7.81 (s, 2H).

Characterization

Characterization Data for the *hb*-PPO-*co*-PG copolymer macroinitiators

Figure S1 shows the ^{1}H NMR spectrum of a typical PPO-*co*-PG copolymer. Both the initiator core and the hydroxyl protons are clearly visible. The fraction of glycerol units incorporated into the polymer was calculated by referencing to the methyl group of the initiator (0.78 ppm) and comparing this value with the integral of the methyl group of the propylene oxide units (0.99-1.05 ppm) and the methylene and methine groups of the polymer backbone (3.1-3.9 ppm). In addition, the total number of glycidol units of each macromolecule corresponds to the total number of hydroxyl groups (4.4-4.7 ppm) minus the number of hydroxyl groups introduced by the initiator moiety (assuming that the core is fully incorporated into all chains of the polymer distribution). In the case of a trimethylolpropane core, n(OH) core equals a value of 3. The other five protons of each glycerol unit as well as three propylene oxide protons generate a broad resonance between 3.1 and 3.8 ppm. Hence, the ratio of propylene oxide and glycerol repeat units can be directly calculated.

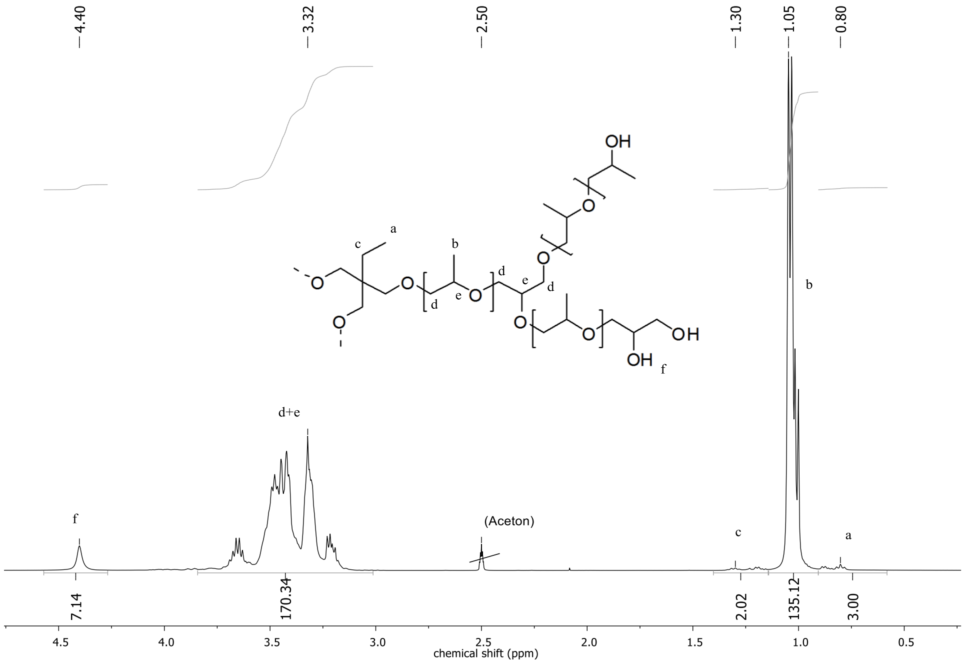

Figure S1. ^{1}H NMR spectrum of a typical hyperbranched PPO-*co*-PG copolymer.

$$\#PO = \frac{I_{Methyl}}{3}$$

$$\#G = \frac{I_{Backbone} - 3\times\#PO}{5}$$

$$\#G = n(OH)_{total} - n(OH)_{core}$$

Both equations for the calculation of the number of glycidol units are in good agreement. These values become incorrect if the core is not fully incorporated into the polymer and/or if the intensity of the hydroxyl groups is very low (e.g., at low glycidol feed ratios).

$$DP_n = \#G + \#PO$$

$$\%G = \frac{\#G}{DP_n}$$

The overall degree of polymerization (DP_n) is the sum of both comonomers, and the glycidol content is calculated by dividing the number of G units by the DP_n. All values are rounded to integer.

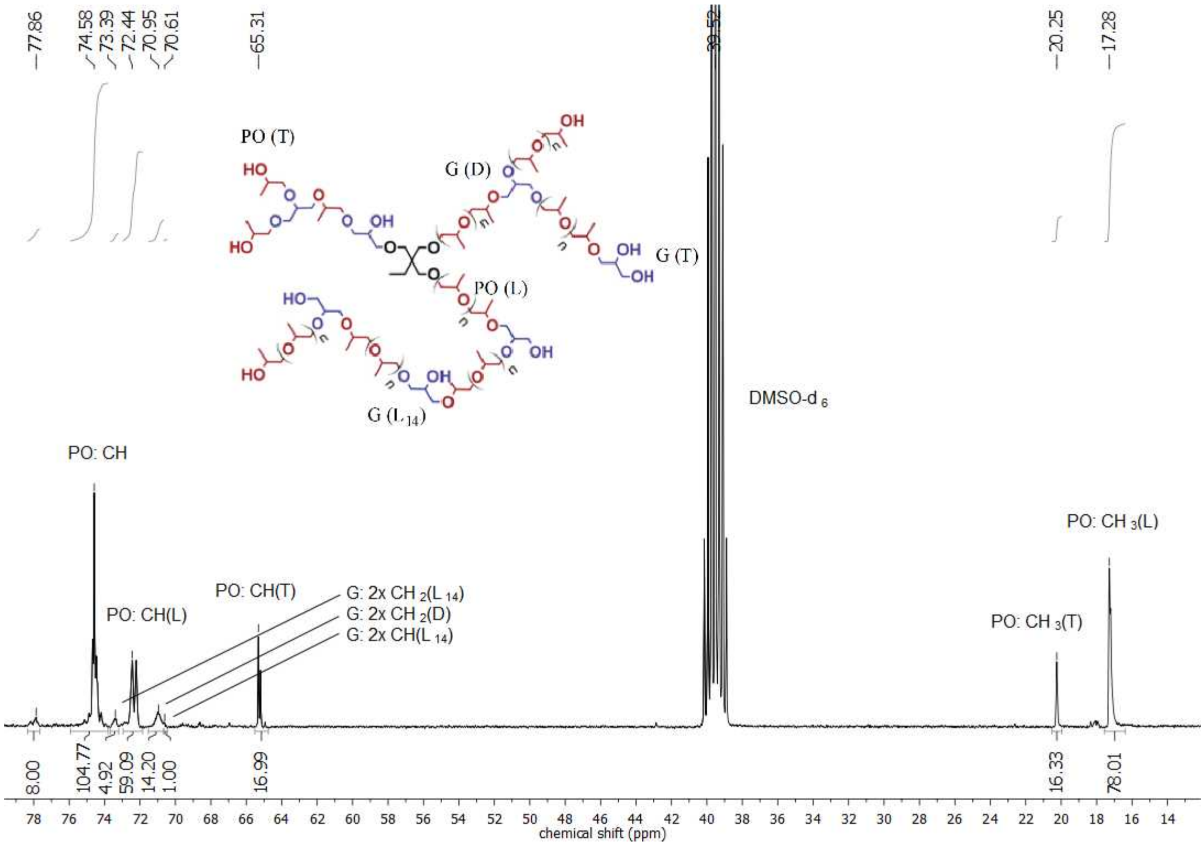

Figure S2. ^{13}C NMR spectrum of a typical PPO-*co*-PG copolymer.[1]

The degree of branching DB was calculated using the equation introduced by Hölter and Frey for random copolymerization of AB/AB$_2$ systems.[1]

$$DB_{AB/AB_2} = \frac{2D}{2D + L}$$

Figure S3 shows typical SEC traces of hb-PPO-*co*-PGs, measured in DMF with linear PEG standards.

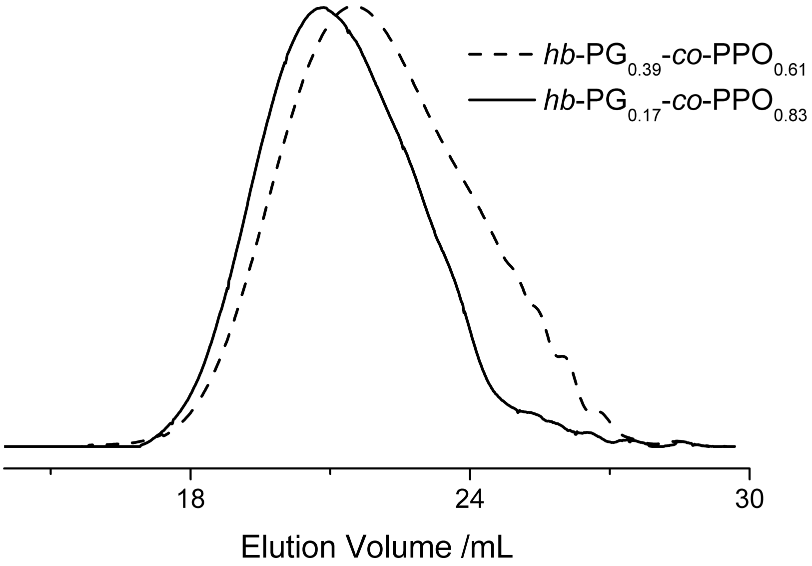

Figure S3. SEC Results for hyperbranched core molecules.

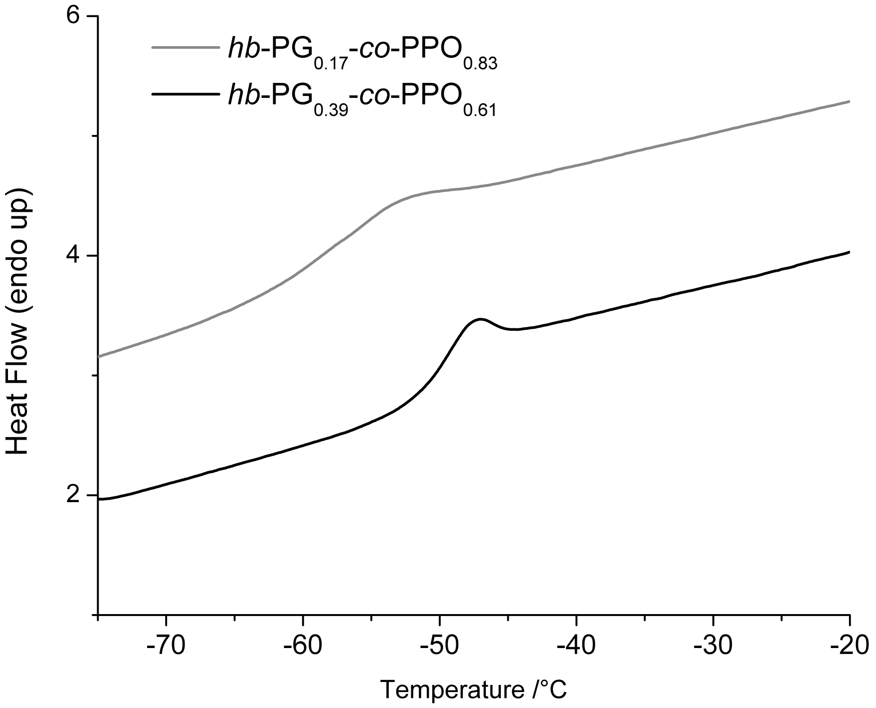

Figure S4. DSC Results for the hyperbranched core molecules.

Characterization Data for (PPO-*co*-PG)-*g*-PPC star copolymers

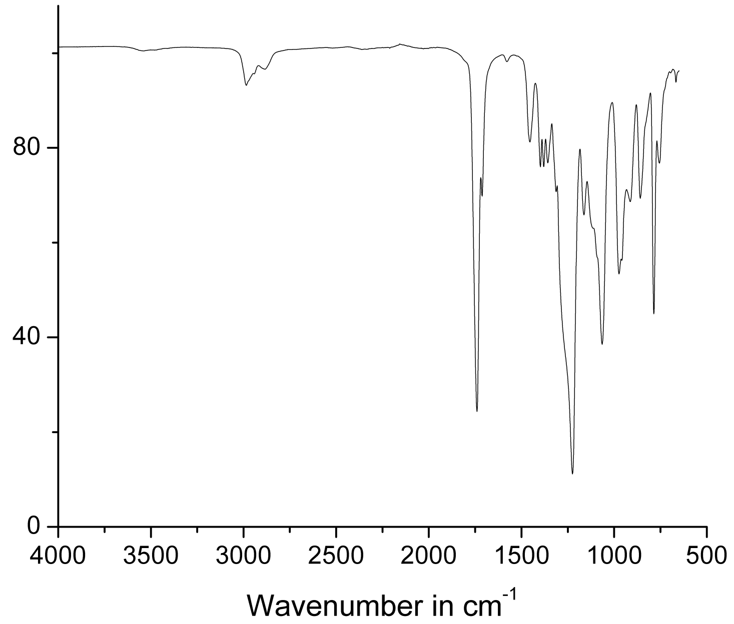

Figure S5. FT-IR spectrum of a typical (PPO-*co*-PG)-*g*-PPC star copolymer.

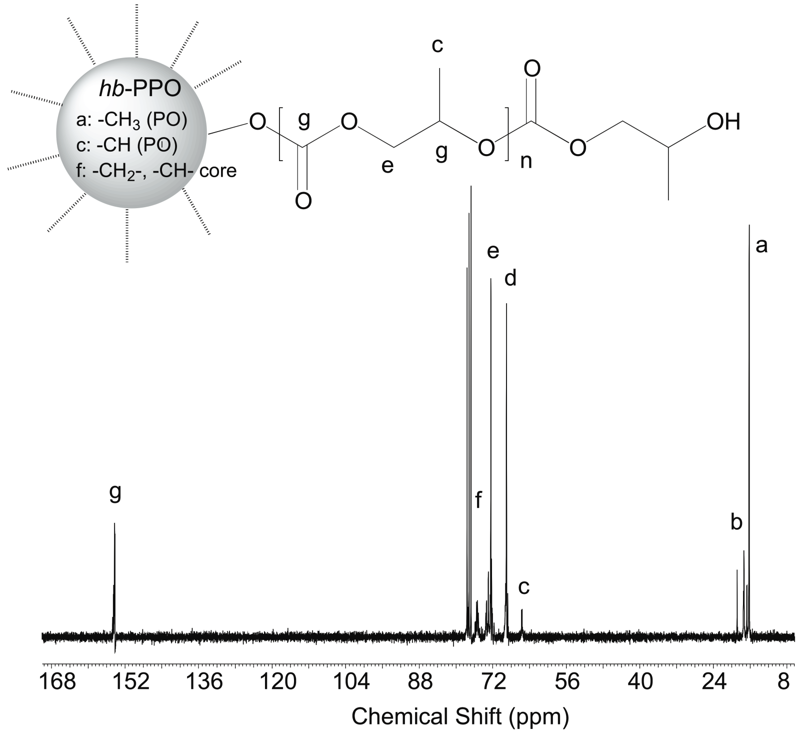

Figure S6. ^{13}C NMR spectrum of *hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{19} (Table 1, sample 3).

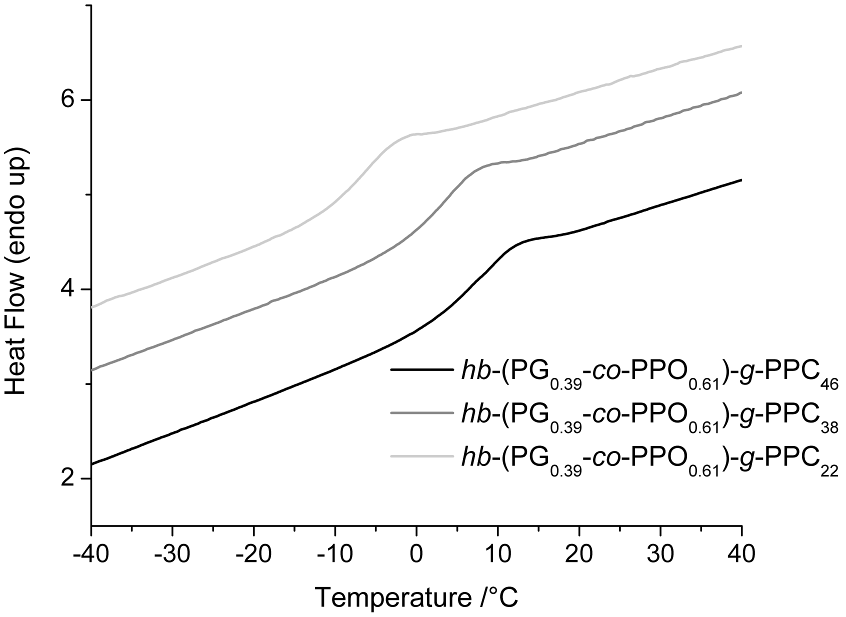

Figure S8. DSC results for the (PPO-*co*-PG)-*g*-PPC star copolymers.

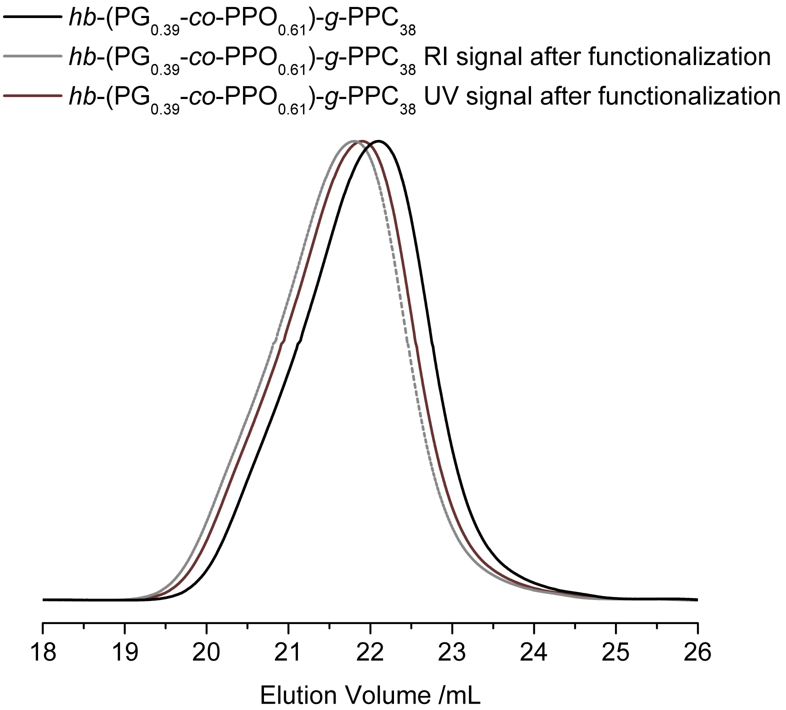

Figure S9. SEC results before and after functionalization with phenylisocyanate.

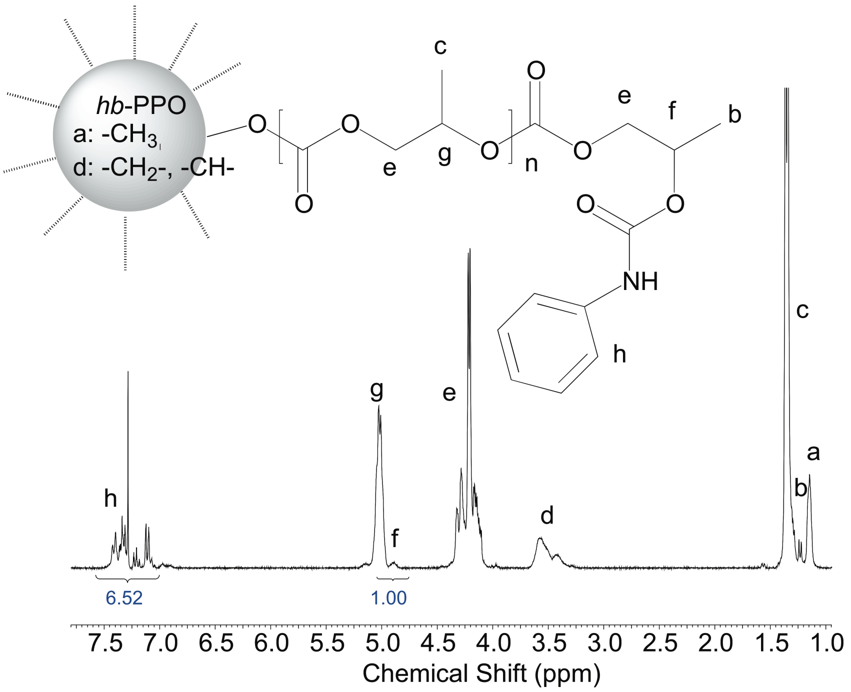

Figure S10. ^{1}H NMR spectrum of *hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{19} (Table 1, sample 3) after reaction with phenylisocyanate in $CDCl_3$.

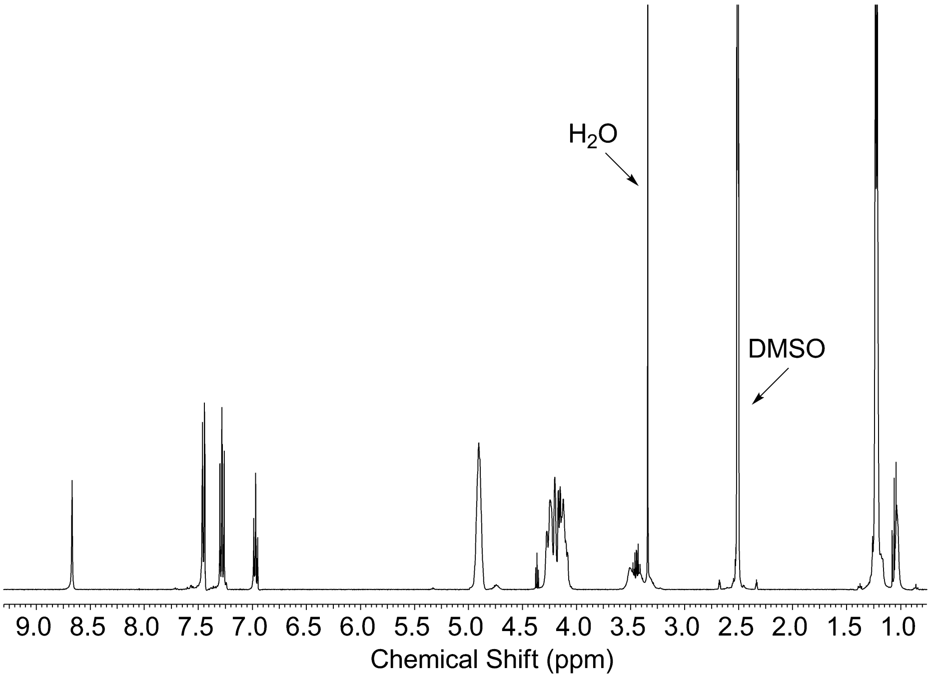

Figure S11. ^{1}H NMR spectrum of *hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{19} (Table 1, sample 3) after reaction with phenylisocyanate in DMSO.

Determination of the intrinsic viscosity in chloroform at 25 °C

***hb*-$PG_{0.17}$-*co*-$PPO_{0.83}$ (sample 1):**

#	Concentration (g/cm^3)	Reduced Viscosity (cm^3/g)
1	0.0554	5.6776
2	0.0523	5.6782
3	0.0496	5.5844
4	0.0471	5.4530
	Intrinsic Viscosity	***5.8847 cm^3/g***

***hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_9(sample 2):**

#	Concentration (g/cm^3)	Reduced Viscosity (cm^3/g)
1	0.0441	12.3249
2	0.0416	12.1737
3	0.0394	12.0034
4	0.0375	11.8464
	Intrinsic Viscosity	***9.0658 cm^3/g***

***hb*-($PG_{0.17}$-*co*-$PPO_{0.83}$)-*g*-PPC_{19} (sample 3):**

#	Concentration (g/cm^3)	Reduced Viscosity (cm^3/g)
1	0.0783	17.4745
2	0.0718	17.0068
3	0.0664	16.6044
4	0.0618	16.2729
	Intrinsic Viscosity	***11. 6199 cm^3/g***

_hb_-($PG_{0.17}$-_co_-$PPO_{0.83}$)-_g_-PPC_{27} (sample 4):

#	Concentration (g/cm^3)	Reduced Viscosity (cm^3/g)
1	0.0535	17.6031
2	0.0505	17.3698
3	0.0478	17.1377
4	0.0433	16.6439
	Intrinsic Viscosity	***12.5777 cm^3/g***

_hb_-$PG_{0.39}$-_co_-$PPO_{0.61}$ (sample 5, hyperbranched polyether):

#	Concentration (g/cm^3)	Reduced Viscosity (cm^3/g)
1	0.1034	6.7147
2	0.0976	6.6653
3	0.0925	6.5750
4	0.0837	6.3701
	Intrinsic Viscosity	***4.9413 cm^3/g***

References

1. M. Schömer, J. Seiwert, H. Frey, *ACS Macro Lett.* **2012**, *1*, 888-891.

Chapter 3: Functional Polycarbonates with Glycidyl Ether Monomers

3.1. Poly(1,2-glycerol carbonate): A Fundamental Polymer Structure Synthesized from CO_2 and Glycidyl ethers

Jeannette Geschwind[1†] **and Holger Frey**[*1]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg 10-14, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany

[†]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

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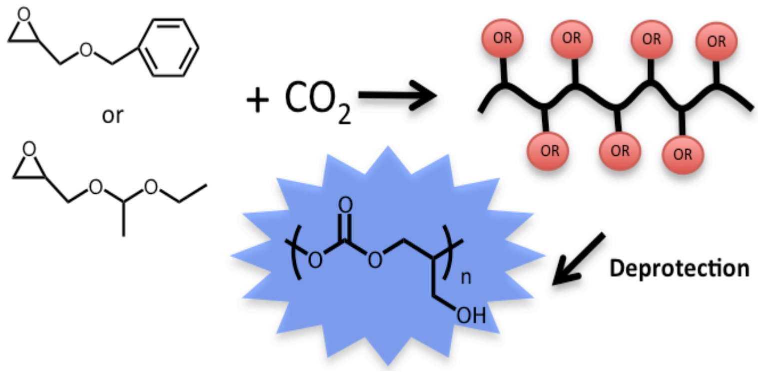


Abstract

The functional, aliphatic poly(1,2-glycerol carbonate) as a fundamental, simple polymer structure based on glycerol and CO_2 was prepared by combination of glycidyl ether monomers with carbon dioxide via two different approaches. The material was obtained by two-step procedures either from copolymerization of (i) ethoxy ethyl glycidyl ether (EEGE) or (ii) benzyl glycidyl ether (BGE) with CO_2, followed by removal of the protecting groups via acidic cleavage for (i) and hydrogenation for (ii). The resulting protected polycarbonate structures and the targeted poly(1,2-glycerol carbonate) were investigated with ^{1}H NMR and ^{13}C NMR spectroscopy as well as 2D-NMR methods. Removal of the respective protecting groups was possible without backbone degradation. All new poly(carbonate)s have been characterized with respect to their thermal behavior in bulk. Protected and deprotected poly(1,2-glycerol carbonate) was obtained with molecular weights in the range of 5000-25,200 g/mol and a PDI from 1.24 to 2.33. The degradation kinetics of poly(1,2-glycerol carbonate) in DMF has also been studied, demonstrating fast degradation to cyclic carbonates.

Introduction

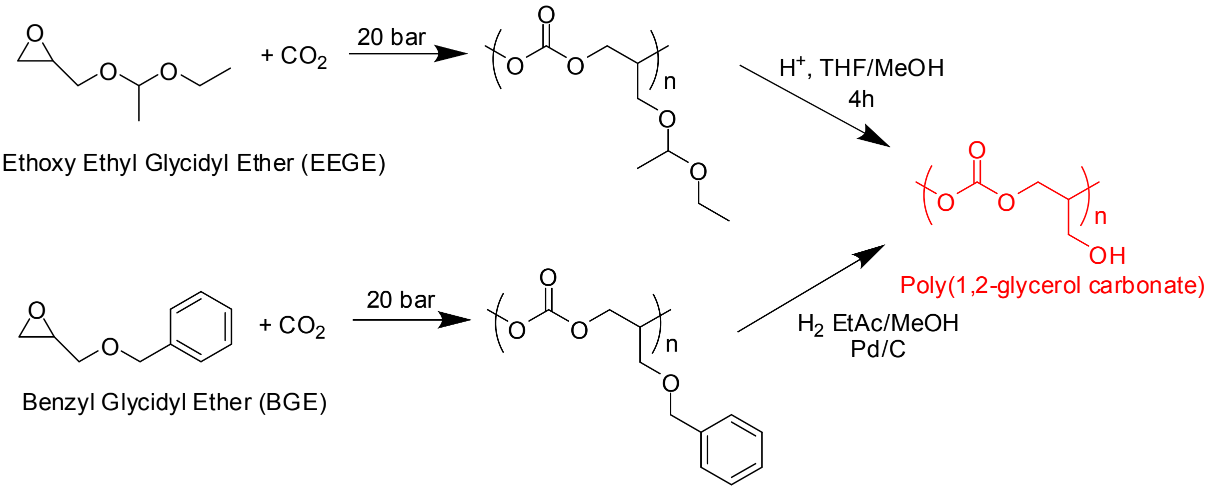
Aliphatic poly(carbonate)s (PCs) represent a promising class of biodegradable polymers for a variety of applications. [1–4] Currently, there is an increasing interest in functional, aliphatic polycarbonates that can be prepared directly from carbon dioxide (CO_2).[5–10,11] Functional groups that are distributed randomly at the polymer backbone could be employed to tailor the chemical properties of the materials, such as hydrophilicity/hydrophobicity, biocompatibility and biodegradability. Ring-opening polymerization (ROP) of six-membered cyclic carbonates is the established pathway for the synthesis of functional aliphatic PCs.[12,13,14,15–20] For the synthesis of poly(trimethylene carbonate) (PTMC) and poly(dimethyl trimethylene carbonate) and their functional derivatives[21,22] cyclic carbonates bearing different functional groups have been investigated. An overview of currently known cyclic carbonate monomers was recently given by Zhang and coworkers.[2]

An alternative method for the synthesis of aliphatic PCs is the copolymerization of epoxides and carbon dioxide (CO_2). Since 1969 various catalysts for this reactions have been developed.[23–25] Mostly cobalt(III)-salen, phenoxide zinc or β-diiminate-zinc complexes are used.[26,27,28–31] For example styrene oxide[32], limonene oxide[33], indene oxide[34] and epichlorohydrin[5] have been copolymerized with CO_2. However, the selective synthesis of polycarbonates from epoxides with electron-withdrawing groups still remains a challenge, and most often propylene oxide and cyclohexene oxide have been used.[23–25,35] To date, glycidyl ethers have rarely been employed, since copolymerization with carbon dioxide using common catalysts is not possible.

We are particularly interested in the basic poly(glycerol carbonate) structures that merely consist of glycerol and CO_2 as building units. Both carbon dioxide as well as glycerol are readily available resources, and the characteristics of these fundamental polymer structures are of interest with respect to potential application in various areas. There are two poly(glycerol carbonate) isomers, poly(1,2-glycerol carbonate) and poly(1,3-glycerol carbonate). The widely known poly(1,3-glycerol carbonate) is prepared by ROP of 5-benzoyl 1,3-dioxan-2-on (BTMC), followed by hydrogenation to remove the benzyl protecting group.[36–38] Unfortunately, the monomer has to be prepared in a three step procedure. Poly(1,2-glycerol carbonate) would have to be prepared by ROP of the five membered cyclic glycerol carbonate. However, the ROP of five-membered carbonates usually results in elimination of CO_2, leading to the formation of a polycarbonate containing a significant fraction of ether groups in the polymer backbone.[12]

Thus, we targeted the preparation of poly(1,2-glycerol carbonate) directly from carbon dioxide (CO_2) and suitable glycidyl ethers with a subsequent deprotection step. It is known that glycidyl ethers can be polymerized with the simple zinc catalyst systems already developed by Inoue in 1969.[39–41] It was suggested that the epoxide/CO_2 copolymerization proceeds via alternating insertion of CO_2 and epoxide into the Zn-O bond.[42,43] However, in the last decades only scattered efforts have been made to copolymerize glycidyl ethers with CO_2.[9,44] For instance, crosslinkable poly(propylene carbonate) was prepared by Tao et al.[41] and Listos and coworkers using allyl glycidyl ether as a comonomer.[45] Other epoxides such as phenyl glycidyl ether[46] or linear aliphatic glycidyl ethers and their copolymers with carbon dioxide have been explored as novel ion conducting materials.[44] Furthermore, in a recent work we described the copolymerization of stable, hydroxyl-functional polycarbonates with glycerol side chains using isopropylidene(glyceryl glycidyl ether) and carbon dioxide.[11]

Various epoxides suitable for the preparation of poly(1,2-glycerol carbonate) have been used by our group and others for the preparation of functional polyethers, including ethoxy ethyl glycidyl ether (EEGE) and benzyl glycidyl ether (BGE).[47,48] After deprotection, EEGE and BGE release hydroxyl groups.



Scheme 1. Synthetic strategies for the preparation of the elusive poly(1,2-glycerol carbonate) via copolymerization of CO_2 and EEGE or BGE and subsequent deprotection.

Using EEGE or BGE in a copolymerization reaction with carbon dioxide, poly(1,2-glycerol carbonate) is accessible (Scheme 1). The respective glycidyl ether monomers can be prepared in one-step procedures, starting from commercially available reagents. Polymerization with carbon dioxide leads to the hitherto unknown polycarbonate structures poly(ethoxy ethyl glycidyl ether carbonate (P(EEGE C)) and poly(benzyl glycidyl ether carbonate) (P(BGE C)) . From both polymers, the fundamental poly(1,2-glycerol carbonate) polymer structure can be obtained after deprotection. This structure was mentioned by Inoue et al. in 1979, however no further characterization was given.[39] To the best of our knowledge poly(1,2-glycerol carbonate) has not been studied and characterized to date. In contrast to the other isomer poly(1,3-glycerol carbonate) which is a widely known biocompatible copolymer possessing secondary hydroxyl groups after deprotection, poly(1,2-glycerol carbonate) contains primary hydroxyl groups.[36,37] Recently, poly(1,3-glycerol carbonate) gained a lot of interest for biomedical applications. For example Grinstaff and coworkers studied the structure–property effects of conjugating various hydrophobic biocompatible side chains to poly(glycerol-co-caprolactone) copolymers with the goal of achieving prolonged and controlled release of a chemotherapeutic agent and other functionalized poly(glycerol-*co*-caprolactone) films.[53-56] Whereas Putnam and coworkers reported the synthesis of statistically random poly(carbonate-ester)s derived from lactic acid and dihydroxyacetone by ring-opening polymerization.[57-58]

This current report describes both the novel poly(glycerol carbonate)s available from the combination of glycidyl ether chemistry with CO_2 as well as the synthesis and properties of poly(1,2-glycerol carbonate).

Experimental Section

Instrumentation.

^{1}H NMR spectra (300 MHz and 400 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC300 or a Bruker AMX400 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in DMF (containing 0.25 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column ($10^6/10^5/10^4$ g mol^{-1}), a UV (275 nm) and a RI detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service. DSC measurements were performed using a PerkinElmer DSC 8500 with PerkinElmer CLN2 in the temperature range from – 100 to 150 °C at heating rates of 10 K min^{-1} under nitrogen.

Reagents.

Benzyl glycidyl ether, epichlorohydrin (99%), sodium hydroxide as well as dimethyl sulfoxide (puriss, over molecular sieve), tetrahydrofurane (puriss, over molecular sieve), and toluene (puriss, over molecular sieve) were purchased from Aldrich. Pyrogallol was recrystallized from Benzene/EtOH. Deuterated chloroform-d_1 and DMSO-d_6 were purchased from Deutero GmbH. Carbon dioxide (99.995%) was purchased from Westfalen AG and used as received. All other solvents and reagents were purchased from Acros Organics. The synthesis of ethoxy ethyl glycidyl ether (EEGE) is described elsewhere.[47,50]

Preparation of the Zinc catalyst.

The catalyst was prepared under argon immediately before use following the procedure described previously.[49] A solution of pyrogallol (0.47 g 4 mmol in 10 mL of 1,4-dioxane) was slowly added to a stirred solution of $ZnEt_2$ (2 mmol in 35 cm3 of dioxane) at room temperature. After the addition was complete, stirring was continued until the evolution of ethane stopped.

Polymerization.

The copolymerization was carried out in dioxane in the presence of a catalytic system based on $ZnEt_2$ and pyrogallol at a molar ratio of 2:1. The above described catalyst solution (2 mmol) and 50 mmol epoxide were placed into a stainless steel autoclave filled with argon. CO_2 was then introduced at a pressure of approx. 20 bar. The reaction was carried out for at room temperature for 72 h. The reaction was stopped by decompression of the autoclave. The resulting solution was diluted with $CHCl_2$, washed with 10% HCl and twice with water, dried with $MgSO_4$, precipitated in cold methanol and dried in vacuum. Yields of the crude products were ca. 60% for P(EEGE C) and > 80% P(BGE C). The purified polymers are white, soft solids that are soluble in acetone, chlorinated and aromatic solvents, and insoluble in water, lower alcohols and diethyl ether.

Deprotection of Poly(EEGE carbonate)

The acetal protecting groups were removed by the addition of 10 wt% acidic ion exchange to a 20% solution of the polymer in MeOH/THF, stirring at room temperature for a period of 3h. The ion exchange resin was removed by centrifugation, and the reaction solution was concentrated in vacuum and then dried in vacuum overnight. Yields: 90-100%.

Deprotection of Poly(BGE carbonate)

Poly(benzyl glycidyl ether carbonate) was dissolved in a 1:1 mixture of ethyl acetate and methanol and palladium on activated charcoal (10%) was added. The reaction vessel was flushed with hydrogen (40bar) and the reaction was allowed to stir for 24 h at 40 °C. The solution was filtered, concentrated and the product dried in vacuum. Poly(1,2-glycerol carbonate) was obtained as a soft, clear solid in 90% yield.

Results and Discussion

The synthesis of the zinc catalyst is based on the reaction of diethyl zinc with pyrogallol in 1,4-dioxane. The ratio of 2:1 guarantees fast and complete conversion under ethane evolution. When the addition of pyrogallol to the diethyl zinc solution was completed, stirring was continued until no more ethane was formed. The concentration of the catalyst can be calculated from the volume ethane formed.

Reasonable-molecular-weight polycarbonates with hydroxyl groups were synthesized by combination of glycidyl ether chemistry and copolymerization of epoxides with CO_2. The synthesis was accomplished in a facile two-step procedure using protected glycidyl ethers as epoxide monomers. Two routes for the deprotection were investigated **(Scheme 1).**

Starting from commercially available benzyl glycidyl ether (BGE), poly(benzyl glycidyl ether carbonate) (P(BGE-C)) was prepared in good yields (> 80%). Neither polyether linkages nor cyclic carbonate were detected by ^{1}H NMR spectroscopy. Ethoxy ethyl glycidyl ether was prepared as described previously.[47,50] Both copolymer syntheses were carried out at room temperature in a high pressure autoclave (20 bar carbon dioxide pressure) for 72 h using a diethyl zinc/pyrogallol catalyst system. Copolymerization with carbon dioxide led to poly(ethoxy ethyl ether carbonate) (P(EEGE-C) copolymers without ether linkages. Increasing the temperature led to an increasing amount of a cyclic carbonate side product.[51]The resulting NMR spectra for both copolymers are shown in **Figure 1** and **2**.

After a certain period of reaction time the pressure was reduced to atmosphere to terminate the reaction. The purification process was followed as reported in the experimental part. The resulting samples were clear rubber-like and colorless amorphous solids. The structure of the copolymers obtained is shown in **Scheme 1**.

Table 1. Overview of the Characterization Data for All Copolymer Samples Prepared

#	Sample	% Carbonate linkages[a]	M_n g/mol (SEC)[b]	PDI (SEC)	T_g /°C (DSC)
1	P(EEGE-C)	> 99	17 000	1.46	- 18.0
2	P(EEGE-C)	> 99	16 400	1.39	- 17.3
3	P(BGE-C)	> 99	21 100	1.24	- 22.0
4	P(BGE-C)	> 99	25 200	1.80	- 21.6
5	P(G-C)[c]	> 99	5 370	2.33	- 4.0
6	P(G-C)[d]	> 99	17 800	1.67	- 3.9

[a]Determined by ^1H NMR spectroscopy, [b]Determined by SEC calibrated with a polystyrene standard in DMF at 40 °C, [c]Obtained from P(EEGE C), [d]Obtained from P(BGE C).
Polymerization conditions: catalyst/epoxide 1:25, reaction time 72h, CO_2 pressure 20 bar.

All synthesized polycarbonates were characterized by ^1H NMR and ^{13}C NMR spectroscopy. Molecular weights and polydispersities were estimated using size exclusion chromatography (SEC, cf. **Table 1**).

Most SEC results of the protected copolymers show a monomodal distribution in the molecular weight range from 16 400 to 25 200 with a moderate PDI between 1.39 to 1.80. Some of the copolymers exhibited bimodal distributions, which is a typical phenomenon in the copolymerization of CO_2 and epoxides, when using binary catalyst systems. This effect is caused by two reactive catalyst species and possible initiation by traces of water.

The alternating structure of the product was confirmed by IR and ^1H NMR spectroscopy. All polymers show a strong IR absorption at around 1750 cm^{-1}, which can be assigned to the C=O group of the linear carbonate, confirming the incorporation of carbon dioxide into the polymer as a carbonate structure. The characteristic vibration band of cyclic carbonate side products can usually be found at around 1800 cm^{-1} and cannot be seen in the resulting spectra (**Figure S8)**.

In **Figure 1,** an exemplary ^1H NMR spectrum of P(EEGE-C in $CDCl_3$ is shown (sample 1). In addition to the polycarbonate backbone signal (d = 5.00 ppm, signal b and d = 4.30 ppm, signal a), the resonances for the side group (d = 3.3-3.8 ppm, signal c) and the acetal protecting (signal d-f) group can be found. The glycidyl ether methylene signal (signal c) splits up, clearly observable in 2D NMR spectroscopy (Figures S3-S6).

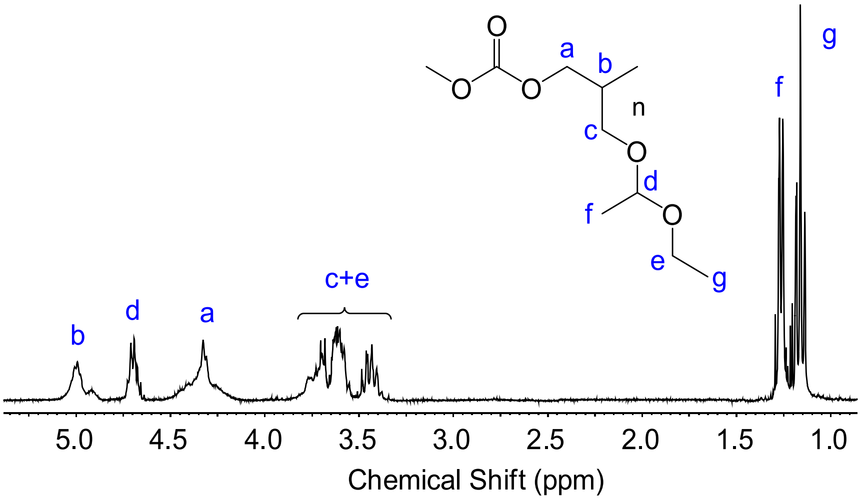


Figure 1. ^{1}H NMR spectrum of a poly(ethoxy ethyl glycidyl ether carbonate) copolymer

No epoxide homopolymer, i.e. ether linkages, can be detected from the ^{1}H NMR spectra. Such structures would result in additional signals between δ 3-4 ppm. This supports the strictly alternating placement of ethoxy ethyl glycidyl ether or benzyl glycidyl ether and CO_2. For signal b a small shoulder can be seen. Since workup was done under acidic conditions, as can be seen in the experimental part, some acetal protecting groups might be already cleaved, however we could not see this effect for all samples.

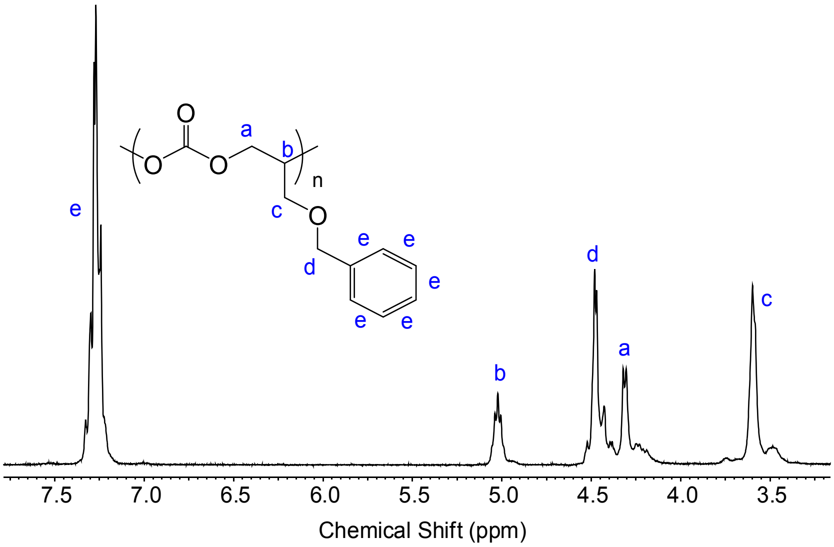


Figure 2. ^{1}H NMR spectrum of the poly(benzyl glycidyl ether carbonate) copolymer.

The structure of poly(benzyl glycidyl ether carbonate) was also confirmed by ^{1}H NMR spectroscopy. The polycarbonate backbone peaks, signal a and b, can be found at d = 4.28 ppm and 5.05 ppm, the benzyl proton signal can be found at d =7.30 ppm (signal e). Signal d (d =4.50 ppm) and signal c (d =3.6 ppm) can be assigned to the four side chain methylene protons.

All assignments were confirmed by 2D NMR spectroscopy **(Figure S5)**. ^{13}C NMR measurements for both polymers show a signal at around d =154 ppm of the carbonyl group (C=O) in the main chain.

To the best of our knowledge, the thermal properties of random copolymers of poly(ethoxy ethyl ether carbonate) and poly(benzyl glycidyl ether carbonate) have not been studied to date. They were examined by differential scanning calorimetry (DSC). No melting point was observed for any of the copolymers, confirming their amorphous character. The results are summarized in **Table 1**. The glass-transition temperature (T_g) of P(EEGE-C) and P(BGE-C) is -17.3 °C and -21.6 °C. Compared to benzyl protected poly(1,3-glycerol carbonate) having a glass transition temperature of 0°C, which was described by Liu et. al., the Tg is lower in our case.[38] Both P(EEGE-C) and P(BGE-C) are colorless, rubber like solids, which are soluble in toluene, benzene, chloroform ,DMF and DMSO.

Deprotection

Acidic removal of the ethoxy ethyl protecting group yielded linear 1,2-poly(glycerol carbonate). Deprotection of the P(EEGE-C) polymer obviously is not trivial, since acidic deprotection can not only cleave the acetal protection group, but also affects the polycarbonate backbone, when the conditions are too harsh. However, acetal cleavage in our experience is usually to be faster than carbonate degradation. In order to study the kinetics of the deprotection, the reaction was monitored by ^{1}H NMR spectroscopy. The reaction was carried out in a THF/methanol mixture, using acidic ion exchange resin (Dowex 50WX8) and sample were taken in increasing intervals from 5 to 30 minutes for 4 h. The results of the kinetic study are shown in **Figure 3**.

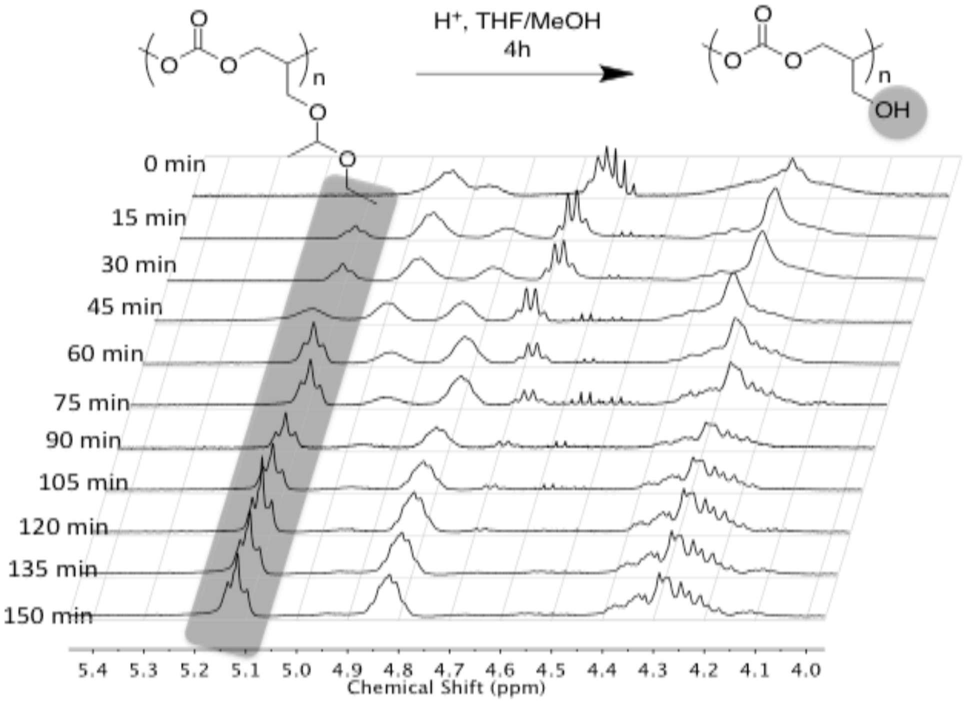


Figure 3. Time-resolved 300 MHz ^{1}H NMR spectra for the acidic deprotection of poly(ethoxy ethyl glycidyl ether carbonate).

In **Figure 3**, the region from d =5.4 to 4.0 ppm is shown. Deprotection was monitored by comparison of the intensity of the decreasing methylene signal of the glycidyl ether and the integration of the increasing hydroxyl group proton signal. The reaction was completed after 3.5 h, since longer reaction times led to polymer degradation. Moreover crosslinking occurred, while using hydrochloric acid as a proton source for the deprotection, and the resulting copolymer became insoluble in both organic and aqueous solvents.

Deprotection of the benzyl groups of poly(benzyl glycidyl ether carbonate) by hydrogenation using Pd/C as a catalyst is also shown in **Scheme 1** (vide supra). The reaction was not successful when using THF, DMF or 1,4-dioxane as solvents, even if the temperature was raised to 60 °C. However removal of the benzyl groups could be carried out using an ethyl acetate (EtOAc) methanol mixture 1:1 as a solvent at 40 °C for 24 h and 40 bar. At room temperature the reaction remained incomplete. When running the deprotection reaction for more than 24 h, degradation of the polymer backbone commenced. The ^{1}H NMR spectrum of the deprotected sample obtained in DMSO-$d_6$demonstrates complete disappearance of the benzyl proton signals (d = 7.1 ppm) (**Figure 4**).

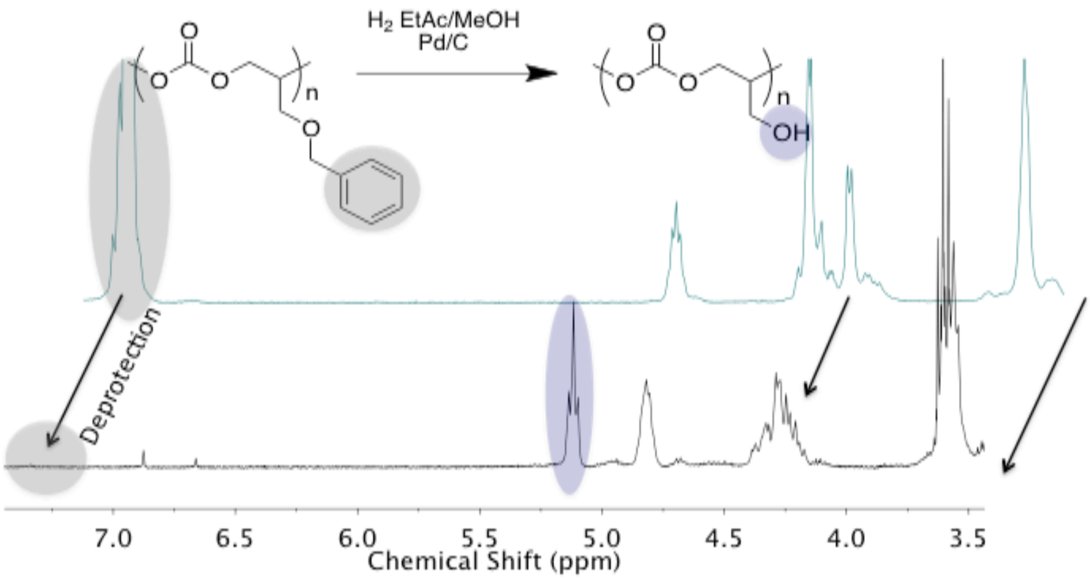


Figure 4. ^{1}H NMR spectra for the acidic deprotection of poly(benzyl glycidyl ether carbonate); middle spectrum: incomplete deprotection.

Poly(1,2-glycerol carbonate).

Both synthesis and deprotection strategies lead to the same product, the poly(1,2-glycerol carbonate), which can be seen in **Figure 5**, however with different molecular weights. In both cases the protecting groups were fully removed. Size exclusion chromatography evidences that the polymer structure is preserved. The backbone signals are found at d = 4.85 and 4.25 ppm, whereas the side group methylene signal and the hydroxyl group signal are observed at d = 3.55 and 5.12 ppm. No cyclic carbonate degradation products were found in the NMR as well as in IR spectroscopy, and no cyclic carbonate signal typical for degradation can be found. ^{13}C NMR spectroscopy also confirmed the structure of poly(1,2-glycerol carbonate) as can be seen in **Figure 6**. Signal a in Figure 6 at around d =154 ppm can be assigned to the carbonyl group (C=O) in the main chain and all signals from the protection groups vanished (compare Figure S5 and S8).

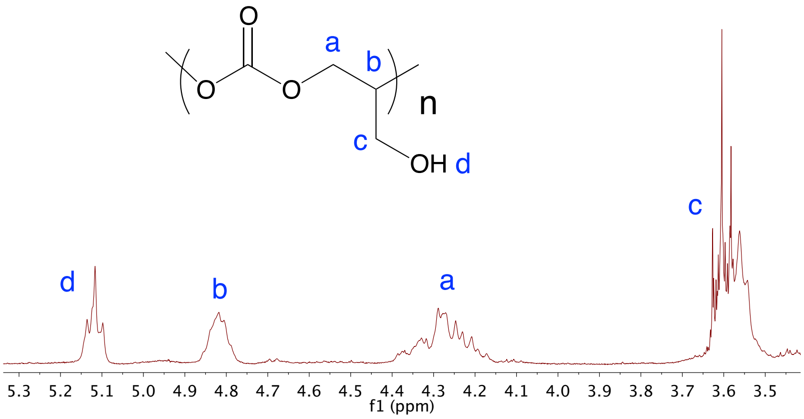


Figure 5. ^{1}H NMR spectrum for poly(1,2-glycerol carbonate).

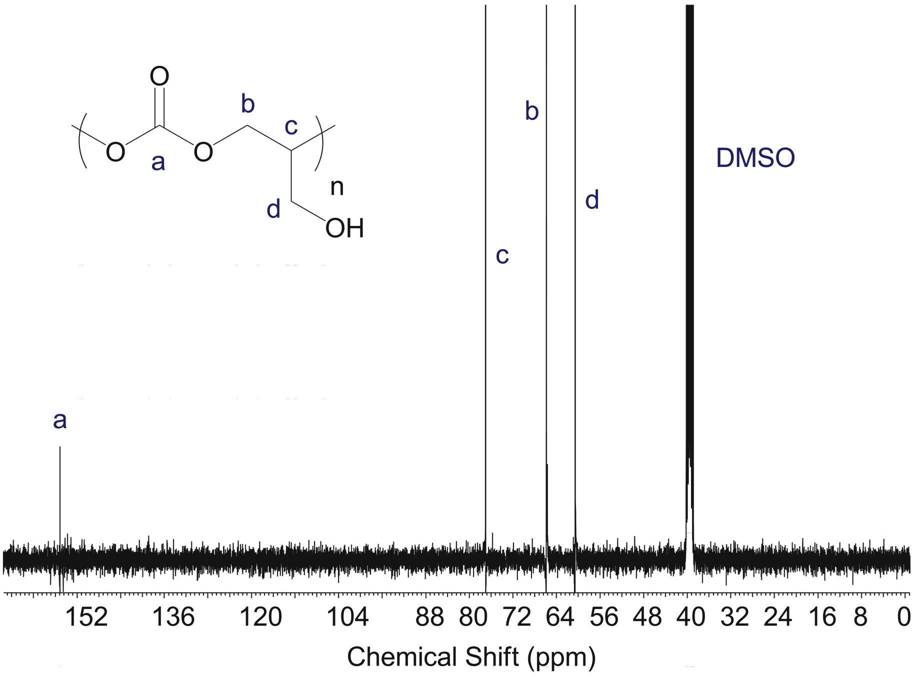


Figure 6. ^{13}C NMR spectrum for poly(1,2-glycerol carbonate).

Figure 5 shows the expected, simple ^{1}H NMR spectrum for the fundamental poly(1,2-glycerol carbonate). For the polymer obtained from the P(BGE-C) copolymer, GPC analysis results reveals that the deprotection reaction did not result in a remarkable decrease in molecular weight or significantly broader molecular weight distributions. In contrast, the poly(1,2-glycerol carbonate) copolymers obtained from P(EEGE-C) showed slightly lower molecular weights than the precursor, maybe due to a low extent of degradation of the polymer backbone. However all poly(1,2-glycerol carbonate) samples obtained showed unimodal distributions with moderate PDIs. (**Figure 7**).

Properties of Poly(1,2-glycerol carbonate) and Degradation

The resulting colorless, rubber like poly(1,2-glycerol carbonate) was insoluble in toluene, benzene and chloroform, but soluble in DMF and DMSO. In methanol and water swelling of the copolymer was observed. Poly(1,3-glycerol carbonate) on the other hand is also soluble in DMF and DMSO, partially soluble in CH_3OH, but its solubility in $CHCl_3$ and ether is poor.[38]

Compared to the protected copolymers, the glass-transition temperature of the poly(1,2-glycerol carbonate) is around -4 °C and therefore higher than that of the protected copolymers, which we ascribe to the influence of the hydroxyl groups. No glass transition temperatures for poly(1,3-glycerol carbonate) are described in current literature so far.

One of the central properties of poly(glycerol carbonate)s is their degradability. The degradation behavior of 1,2-poly(glycerol carbonate) in solution was investigated at neutral pH in bulk, DMF and THF. Size exclusion chromatography measurements were performed in DMF and THF for several days, and the decrease in molecular weight was followed. The results can be seen in Figure 7 and Figure S14.

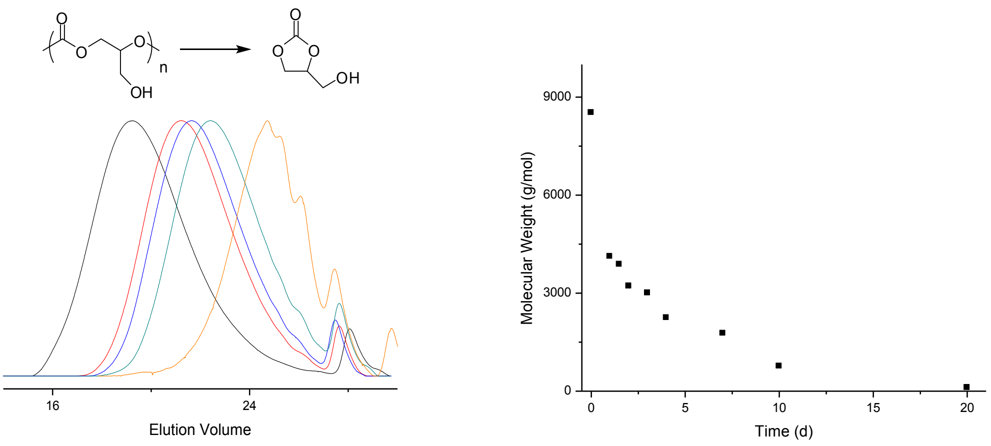


Figure 7. SEC results for the degradation of poly(1,2-glycerol carbonate) in DMF; and the same results plotted molecular weight versus time.

During degradation the more thermodynamically stable cyclic 1,2-glycerol carbonate with a molecular weight of 118.09 g/mol is formed. The decrease in molecular weight can clearly be seen in the SEC traces. For the degradation in DMF after 20 days only oligomers are left in the solution (**Figure 7**). For the degradation in THF the degradation was faster and after around two weeks only the cyclic five-membered glycerol carbonate was left (**Figure S14**). To investigate the degradation in bulk a poly(1,2-glycerol carbonate) sample was stored at -28 °C for several weeks. After eight week a significant amount of cyclic carbonate was formed, as can bee seen in **Figure S15**. Compared to other poly(carbonate)s used in biomedical application such as poly(trimethylene carbonate) the degradation rate of poly(1,2-glycerol carbonate) is much faster, whereas poly(1,2-propylene carbonate), which can be prepared by carbon dioxide and propylene oxide, completely suppresses enzymatic attack and is also stable in solution. [59-60]

Degradation took also place in the solid state in moist atmosphere, as indicated by the appearance of an infrared absorption at about 1800 cm^{-1} at the expense of that at 1750 cm^{-1}, belonging to the carbonyl stretching vibration of the five-membered cyclic glycerol carbonate produced. The rapid degradation of poly(1,2-glycerol carbonate) compared to poly(propylene carbonate) (PPC) or also poly(1,3-glycerol carbonate) results in an intramolecular attack of the pendant hydroxyl groups towards the carbonate linkage and the formation of the thermodynamically stable 5-membered cyclic glycerol carbonate (**Figure 7**). Water absorption is a simple way to evaluate the hydrophilicity of polymers and it is defined as the weight percentage of water in wet polymer. It was measured after the polymer had been immersed in distilled water to equilibrium at room temperature.p[52] The water absorbance of poly(1,2-glycerol carbonate) compared to the protected analogues is much higher, this fact indicated that the presence of hydroxyl groups at the polymer chains result in an enhancement of chain hydrophilicity. The same results were also found for poly(1,3-glycerol carbonate).

Conclusions

Two innovative routes for the synthesis of the fundamental polymer structure 1,2-poly(glycerol carbonate) were described. Since glycerol and carbon dioxide represent readily available resources, the behavior of such a simple polymer structure is interesting. On the one hand a huge amount of almost pure carbon dioxide is formed as by-product in most types energy production and glycerol is obtained as side product in the production of bioethanol. Reacting ethoxy ethyl glycidyl ether and benzyl glycidyl ether in a copolymerization with carbon dioxide using a simple zinc catalyst system, protected 1,2-poly(glycerol carbonate)s were obtained. ^{1}H NMR spectra as well as ^{13}C NMR and IR spectroscopy confirmed the structure of the resulting polymers. The protecting groups could be cleaved in both cases, either by acidic treatment or by hydrogenation, respectively. However, hydrogenation turned out to be the more effective way, since no loss in molecular weight was observed. For poly(ethoxy ethyl glycidyl ether carbonate) the protection groups had to be removed under acidic conditions, which lead to degradation of the polymer backbone and smaller molecular weight after deprotection, since the carbonate bonds are also acid labile. Therefore the synthesis of poly(1,2-glycerol carbonate) using a benzyl glycidyl ether/CO_2 copolymerization was preferred. Furthermore thermal properties and degradation behavior of all new polycarbonates have been studied. DSC results show that all synthesized polymers are amorphous with glass transition temperature below 0 °C. Preliminary examination in solution as well as in bulk revealed that hydrophilic degradable materials were obtained. Moreover poly(1,2-glycerol carbonate) can enable covalent attachment of small substances as well as other functionalizations. The combination of CO_2 and glycidyl ether chemistry is an innovative way for the synthesis of poly(1,2-glycerol carbonate), a polymer, which consists only of carbon dioxide and glycerol, two prominent non-toxic side products in chemical industry .

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Supporting Information for: Poly(1,2-glycerol carbonate): A Basic Polymer Structure Synthesized from CO_2 and Glycidyl ethers

Jeannette Geschwind[1,†] and Holger Frey[*1]

Overview over all polymers

#	Sample	% Carbonate linkages[a]	M_n g/mol (SEC)[b]	PDI (SEC)	Tg /°C (DSC)
1	**P(EEGE-C)**	**> 99**	**17 000**	**1.46**	**- 18.0**
1b	P(EEGE-C)	> 99	17 800	1.43	- 17.7
1c	P(EEGE-C)	> 99	16 500	1.48	- 17.6
2	**P(EEGE-C)**	**> 99**	**16 400**	**1.39**	**- 17.3**
3	**P(BGE-C)**	**> 99**	**21 100**	**1.24**	**- 22.0**
3b	P(BGE-C)	> 99	22 300	1.26	- 22.1
3c	P(BGE-C)	> 99	23 400	1.32	- 21.8
4	**P(BGE-C)**	**> 99**	**25 200**	**1.80**	**- 21.6**
5	**P(G-C)[c]**	**> 99**	**5 370**	**2.33**	**- 4.0**
5b	P(G-C)[c]	> 99	6 500	2.33	- 3.8
5c	P(G-C)[c]	> 99	7 300	2.33	- 4.1
6	**P(G-C)[d]**	**> 99**	**17 800**	**1.67**	**- 3.9**
6b	P(G-C)[d]	> 99	18 600	1.69	- 3.8
6c	P(G-C)[d]	> 99	19 100	1.68	- 4.0

[a]Determined by ^1H NMR spectroscopy, [b]Determined by SEC calibrated with a polystyrene standard in DMF at 40 °C, [c]Obtained from P(EEGE C), [d]Obtained from P(BGE C).

Deprotection of P(BGE C)

Solvent	Temperature	Time/ h	Pd/C gw%	Pressure	Result
THF	RT	24	10	40	no reaction
THF	60°C	24	10	40	no reaction
THF/MeOH	RT	24	5	40	no reaction
THF/MeOH	40°C	24	10	40	no reaction
THF/MeOH	60°C	24	5	40	no reaction
Dioxan/Me	RT	24	10	40	no reaction
Dioxan/Me	60°C	24	10	40	no reaction
DMF/MeOH	RT	24	5	40	no reaction
DMF/MeOH	60°C	24	10	40	no reaction
Ethylacetat	RT	24	10	40	degradation
Ethylacetat/	RT	24	10	40	incomplete
Ethylacetat/	40°C	24	10	40	complete

Size Exclusion Chromatography

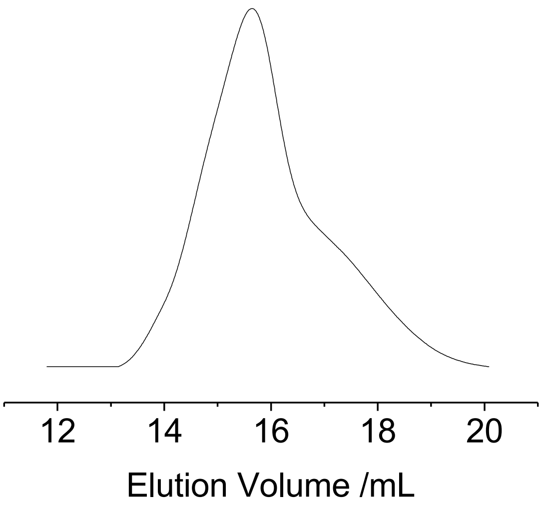

Figure S1. SEC trace of Poly(ethoxy ethyl glycidyl ether carbonate) (P(EEGE-C)).

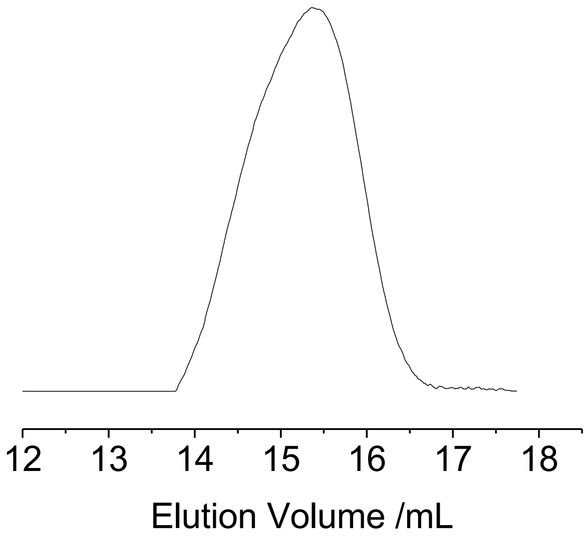

Figure S2. SEC trace of Poly(benzyl glycidyl ether carbonate) (P(BGE-C)).

2 D NMR Spectroscopy

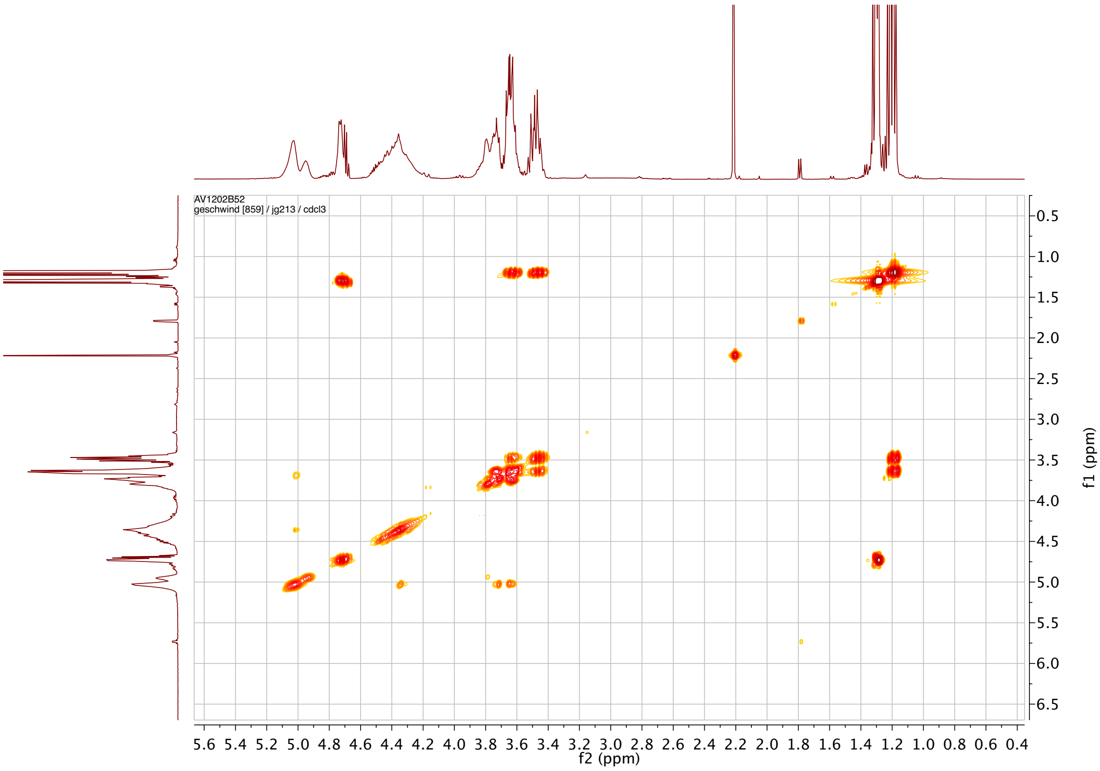

Figure S3. HSCQ of Poly(ethoxy ethyl glycidyl ether carbonate).

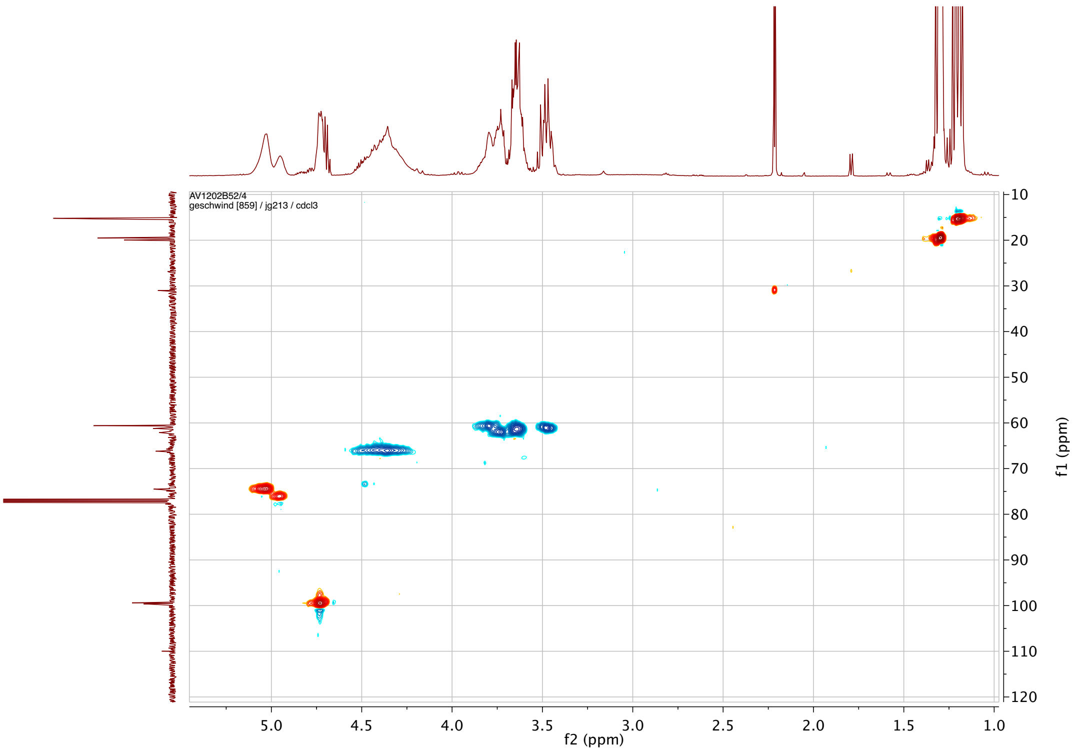

Figure S4. COSY of Poly(ethoxy ethyl glycidyl ether carbonate).

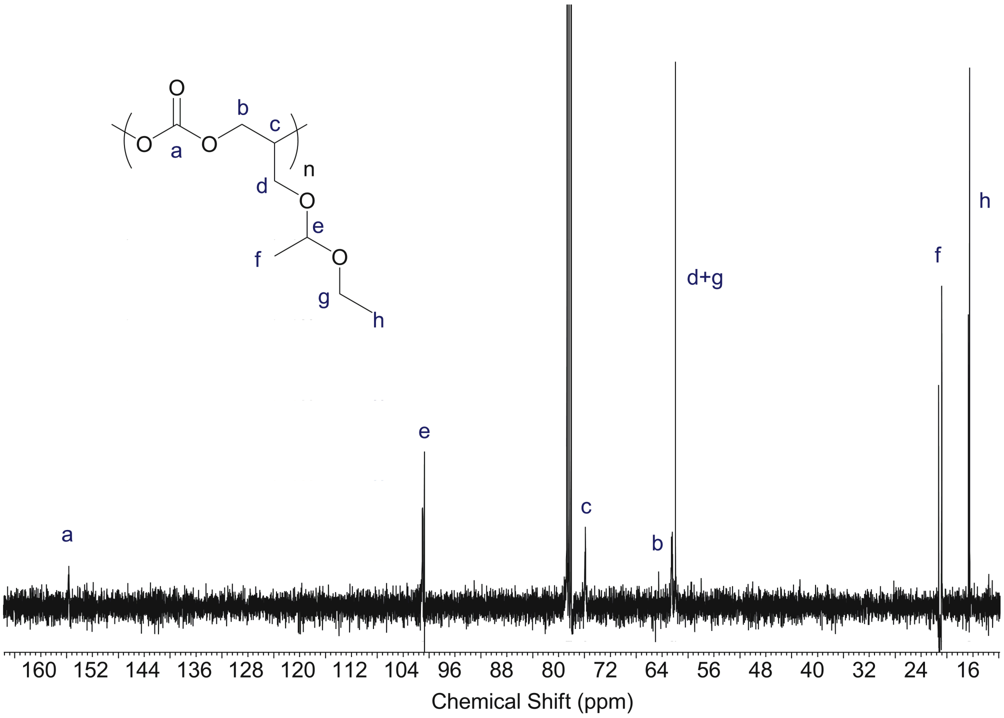

Figure S5. ^{13}C of Poly(ethoxy ethyl glycidyl ether carbonate).

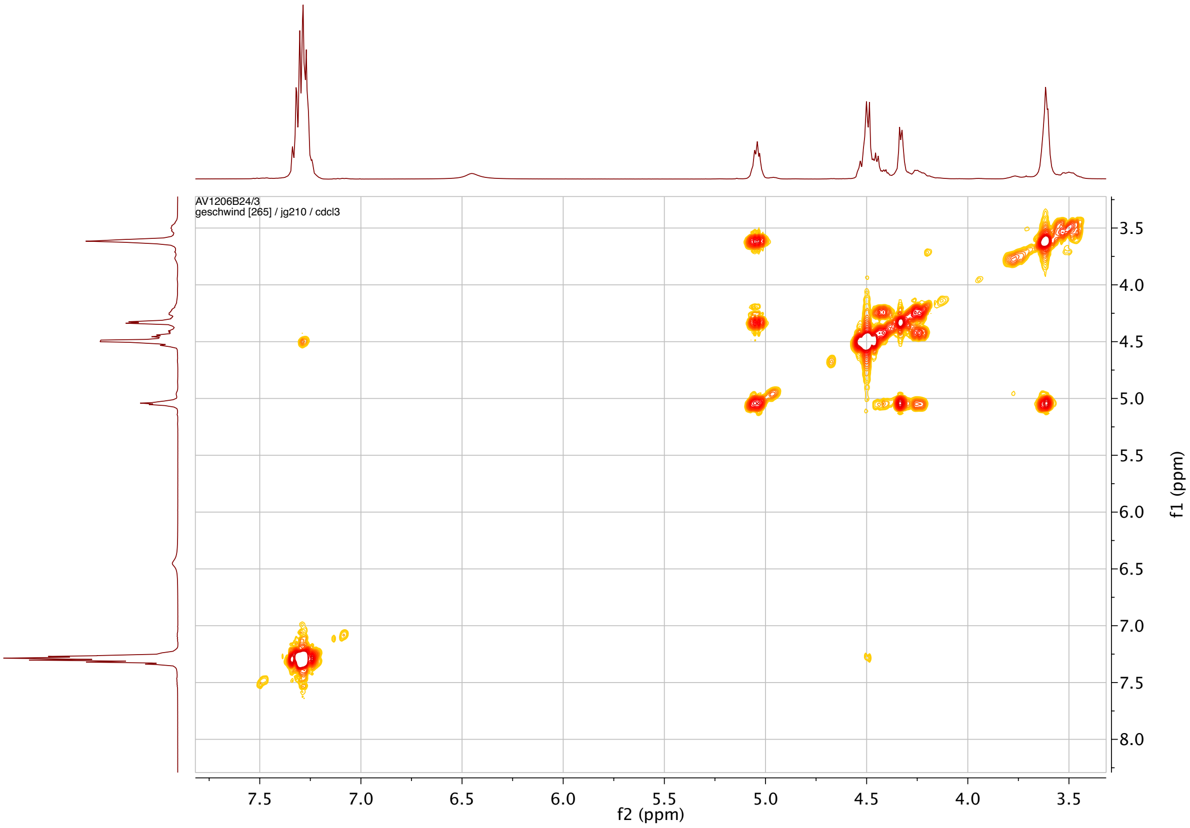

Figure S6. HSQC Poly(benzyl glycidyl ether carbonate).

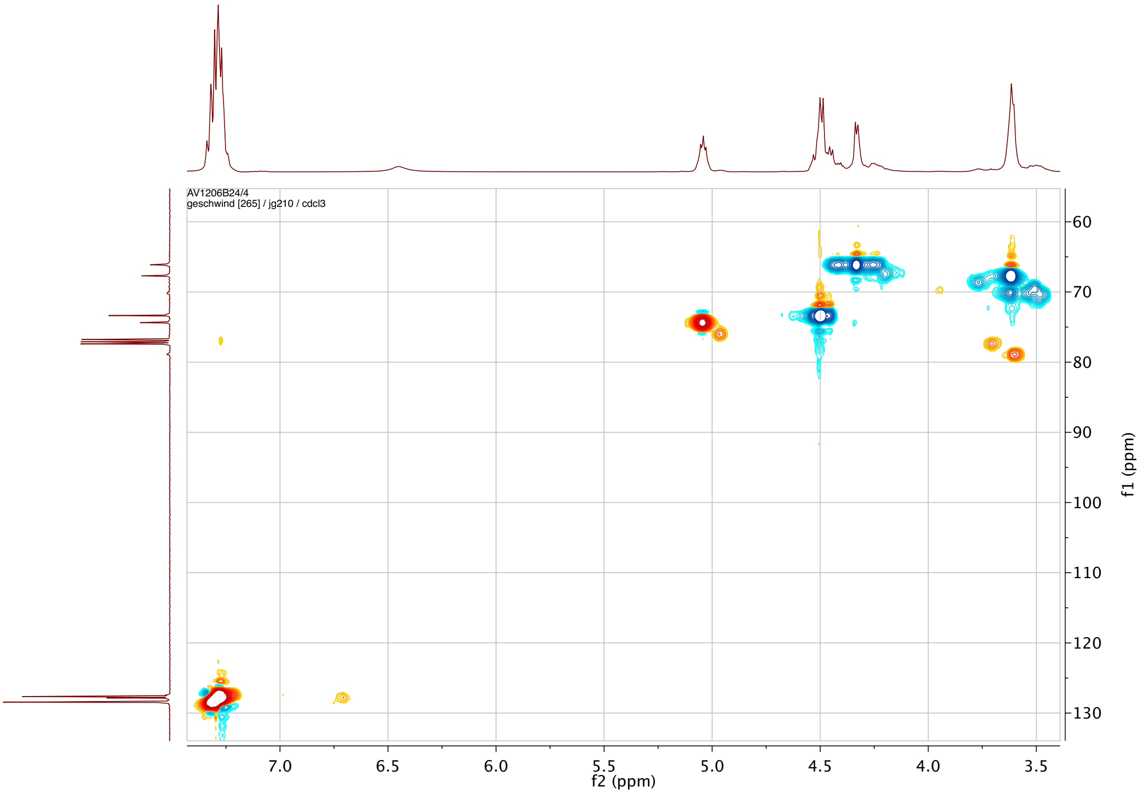

Figure S7. COSY of Poly(benzyl glycidyl ether carbonate).

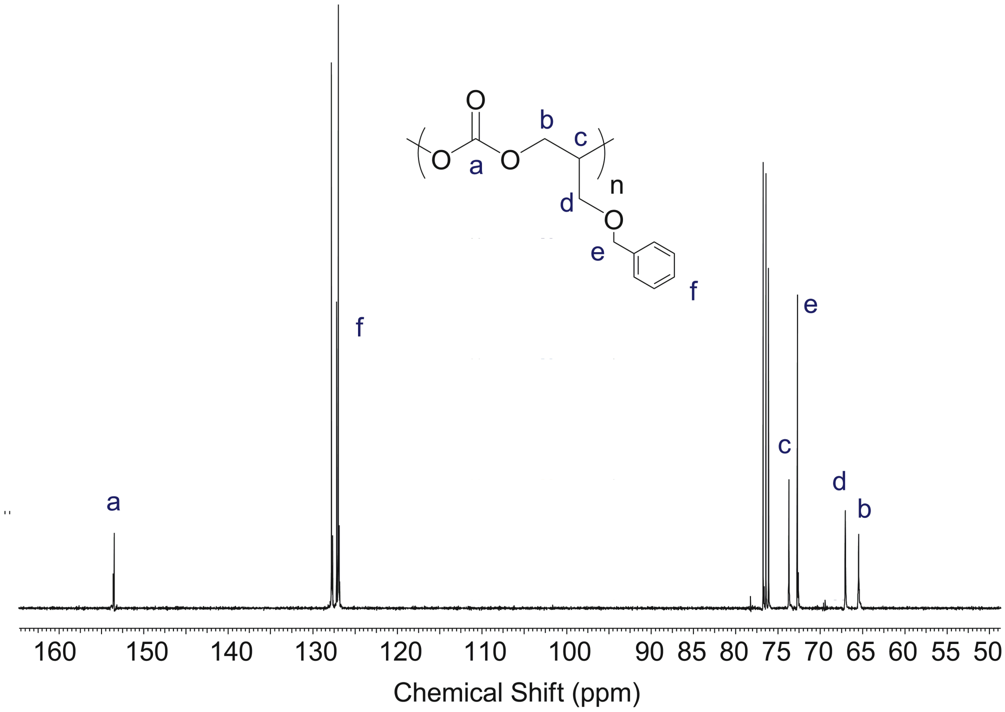

Figure S8. ^{13}C of Poly(benzyl glycidyl ether carbonate).

IR Spectroscopy

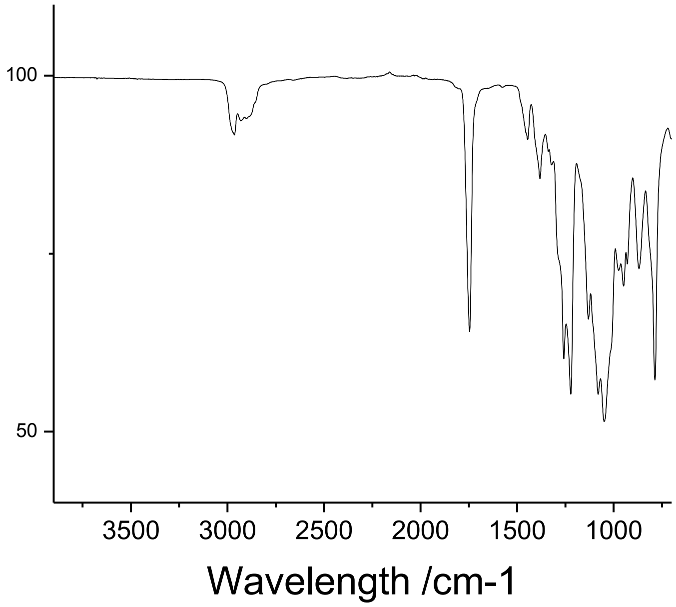

Figure S9. IR spectrum of Poly(ethoxy ethyl glycidyl ether carbonate).

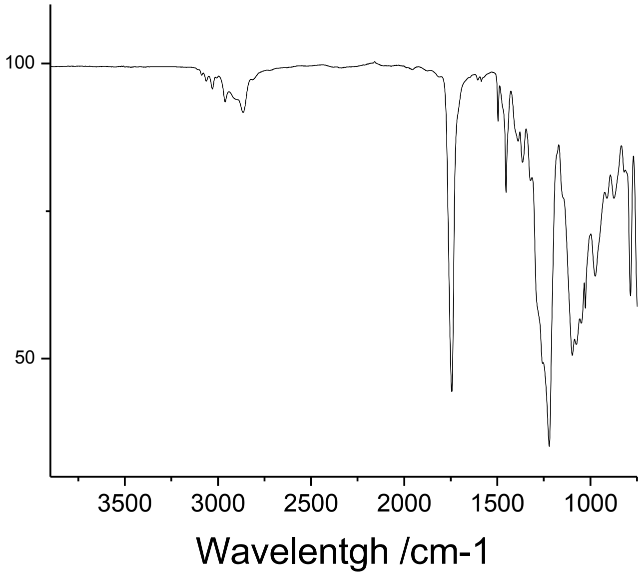

Figure S10. IR spectrum of Poly(benzyl glycidyl ether carbonate).

Deprotection

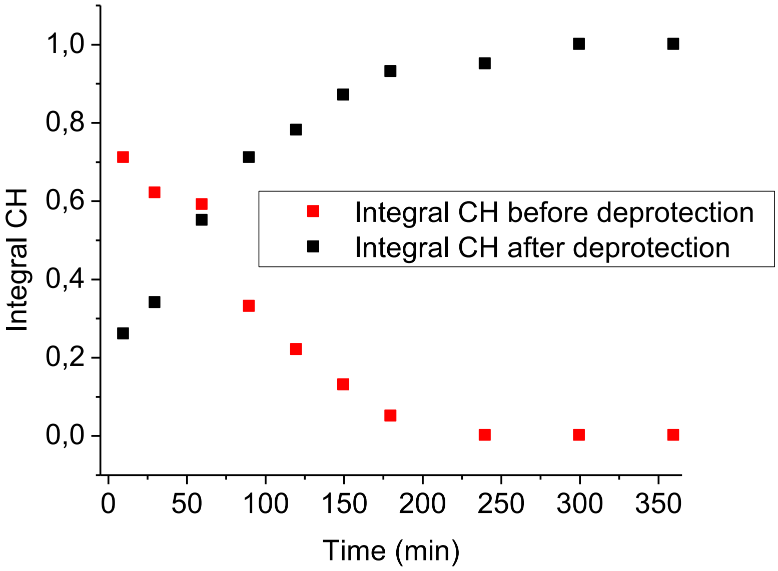

Figure S11. Time resolved integration of the polycarbonate backbone methane signal during acidic deprotection of poly(ethoxy ethyl glycidyl ether carbonate).

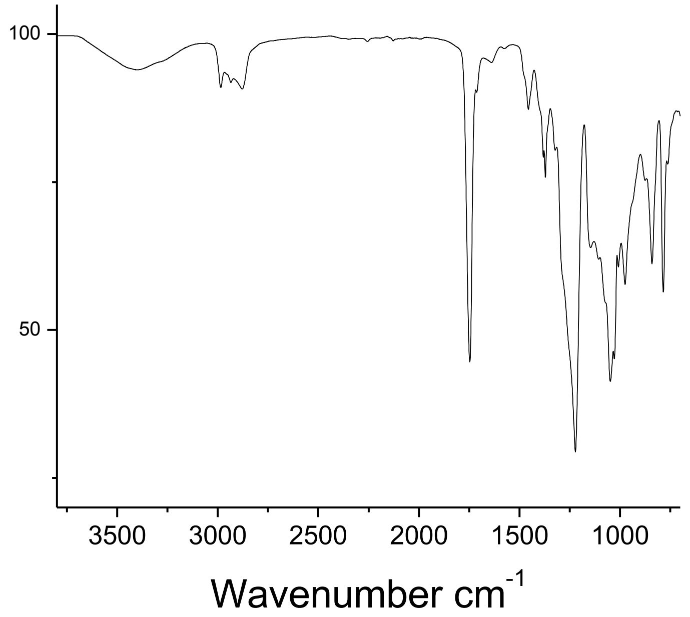

Figure S12. IR spectrum of poly(1,2-glycerol carbonate).

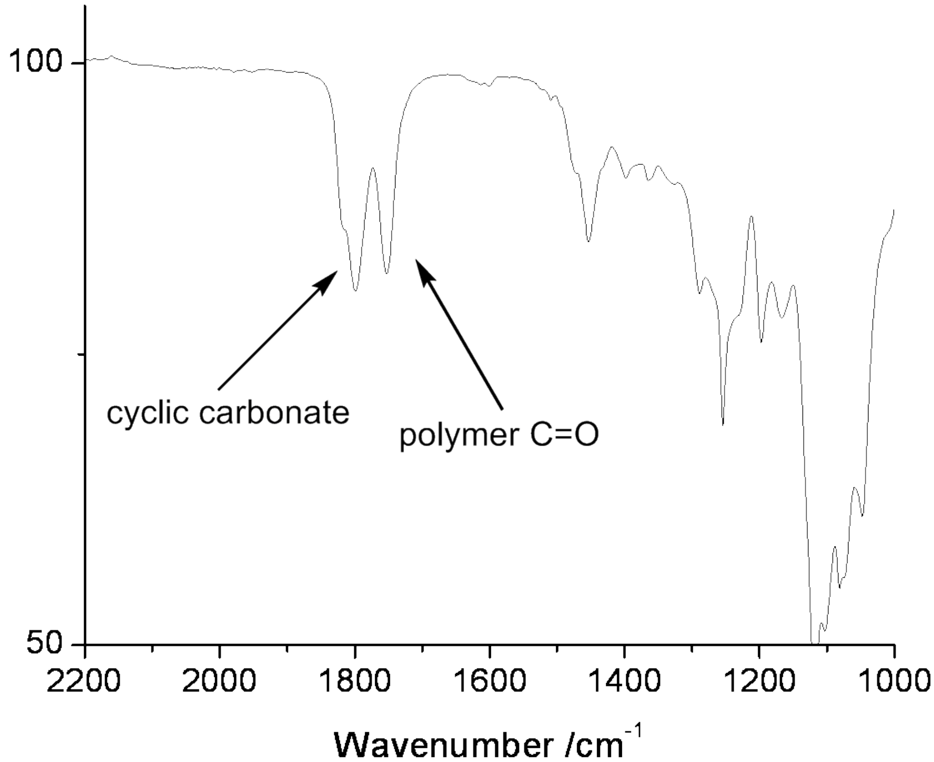

Figure S13. IR spectrum of poly(1,2-glycerol carbonate) degradation and formation of cyclic glycerol carbonate.

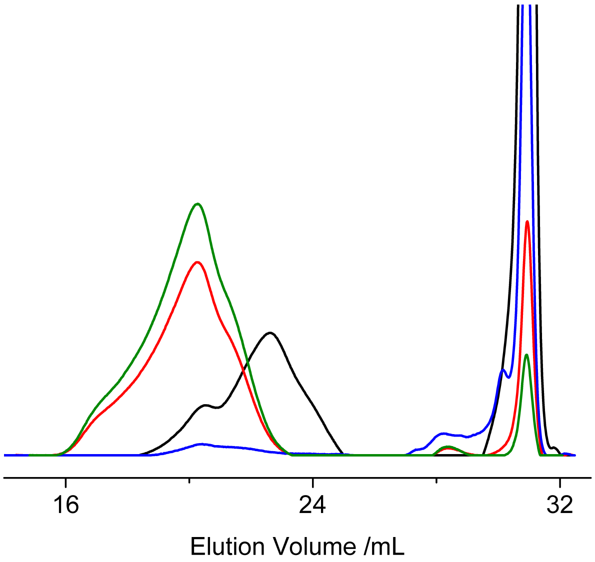

Figure S14. Degradation in THF, almost full degradation after 2 weeks (blue trace).

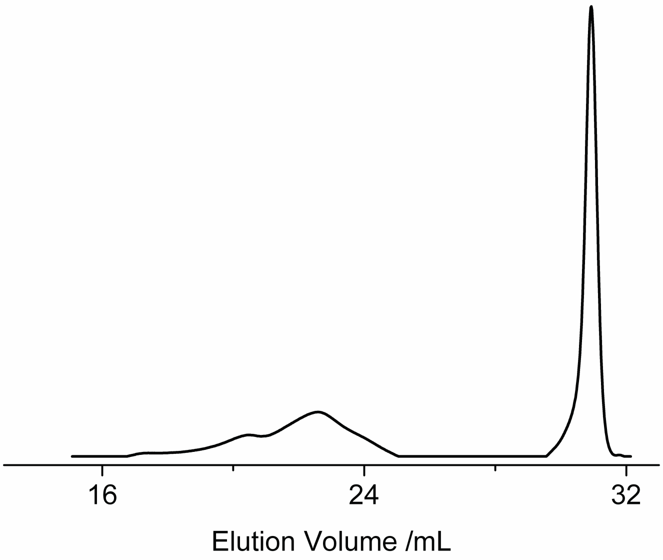

Figure S15. Degradation in bulk at -28°C, significant degradation after 2 weeks.

3.2. Poly(carbonate) Copolymers with Tailored Number of Hydroxyl Groups from Glycidyl Ethers and CO_2

Jeannette Geschwind[1,2], Andrew Phillips[1] and Holger Frey[*1]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg 10-14, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany

[2]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

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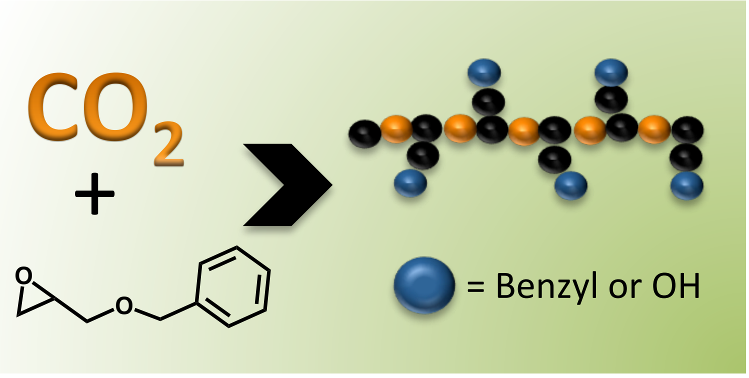


Abstract

Functional poly(carbonate)s with multiple hydroxyl functionalities have been prepared by copolymerization of carbon dioxide (CO_2) with glycidyl methyl ether (GME) and benzyl glycidyl ether (BGE) in various ratios. Subsequent catalytic hydrogenation was employed for removal of the benzyl protecting groups at the polymer backbone. A series of copolymers with varying comonomer fractions from 0 to 100% was obtained. The copolymers possessed a broad range of molecular weights from 9000 to 30 000 g/mol and showed polydispersities M_w/M_n between 2.4 and 3.6. The materials were characterized via ^1H and ^{13}C NMR, SEC and differential scanning calorimetry (DSC). The deprotected copolymers are structurally simple materials consisting of carbon dioxide, GME and glycerol. These functional poly(carbonate)s represent degradable materials with tailored functionality.

Introduction

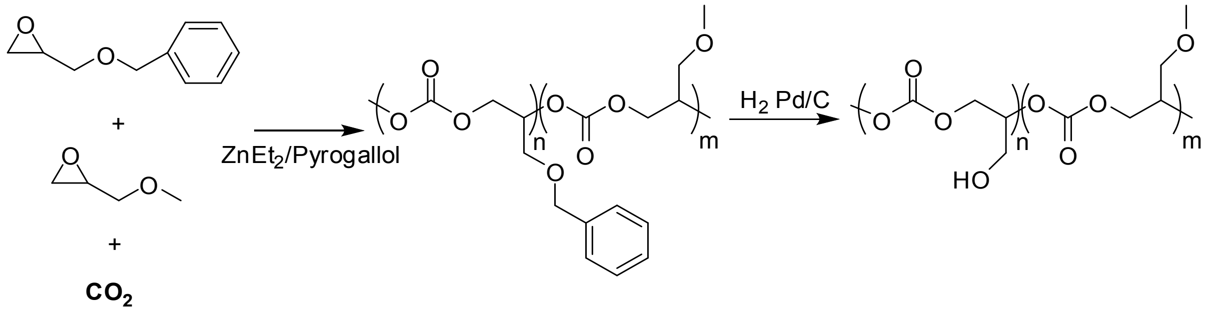
Aliphatic poly(carbonate)s are an important class of biodegradable polymers and have been commonly used as integral components of engineered tissues, medical devices and drug delivery systems.[1,2–4] They have recently attracted increasing attention because of their significant application potential as potentially sustainable materials and in the medical field, owing to their unique combination of biodegradability and biocompatibility.[5,6] Functional aliphatic polycarbonates are usually synthesized by ring opening polymerization (ROP) of six membered cyclic carbonates, and the respective monomers have to be prepared in a multistep procedure.[7–9 10–13,14–17]

An innovative way for the synthesis of aliphatic poly(carbonate)s is the preparation by copolymerization of carbon dioxide with epoxides.[18–20,21,22, 42] The use of carbon dioxide as a C_1 building block is one of the most important current targets in synthetic chemistry, because CO_2 is an inexpensive, non-toxic, and non-flammable monomer. The CO_2/epoxide copolymerization was pioneered by Inoue more than thirty years ago.[23] He employed a heterogeneous catalyst system derived from a 1:1 mixture of diethylzinc and H_2O. However, in the last decade many new catalysts, mainly homogeneous systems, have been developed.[18–20] For the copolymerization of epoxides and carbon dioxide salen complexes, especially of cobalt, have come into focus.[18,24–26]

In most recent works propylene oxide (PO) and cyclohexene oxide (CHO) have been used as epoxide monomers, resulting in poly(carbonate)s with a maximum of two functional groups at the end of the polymer chain. However, the use of functional epoxides can be exploited to generate poly(carbonate)s carrying various functionalities at the polymer backbone.[25] For example, Coates and coworkers synthesized multiple block copolymers via sequential addition of functionalized cyclohexene oxides with a high degree of control over the block length.[27,28]

Another prominent group of functional epoxides are glycidyl ethers, which have recently been used for the synthesis of functional poly(ethylene glycol) derivatives.[29–31] The functionality at the polymer backbone is introduced by copolymerization of ethylene oxide (EO) with an epoxide comonomer bearing an additional functional group, which is typically protected and can be released without backbone degradation after polymerization. A variety of glycidyl ether monomers like allyl glycidyl ether (AGE),[32] ethoxy ethyl glycidyl ether (EEGE),[30] ethoxy vinyl glycidyl ether (EVGE)[29] or 1,2-isopropylidene glyceryl glycidyl ether (IGG)[33] have been introduced for polyether synthesis by our group.

Glycidyl ethers can also be used for the copolymerization with carbon dioxide.[39-41] However, the often used heterogeneous cobalt catalysts are not suitable for this reaction due to the coordination of both glycidyl ether oxygens to the metal center, which leads to deactivation of the catalyst. Listos and coworkers showed that glycidyl ether and carbon dioxide can be copolymerized with a simple diethylzinc/pyrogallol catalyst system via a coordination-insertion mechanism.[34] In a recent work, we demonstrated that this catalyst system is also capable of copolymerizing carbon dioxide with isopropylidene(glyceryl glycidyl ether) (IGG) to form a protected poly((glycidyl methyl ether)-*co*-(glyceryl glycerol) carbonate), which can be deprotected by acidic cleavage of the acetal group.[35] This leads to a stable polycarbonate with two pendant hydroxyl groups at each IGG unit, consisting merely of carbon dioxide and glycerol. Furthermore, Grinstaff et. al. as well as our group reported the synthesis of aliphatic polycarbonates only consisting of glycerol and carbon dioxide by using benzyl glycidyl ether or ethoxy ethyl glycidyl ether in combination with CO_2 and subsequent deprotection.[40,41]



Scheme 1: Synthesis of P((GME-*co*-BGE) C) copolymers and their deprotection.

In this work we describe the synthesis and characterization of a series of random poly((glycidyl methyl ether-*co*-benzyl glycidyl ether) carbonate) (P((GME-*co*-BGE) C)) copolymers by copolymerization of benzyl glycidyl ether (BGE), glycidyl methyl ether (GME) and carbon dioxide (CO_2). The benzyl protecting group can be conveniently removed by catalytic hydrogenation without backbone degradation to release pendant hydroxyl groups (Scheme 1). The amount of hydroxyl groups in the resulting polycarbonate copolymers can be controlled via the BGE/GME comonomer ratio.

Results and Discussion

The synthetic strategy developed to obtain multifunctional aliphatic polycarbonate structures is depicted in **Scheme 1**. The synthesis was carried out using a two-step procedure and commences with the copolymerization of CO_2/(GME,BGE), using a diethylzinc/pyrogallol catalyst system and subsequent hydrolytic deprotection using palladium on activated charcoal as a catalyst results in pendant hydroxyl groups. Glycidyl methyl ether was used to control the number of functional groups in the resulting polymer, since cleavage of the methyl ether does not occur under the reaction conditions used in this work. All polymerizations were carried out in 1,4-dioxane, stirred for at least 72 h, and quenched with 10% hydrochloric acid added in a dropwise manner. A significant amount of cyclic carbonate side product and unreacted epoxide monomers were found in the crude reactions mixture, but pure copolymer could be isolated by repeated precipitation in cold methanol. The overall yield of the polymers was The BGE comonomer content has been varied in a systematic manner from 0-100%. **Table 1** summarizes the results for the series of copolymers prepared in this study. Molecular weights were in the range of 9000 to 30 000, and polydispersities were generally between 2.4 and 3.6 (samples 1-9). From a comparison of the composition of the monomer feed and the copolymer composition characterized by ^{1}H NMR, it can clearly be stated that the monomer feed corresponds to the incorporated BGE/GME-ratio. All polycarbonate copolymers were soft, clear and amorphous materials and showed good solubility in chloroform, THF, DMSO and toluene at room temperature.

Table 1: Overview of the characterization data for all copolymer samples prepared

#	Sample	% BGE/G (theory)	% BGE/G[b]	M_n g/mol (SEC)[c]	PDI (SEC)	T_g /°C[d]
1	P(GME-C)	0	0	12 600	3.2	1.7
2	P(($BGE_{0.13}$-*co*-$GME_{0.87}$)-C)	15	13	15 800	3.1	1.3
2	P(($BGE_{0.33}$-*co*-$GME_{0.67}$)-C)	30	33	9800	3.3	0.7
3	P(($BGE_{0.5}$-*co*-$GME_{0.5}$)-C)	50	50	13 400	2.9	-8.2
4	P(($BGE_{0.66}$-*co*-$GME_{0.34}$)-C)	65	66	20 200	3.8	-10.6
5	P(($BGE_{0.75}$-*co*-$GME_{0.25}$)-C)	75	75	11 800	2.8	-15.0
6	P(($BGE_{0.9}$-*co*-$GME_{0.1}$)-C)	90	90	29 200	2.8	-17.3
9	P(BGE-C)	100	100	13 300	3.6	-21.6
10	P(($G_{0.13}$-*co*-$GME_{0.87}$)-C)	15	13	15 200	2.8	6.2
11	P(($G_{0.33}$-*co*-$GME_{0.67}$)-C)	30	33	9200	2.6	5.3
12	P(($G_{0.5}$-*co*-$GME_{0.5}$)-C)	50	50	12 600	2.4	0.2
13	P(($G_{0.66}$-*co*-$GME_{0.34}$)-C)	65	66	18 900	3.1	-2.4
14	P(($G_{0.75}$-*co*-$GME_{0.25}$)-C)	75	75	11 300	2.3	-6.3
15	P(($G_{0.9}$-*co*-$GME_{0.1}$)-C)	90	90	27 800	2.5	-9.8
16	P(G-C)	100	100	12 400	3.2	-

[a]Determined by ^{1}H NMR spectroscopy, [b] Comonomer content (BGE or glycerol (G)) calculated by ^{1}H NMR spectroscopy [c]Determined by SEC calibrated with a PEG standard in DMF at 40 °C,[d]Glass transition temperature obtained from DSC

Typical ^{1}H NMR spectra of a P((BGE-*co*-GME)-C) and a deprotected P((G-*co*-GME)-C) copolymer in DMSO-d_6 are displayed in **Figure 1** and **Figure 2**, respectively. The resonances c (δ = 3.57 ppm), d (δ = 4.44 ppm), and e (δ = 7.26 ppm) correspond to the benzyl ether side chain, and by integration of these signals and comparison with the polycarbonate backbone (signals b δ = 4.98 ppm and signal a δ = 4.26 ppm) the copolymer composition was calculated. No polyether bond were formed and for all samples > 99% carbonate linkages were obtained. The structural parameters given in **Table 1** have been determined using ^{1}H NMR spectroscopy in DMSO-d_6. After deprotection by removal of the benzyl groups the benzyl ether side chain signal (signal e) vanishes, and signal h' occurs at δ = 5.11 ppm, which can be assigned to the newly formed hydroxyl group (Figure 2). The formation of the free hydroxyl group is accompanied by a shift of the backbone methine signal (signal b') from δ = 4.98 ppm to δ = 4.86 ppm. ^{13}C NMR spectroscopy and 2D NMR spectroscopy (COSY and HSQC) also confirmed the incorporation of BGE, GME and CO_2 into the copolymer and the carbonate carbon peak at δ = 154 ppm can clearly be detected in **Figure S2**. All other peaks were assigned as well.

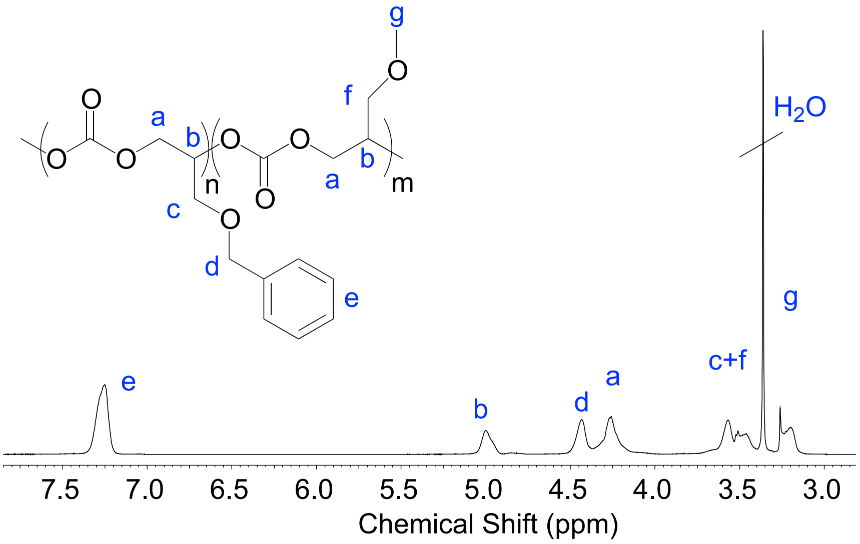


Figure 1: Typical ^{1}H NMR spectra of a protected copolymer (Table 1, sample **5**)

The molecular weight distributions obtained from size exclusion chromatography (SEC) measurements (in DMF with PEG standards) were in the range of M_w/M_n = 2.8-3.8, which is common for the catalyst system employed. The resulting SEC traces are given in the Supporting Information (**Figure S1)**. All molecular weights were determined to be 9000 - 30000 g/mol. The molecular weight could not be calculated from ^{1}H NMR spectra, because no separate end group signals were detected.

In addition, the incorporation of CO_2 into the polymer was confirmed by IR spectroscopy (**Figure S7**). Only one separate carbonate band at 1738 cm^{-1} is visible, which can be assigned to the C=O group of the linear carbonate. No bands typical for a cyclic carbonate at around 1790 cm^{-1} were detected in the IR spectra of the resulting copolymers.[36]

Deprotection and liberation of functional polycarbonates.

Deprotection of the hydroxyl groups of P((BGE-co-GME) C) copolymers by catalytic hydrogenation with palladium on activated charcoal resulted in linear multifunctional P((G-co-GME) C) copolymers (samples 10-18). All deprotection reactions were carried out in a 1:1 ethyl acetate/methanol mixture using a hydrogen pressure of 40 bar for 2 days.

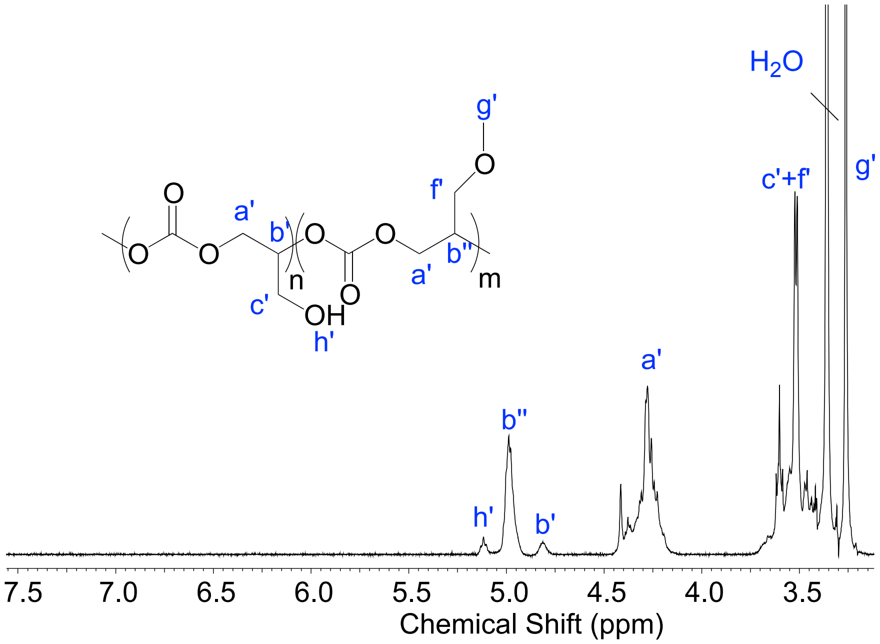


Figure 2: Typical ^{1}H NMR spectra of a deprotected copolymer (Table 1 entry 11)

The cleavage of the benzyl ether can be followed via ^{1}H NMR spectroscopy for the purified samples, monitoring the disappearance of the aromatic signal at 7.26 ppm and the methylene signal (signal d) at 4.45 ppm. (Figure 2). The reaction conditions applied for the hydrogenolysis guarantee full removal of the benzylic protecting groups without degradation of the polymer backbone. The molecular weights obtained from SEC are almost constant for all P((GME-co-G) C) samples after the release of the hydroxyl functions. Like the P((GME-co-BGE) C) copolymers the P((GME-co-GG) C) copolymers were all clear, amorphous and soft materials and showed good solubility in THF and DMSO at room temperature. However the deprotected copolymers were not soluble in toluene and chloroform anymore, indicating that the deprotected copolymers are more hydrophilic than the protected ones. Even after deprotection all polymers were insoluble in aqueous solution, despite the large number of hydroxyl groups. In methanol and water, swelling of the samples occurred.

Hydrolytic Stability.

Since the formation of cyclic 1,2-glycerol carbonate is thermodynamically favored, the glycerol units in the polymer backbone can act as predetermined breaking points. Degradation of the deprotected copolymer samples took place in the solid state in moist atmosphere as well as in solution. The degradation in solution was followed by SEC in DMF for 10 weeks. Figure 2 shows the degradation in solution based on SEC results. Clearly to be seen, after two weeks the SEC curve became broad, and smaller polymer fragments were detected. After around 10 weeks the polymer is completely degraded, and only small fragments can be seen, as indicated by the appearance of infrared absorption at about 1800 cm^{-1} and the decrease of that at 1738 cm^{-1}, which represents the carbonyl stretch of five-membered cyclic glycerol carbonate produced **(Figure S8).** The benzyl-protected copolymers do not degrade under these conditions.

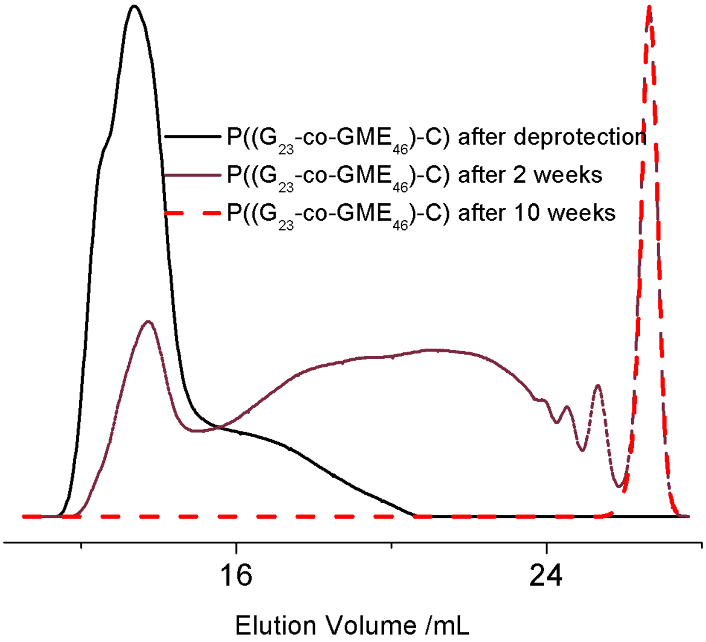


Figure 3: SEC results for the degradation in DMF at room temperature of a P((G-co-GME)-C) copolymer as a typical example.

The considerably easier degradation of P((G-*co*-GME) C) copolymers compared to their protected analogs might be due to an intramolecular attack of the pendant hydroxyl groups at the carbonate linkage and formation of the thermodynamically stable cyclic glycerol carbonate. With increasing GME content the number of potential breaking points in the polymer backbone increases as well. Upon storage of the polymers at -25°C below the glass transition no degradation was observed.

Thermal Properties.

The thermal properties of the protected (P((BGE-*co*-GME) C)) as well as deprotected (P((G-*co*-GME) C)) copolymers have also been investigated. Differential scanning calorimetry (DSC) has been used to quantify the thermal properties of the materials, since behavior and stability is a key parameter with respect to possible applications. All samples exhibited glass transition temperatures (T_g) between those of the two homopolymers. (P(GME C) = 1 °C and P(BGE C) = -21.6°C) first described in this work.

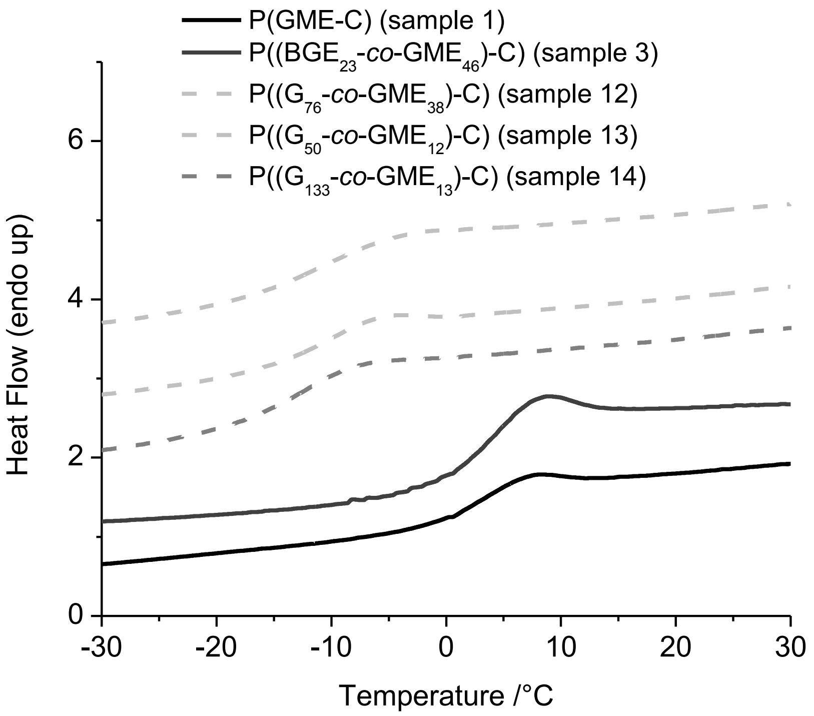


Figure 4: Typical DSC results for some copolymers

However, the T_gs of the materials showed a slight decrease with increasing BGE/GME-ratios, which was expected, since benzyl glycidyl ether contains a sterically demanding group that influences the free volume of the systems. This result illustrates how the inherent flexibility of the polymer backbone can become manifest, if the side chains are sufficiently flexible to allow for facile internal reorientational motions, as also described in the literature.[37] A decrease of the T_g was also observed for the deprotected samples, but their glass transition temperatures (Table 1, samples 10-18) are higher than those of the respective protected precursors, which is explained by the interaction of the hydroxyl groups in these systems. Intramolecular hydrogen bonding serves to restrict skeletal torsional motions.

Conclusion

Novel functional, linear aliphatic polycarbonate random copolymers from CO_2, glycidyl methyl ether (GME), and a protected glycidyl ether derivative (benzyl glycidyl ether (BGE)) have been synthesized. By adjusting the monomer feed composition, the complete range of monomer compositions was prepared with BGE content from 0% to 100%. Via catalytic hydrogenation of the benzyl protecting groups the hydroxyl groups were released and functional polycarbonates with tailored functionality were obtained.

Detailed characterization in terms of composition, thermal properties and hydrolytic stability was performed. Differential scanning calorimetry characterization was carried out for all samples, confirming expectation for the thermal properties of random copolymers. Further studies on the hydrolytic stability of the novel hydroxyl containing polycarbonate materials and their application in the field of drug encapsulation and release are in progress.

Experimental Section

Preparation of the diethylzinc/pyrogallol catalyst.

The catalyst was prepared under argon atmosphere prior to use following the procedure described previously.[38] A solution of pyrogallol (0.47 g, 4 mmol) in 10 mL of 1,4-dioxane was slowly added to a stirred solution of $ZnEt_2$ (2 mmol) in 35 ml of dioxane at room temperature. After the addition was completed, stirring was continued until the evolution of ethane stopped.

Polymerization.

The copolymerization was carried out in dioxane in the presence of the catalytic system based on $ZnEt_2$ and pyrogallol at a molar ratio of 2:1. The earlier described catalyst solution (2 mmol) and 50 mmol epoxide were placed in a stainless steel autoclave filled with argon. CO_2 was then introduced at a pressure of ca. 20 bar. The reaction was carried out at room temperature for 44 h. The reaction was stopped by decompression of the autoclave. The resulting solution was diluted with $CHCl_3$, quenched with 10% HCl added dropwise. The solution was washed twice with water, dried with $MgSO_4$, the product was precipitated in cold methanol and dried in vacuum. Yields of the crude products were between 40–65%. The purified polymers are colorless, soft materials which are soluble in acetone, chlorinated and aromatic solvents and insoluble in water, lower alcohols and diethyl ether.

Deprotection of Poly(benzyl glycidyl ether carbonate)

Benzyl glycidyl ether containing polymers were dissolved in a 1:1 mixture of ethyl acetate and methanol, and palladium on activated charcoal (10%) was added. The reaction vessel was flushed with hydrogen (20 bar) and the reaction was allowed to stir for 24 h at room temperature. The solution was filtered, concentrated and dried in vacuum. Yields of the crude products were about 95%.

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Supporting Information for: Poly(carbonate) Copolymers with Tailored Number of Hydroxyl Groups from Glycidyl Ethers and CO_2

Jeannette Hilf[1,†], Andrew Phillips[1] and Holger Frey[*1]

Experimental Section

Instrumentation.

^{1}H NMR spectra (300 MHz and 400 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC300 or a Bruker AMX400 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in DMF (containing 0.25 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column ($10^6/10^5/10^4$ g mol^{-1}), a UV (275 nm) and a RI detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service. DSC measurements were performed using a PerkinElmer DSC 8500 with PerkinElmer CLN2 in the temperature range from – 100 to 150 °C at heating rates of 10 K min^{-1} under nitrogen.

Reagents.

Benzyl Glycidyl ether, epichlorohydrin (99%), sodium hydroxide as well as dimethylsulfoxide (puriss, over molecular sieve), tetrahydrofurane (puriss, over molecular sieve), and toluene (puriss, over molecular sieve) were purchased from Aldrich. Pyrogallol was recrystallized from Benzene/EtOH. Deuterated chloroform-d_1 and DMSO-d_6 were purchased from Deutero GmbH. Carbon dioxide (99.995%) was purchased from Westfalen AG and used as received. All other solvents and reagents were purchased from Acros Organics.

GPC data for the copolymers

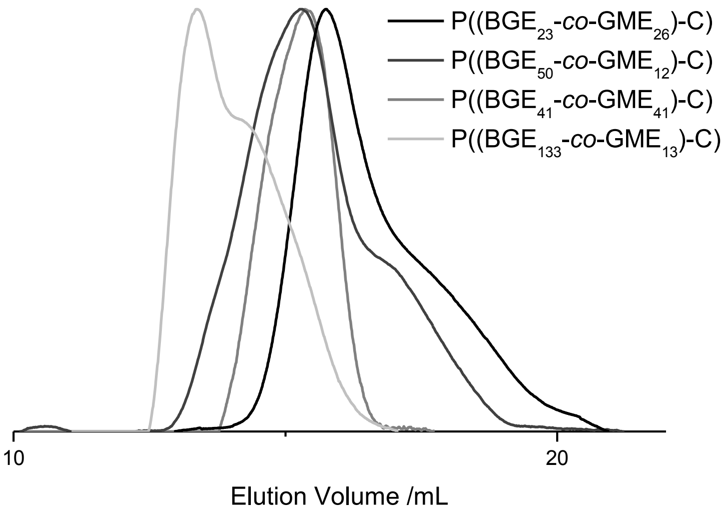

Figure S1. SEC diagrams of the synthesized P((BGE-*co*-GME) carbonate) copolymers.

Representative ^{1}H and ^{13}C of the protected and deprotected P ((BGE-co-GME C) and P ((G-co-GME C) copolymers.

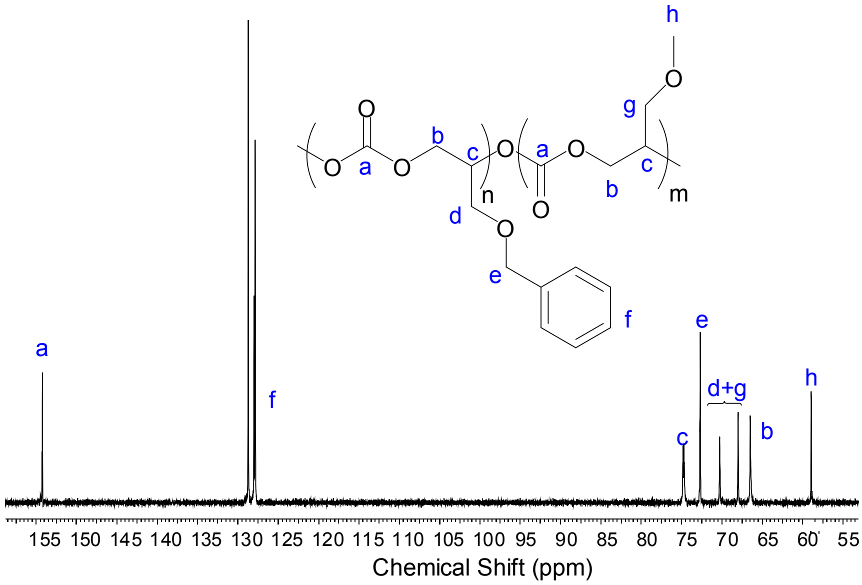

Figure S2. ^{13}C NMR spectrum of the synthesized P((BGE-*co*-GME) carbonate) copolymer (Table 1, sample 4).

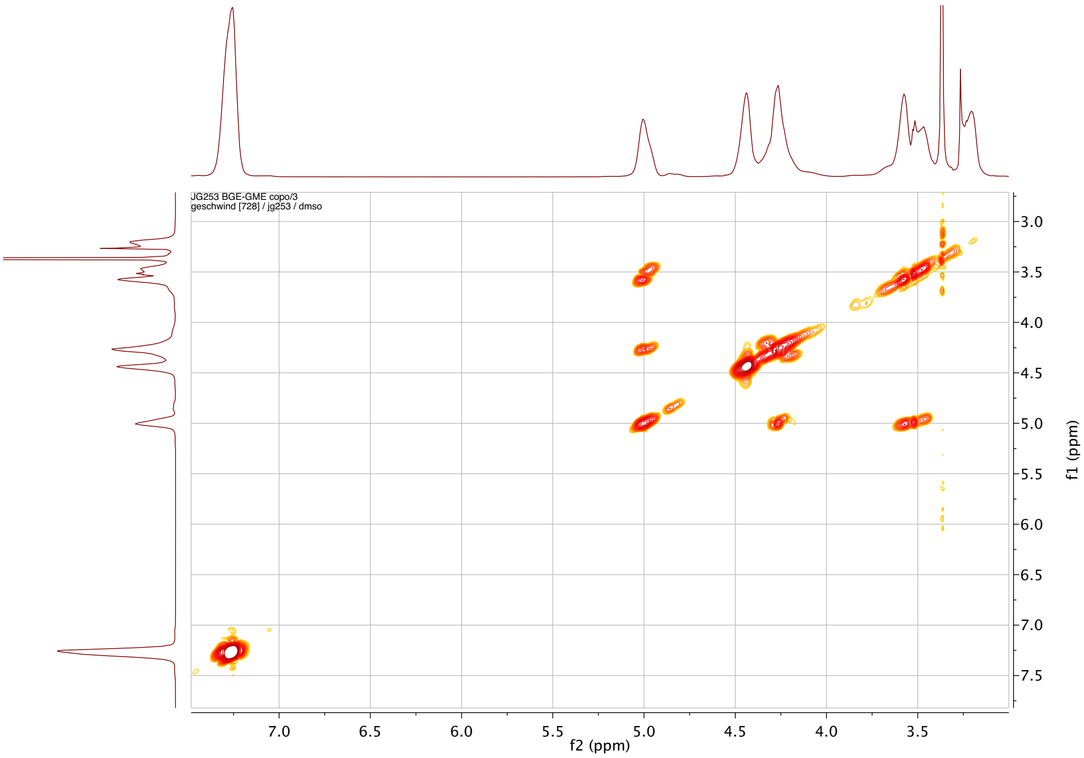

Figure S3. COSY spectrum of the synthesized P((BGE-*co*-GME) carbonate) copolymer (Table 1, sample 4).

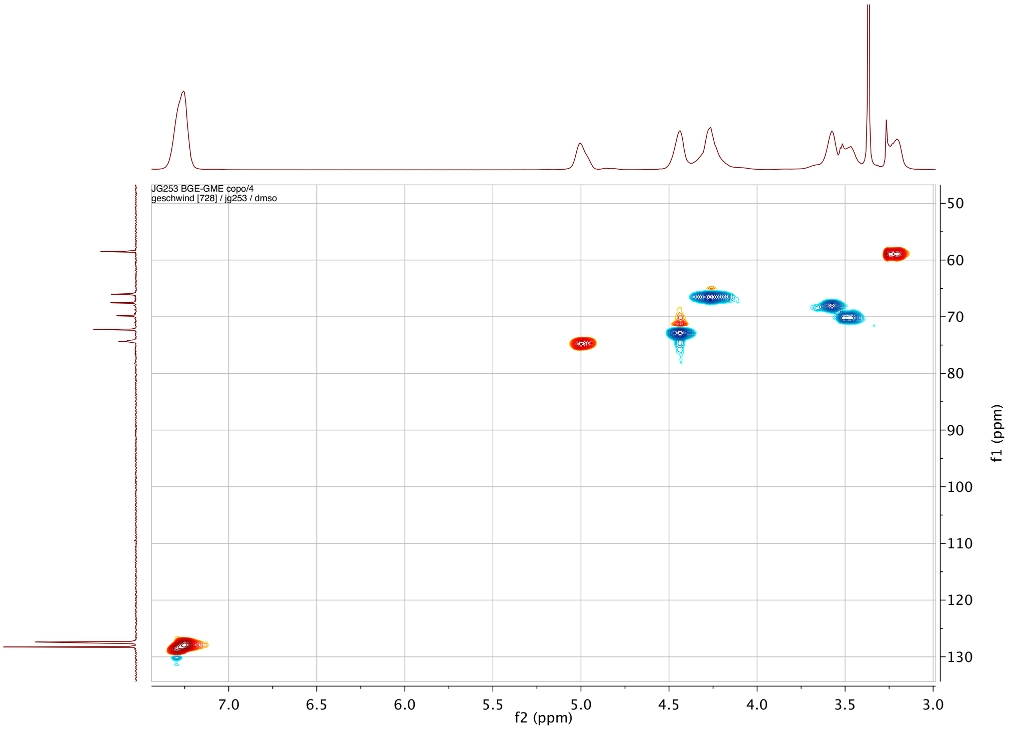

Figure S4. HSQC spectrum of the synthesized P((BGE-*co*-GME) carbonate) copolymer (Table 1, sample 4).

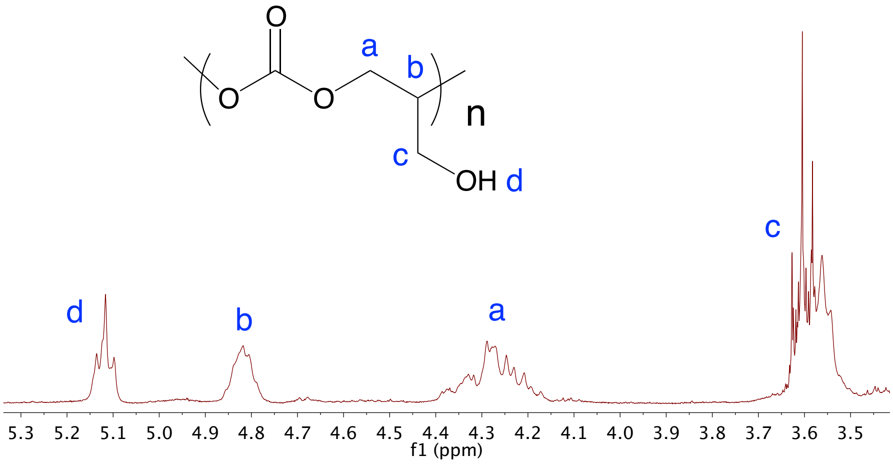

Figure S5. ^{1}H NMR spectrum of the deprotected P((BGE-*co*-GME) carbonate) copolymer (Table 1, sample 18).

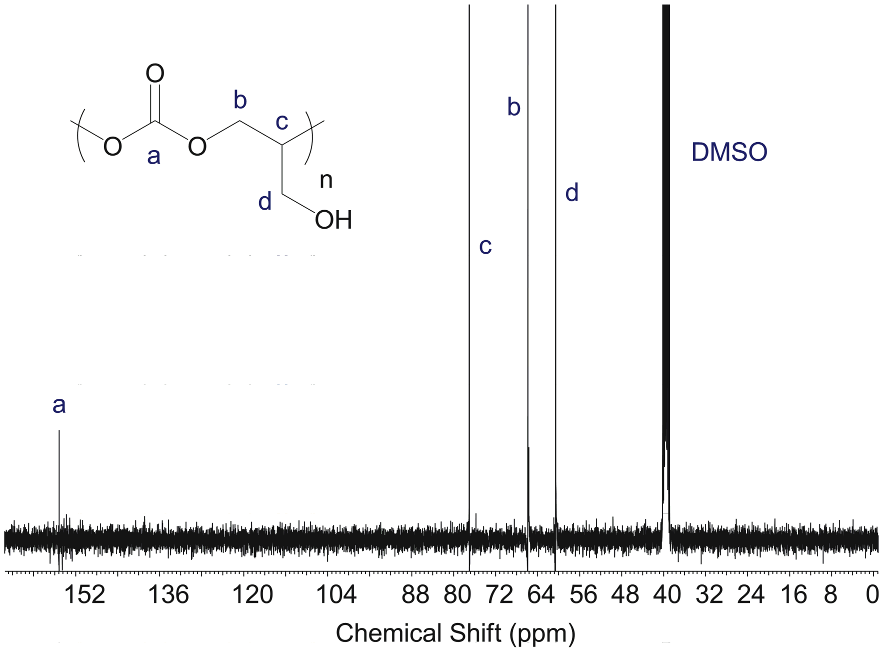

Figure S6. ^{13}C NMR spectrum for poly(1,2-glycerol carbonate).

IR spectra of the resulting polymers

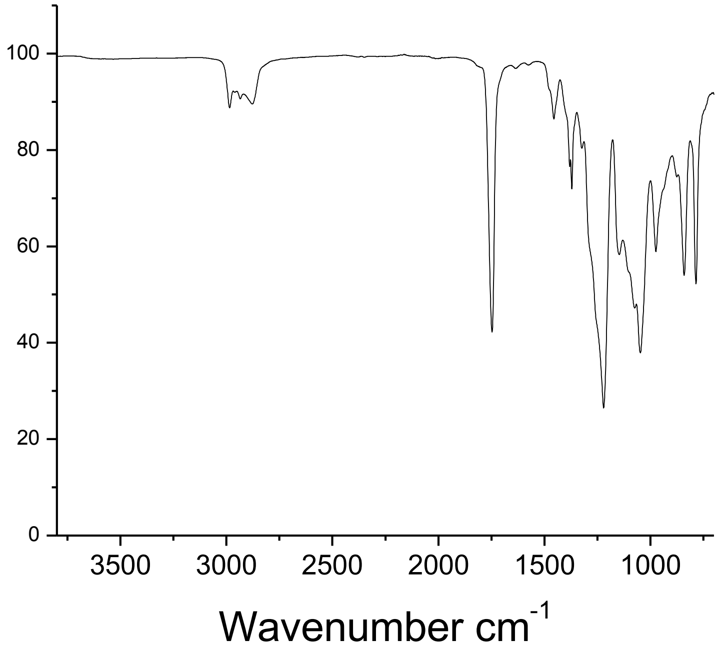

Figure S7. IR spectrum of Poly((benzyl glycidyl ether-*co*- glycidyl methyl ether) carbonate).

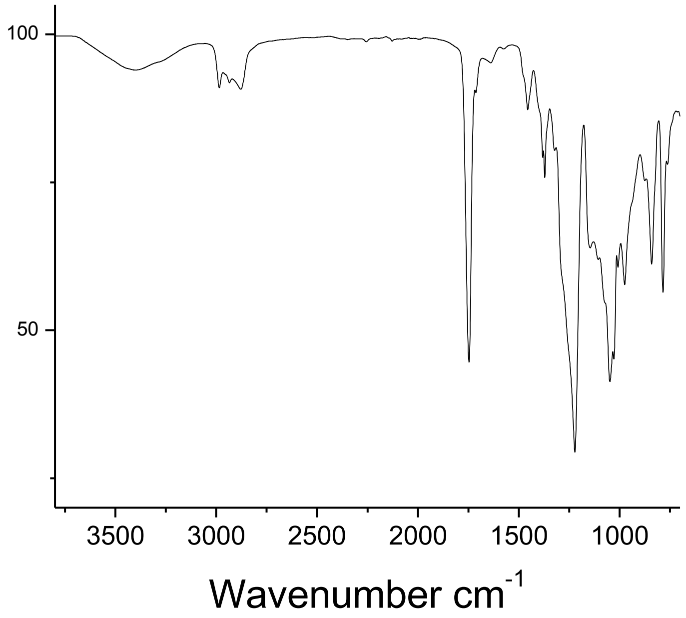

Figure S8. IR spectrum of the deprotected Poly((benzyl glycidyl ether-*co*- glycidyl methyl ether) carbonate).

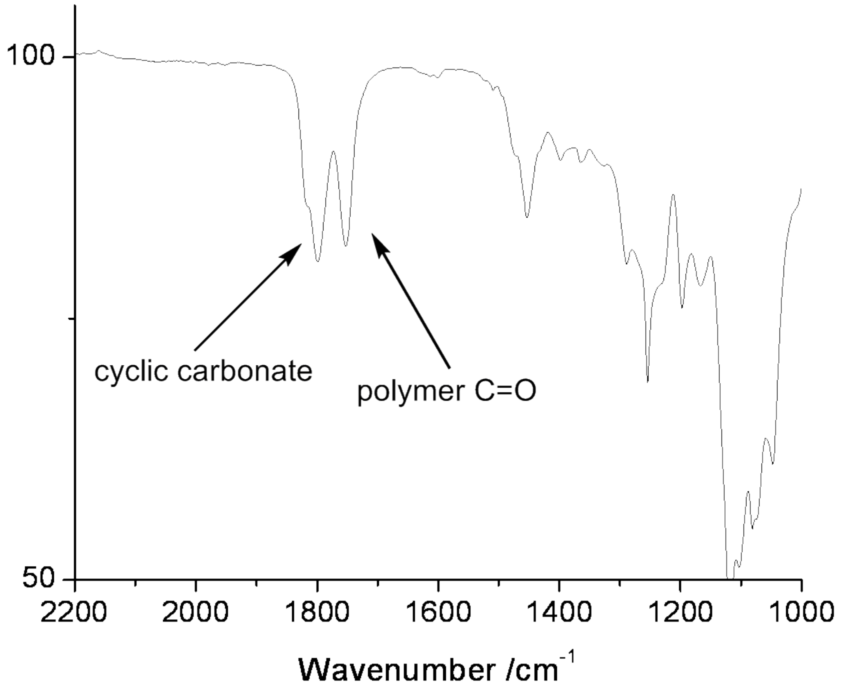

Figure S9. IR spectrum of poly(1,2-glycerol carbonate) degradation and formation of cyclic glycerol carbonate.

3.3. Stable, Hydroxyl-Functional Polycarbonates with Glycerol Side Chains Synthesized from CO_2 and Isopropylidene(glyceryl glycidyl ether)

Jeannette Geschwind[1†] **and Holger Frey**[*1]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg 10-14, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany

[†]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

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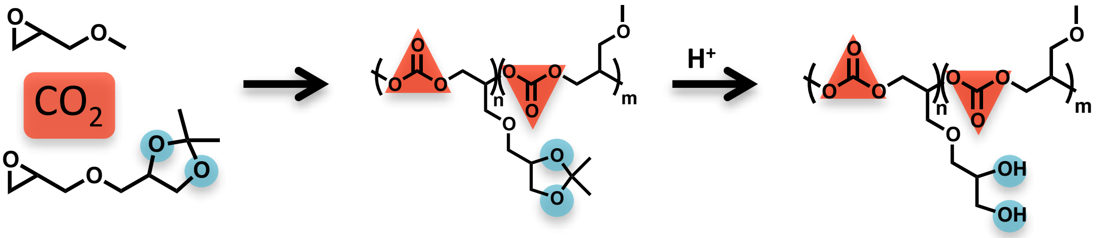


Abstract

A series of functional polycarbonates, poly((glycidyl methyl ether)-*co*-(isopropylidene glyceryl glycidyl ether) carbonate) (P((GME-*co*-IGG) C)) random copolymers with different fractions of 1,2-isopropylidene glyceryl glycidyl ether (IGG) units as a precursor for a glycerol unit, is synthesized. After acidic hydrolysis of the acetal protecting groups a new type of functional polycarbonate obtained directly from carbon dioxide (CO_2) and glycerol is obtained, namely poly((glycidyl methyl ether)-*co*-(glyceryl glycerol) carbonate) (P((GME-*co*-GG) C)). All hydroxyl functional polycarbonate samples exhibit monomodal molecular weight distributions with polydispersities between 2.5 and 3.3 and M_n between 12000 and 25000 g/mol. The formation of undesired ether units is not observed. Thermal properties reflect the amorphous and flexible structure of the polymers. Interestingly, both the protected as well as the deprotected materials are stable in bulk and solution. The aliphatic polycarbonates with tunable hydroxyl functionality are promising materials as support for catalysts, drugs or reagents.

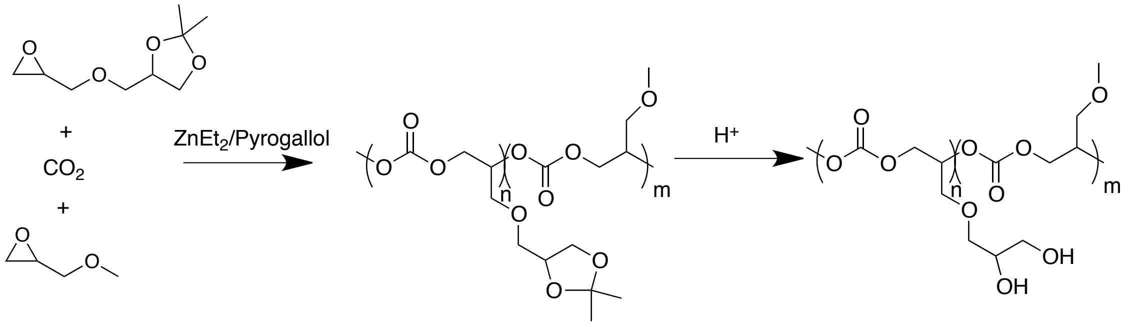
Introduction

The use of carbon dioxide for polymer synthesis is very attractive with respect to resource utilization, as it is non-toxic, renewable and readily available in large quantities and high purity. Various catalysts have been developed for the reaction of carbon dioxide and epoxides to form aliphatic polycarbonate polymers.[1-5] The first catalysts reported by Inoue at al. in 1969 are based on simple heterogeneous zinc dicarboxylate systems.[6–8] To date, heterogeneous zinc catalyst systems are still interesting due to their ease of handling, low toxicity, economic availability, and facile removal after the reaction.[9–11] Another key advantage of these established zinc catalysts is that copolymerization of carbon dioxide and glycidyl ethers is possible.[12] Despite the facile copolymerization of CO_2 with epoxides, glycidyl ethers as monomers have been neglected until today, maybe due to the non-suitability of established, highly efficient catalyst systems based on cobalt complexes. Both oxygens of the glycidyl ether structure can coordinate to the metal catalyst central atom and block one coordination site, terminating the reaction, since the coordination-insertion mechanism is not active any more.

Linear aliphatic functional polycarbonates are one important kind of biodegradable polymers and have gained considerable attention recently.[13–20] They exhibit great potential for medical devices, drug delivery systems and in tissue engineering. Although the possibility of enzymatic degradation of established linear aliphatic polycarbonate copolymers has been discussed, the extent of water absorption is low, and the synthesis of more hydrophilic copolymers is desirable.

The introduction of functional groups into the aliphatic polycarbonate derivatives can either be realized by ring opening polymerization of functional six membered cyclic carbonates,[13,14,17,21–35] by suitable initiator systems,[36] or by the copolymerization of carbon dioxide with functional epoxides, which is the pathway that has been least explored at to date[12,37–41] A detailed overview over the first method has been given in a recent comprehensive review by Zhang et al. and several other groups.[17–20] The preparation of polycarbonates from CO_2 and epoxides with more than two functional groups randomly distributed along the polymer backbone requires a suitable functional comonomer. To incorporate functionalities that do not tolerate or impede the polymerization conditions, e.g., hydroxyl groups, a suitable protected comonomer has to be chosen. One obvious requirement is that the protecting groups can be removed quantitatively in post-polymerization reactions without degradation of the backbone. Suitable comonomers that meet these criteria are glycidyl ethers, as employed by our group for the synthesis of functional polyethers.[42–45] The use of 1,2-isopropylidene glyceryl glycidyl ether (IGG), which is obtained conveniently in one step from epichlorohydrin and solketal (sf. Supp. Inf.)[43,46] should permit the introduction of glycerol side chains with two adjacent hydroxyl functions for each IGG unit after deprotection.

In the current work we have synthesized aliphatic, hydroxy-functional polycarbonates by direct random copolymerization of CO_2 with IGG as a protected bis-hydroxy-functional glycidyl ether (Scheme 1). GME (glycidyl methyl ether) has also been employed in a terpolymerization to tailor both functionality and solubility.



Scheme 1. Synthesis of the poly(IGG-*co*-GME C) and subsequent acidic deprotection.

Subsequent acidic hydrolysis resulted in stable aliphatic PCs with 1,2-diol side chains without degradation of the polymer backbone. The hydroxyl-functional polycarbonates have been studied with respect to their thermal properties and stability in solution and in bulk.

Experimental Section

Monomer Synthesis.

1,2-isopropylidene glyceryl glycidyl ether (IGG) was prepared as described in the Supporting Information and glycidyl methyl ether (GME) was purchased from TCI.

Preparation of the catalyst.

The catalyst was prepared under argon atmosphere immediately before use, following a procedure described previously[12]. A solution of pyrogallol (0.47 g, 4 mmol in 10 mL of 1,4-dioxane) was slowly added to a stirred solution of $ZnEt_2$ (2 mmol in 35 mL of dioxane) at room temperature. After the addition was complete, stirring was continued until the evolution of ethane stopped.

Polymerization.

The copolymerization was carried out in dioxane in the presence of a catalytic system based on $ZnEt_2$ and pyrogallol at a molar ratio of 2:1. The catalyst solution (2 mmol) and 50 mmol epoxide was placed in a stainless steel autoclave filled with argon. CO_2 was then introduced at a pressure of ca. 20 bar. The reaction was carried out at room temperature for 72 h. The reaction was stopped by decompression of the autoclave. The resulting solution was diluted with CH_2Cl2, washed with 10% HCl and twice with water, dried with $MgSO_4$, precipitated in cold methanol and dried in vacuum. Yields of the crude products were ca. 50%. The purified polymers are white solids, which are soluble in acetone, chlorinated, THF and aromatic solvents, and insoluble in water, lower alcohols and diethyl ether.

Deprotection of Poly(IGG carbonate) and Poly(IGG-*co*-GME C).

The acetal protecting groups were removed by addition of 10 wt% acidic ion exchange resin (Dowex 50WX8) to a 20% solution of the polymer in MeOH/THF, stirring at 40°C for 4h. The ion exchange resin was removed by centrifugation and the solution was concentrated in vacuum and then dried in vacuum overnight. Yields: 90-100%.

Results and Discussion

Synthesis and Molecular Characterization.

To copolymerize 1,2-isopropylidene glyceryl glycidyl ether (IGG) and glycidyl methyl ether (GME) with CO_2, a diethyl-zinc/pyrogallol catalyst system[12,47] was used. Glycidyl methyl ether (GME) was used as a comonomer because of the structural similarity to IGG and the absence of functional groups. By varying the IGG/GME ratio, the number of functional groups, in this case protected hydroxyl groups, can be adjusted. All reactions were performed at room temperature in 1,4-dioxane for 72 hours. Size exclusion chromatography (SEC) revealed molecular weights between 12 000 – 25 000 g/mol and PDI values between 2.5 and 3.3. **Table 1** summarizes molecular weights, molecular weight distributions as well as IGG content of typical copolymer samples. (**Figure S1**) Some isolated copolymers showed bimodal distributions, which is a typical phenomenon in the copolymerization of CO_2 and epoxides, as already described by several groups.[1,48,49] The copolymerization of carbon dioxide and epoxides with organozinc catalyst systems is usually accompanied by the formation of cyclic carbonates, which can be completely removed by precipitation of the polymer in cold methanol. They were also found in the current reaction to a low extent.

Removal of the protecting group and release of the two hydroxyl groups was carried out using an acidic ion exchange resin in a THF/methanol mixture. Although a significant decrease would be expected due to the loss of the acetal group, the molecular weights obtained from SEC are almost constant for all P((GME-co-GG) C) sample before and after release of the hydroxyl functions. This effect can most likely be attributed to the interaction between the hydroxyl groups and the column material and to intramolecular hydrogen-oxygen interactions leading to an increased hydrodynamic radius. However, the polydispersity indices decreased after deprotection.

Table 1. Overview of the Characterization Data for All Copolymer Samples Prepared.

#	**Sample**	**% Carbonate linkages**[a]	**% IGG**[b]	**M_n g/mol (SEC)**[c]	**PDI (SEC)**	**T_g °C**[d]
1	P(GME-C)	> 99	0	12 600	3.2	1.7
2	P((IGG$_{50}$-*co*-GME$_{100}$)-C)	> 99	33	23 300	3.3	-5.6
3	P((IGG$_{65}$-*co*-GME$_{65}$)-C)	> 99	50	22 800	3.2	-6.7
4	P((IGG$_{78}$-*co*-GME$_{39}$)-C)	> 99	66	22 700	2.8	-7.9
5	P(IGG-C)	> 99	100	24 800	2.5	-14.8
6	P((GG$_{50}$-*co*-GME$_{100}$)-C)	>99	33	22 400	2.3	-2.8
7	P((GG$_{65}$-*co*-GME$_{65}$)-C)	>99	50	21 700	2.5	-4.3
8	P((GG$_{78}$-*co*-GME$_{39}$)-C)	>99	66	22 300	2.1	-5.1
9	P(GG-C)	>99	100	23 900	2.2	-9.9

[a)] Determined by ^{1}H NMR spectroscopy, [b)] IGG Comonomer content [c)] Determined by SEC calibrated with a PEG standard in DMF at 40 °C, [d)] Glass transition temperature obtained from DSC

The incorporation of carbon dioxide into the polymer was confirmed by IR spectroscopy (**Figure S10**). Only one carbonate band at 1755 cm $^{-1}$ is detected, which can be clearly assigned to the carbonyl group of the linear carbonate. No bands for a cyclic carbonate, which appear at around 1790 cm^{-1}, were found in the IR spectra of the copolymers.

Copolymer composition.

The resulting copolymers were characterized by ^{1}H NMR spectroscopy with respect to their composition. Agreement of the IGG fraction in the copolymers with the composition of the epoxide monomer feed is confirmed by proton NMR from the comparison of the polycarbonate backbone signals a and b (δ = 4.98 and δ = 4.29 ppm), which were set to 1 and 2, with the methyl protecting group signals g at δ = 1.30 and δ = 1.25 ppm. All other side chain signals (c-f) can be found between δ = 3.59-4.14 ppm. No IGG/GME structures without CO_2 incorporation, i.e., ether linkages, can be detected from the ^{1}H NMR spectra. A polyether backbone would generate additional resonances at δ = 3.5 ppm. ^{13}C NMR spectroscopy and 2D NMR spectroscopy also confirmed incorporation of IGG, GME and CO_2 into the copolymer and the typical carbonate resonance at δ = 154 ppm can clearly be detected (**Figure S3-S8**).

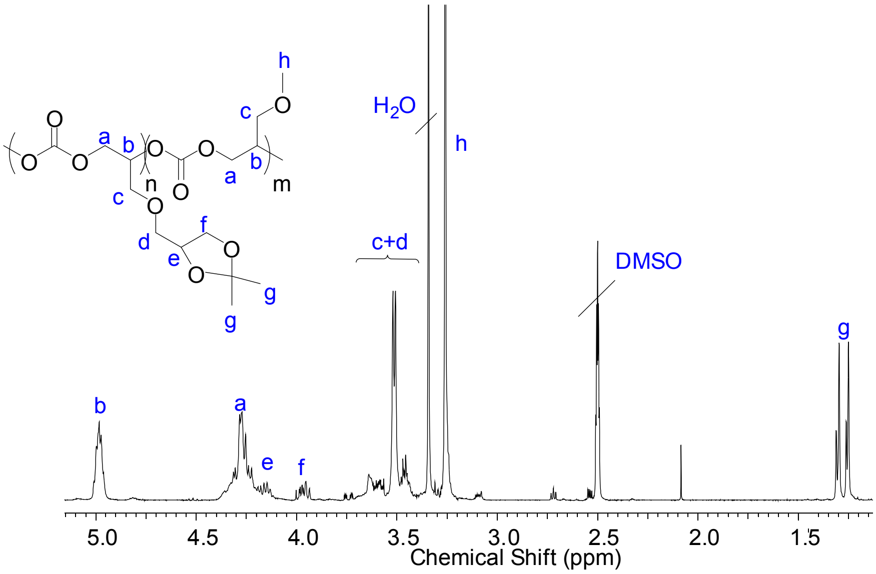


Figure 1. ^{1}H NMR spectrum of the P((IGG$_{50}$-*co*-GME$_{100}$)-C) copolymer (sample 2, 23 300 g/mol).

Detailed investigation of the deprotection kinetics is crucial to confirm that no polymer backbone degradation occurs, since polycarbonates are acid labile. The polymer solution (30 mg in 0.7 mL DMSO-*d*$_6$) was transferred into a NMR tube and 50 µL 20% DCl in D_2O were added. Spectra were measured every 5 minutes. The results are shown in **Figure 2**. Deprotection was studied by following the decrease of the protecting group methyl signals located at δ = 1.30 and δ = 1.25 ppm and the increase of the acetone signal at δ = 2.09 ppm, respectively. All signals are referenced to the backbone methine peak at δ = 4.98 ppm, which was set to one and should be constant in the course of the reaction. Plotting the decrease of the protecting group signal vs. time results in an exponential decay, showing that the deprotection reaction slows down with conversion. (Figure **S11**). As expected the signals next to the protecting group e and f (δ = 4.14 and δ = 3.95 ppm) shift to lower values upon deprotection. The backbone signals remain constant over time, indicating that no backbone degradation takes place. The free hydroxyl group can also be monitored by IR spectroscopy (**Figure S10**).

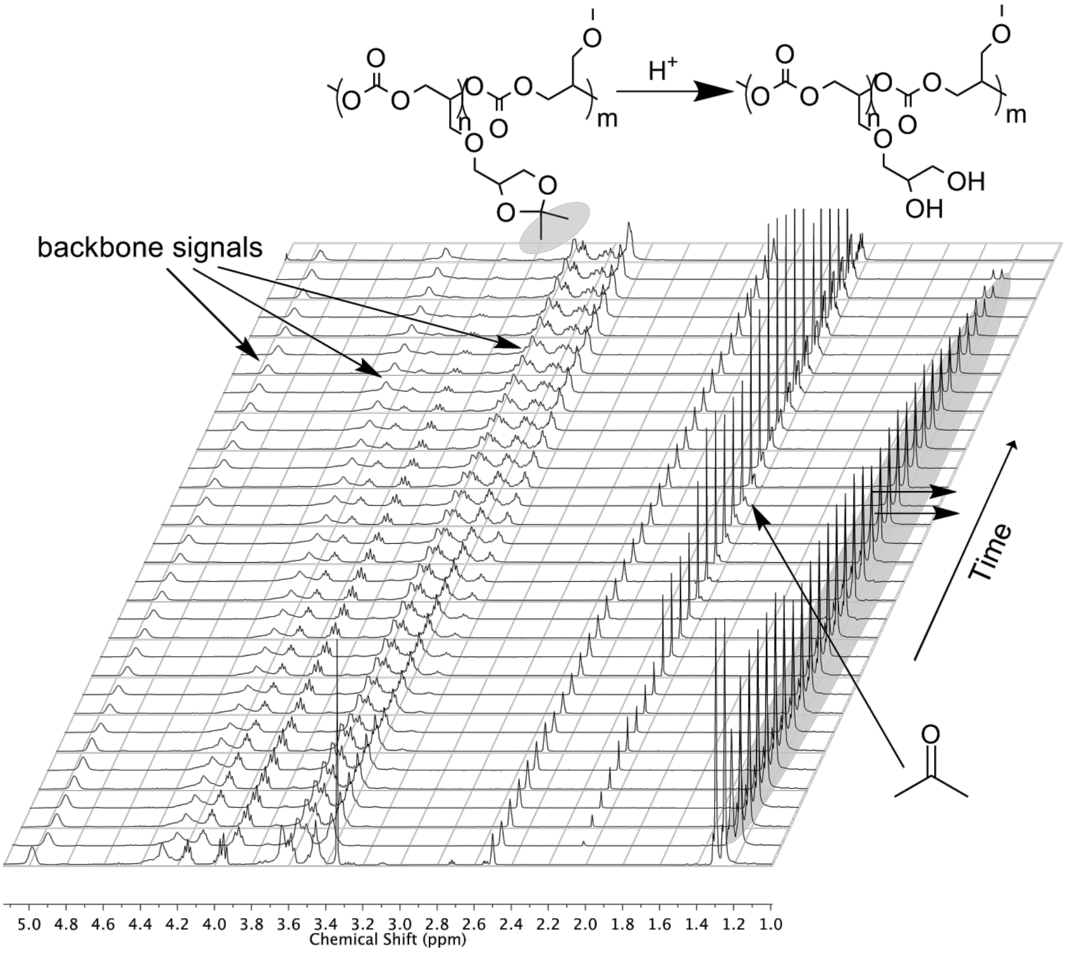


Figure 2. ^{1}H NMR spectra for the deprotection of P(IGG C) with DCl at 25 °C in DMSO-d_6 recorded every 5 minutes.

Properties and Stability.

The thermal properties of the P((GME-*co*-IGG) C) as well as the P(GME-*co*-GG C) copolymers are of central interest for biomedical application. The thermal characteristics studied with differential scanning calorimetry (DSC) are also given in **Table 1** and **Figure S12**. The T_g of the copolymers increases from the T_g of the P(IGG C) homopolymer (-14.7 °C) to the value for the P(GME C) homopolymer (1.7°C). The T_g is -5.6 °C for sample 2 with an IGG content of 33% and decreases slightly with increasing IGG content up to – 9.9 °C for 66% IGG. The deprotected analogues exhibit glass transition temperatures that are approximately 3-5 °C higher than those of the respective protected copolymers. The copolymer T_g may be expected to decrease after deprotection due to the removal of the protecting groups with steric bulk. However, the transformation of the acetal groups to interacting bis-hydroxyl groups appears to counterbalance this effect.[50–52] The hydroxyl groups can form hydrogen bonds increasing the interaction between and within the polymer chains. All P((GME-co-IGG) C) copolymers were obtained as clear, rubber-like materials at room temperature that were soluble in acetone, chlorinated media, THF and aromatic solvents, and insoluble in water, lower alcohols and diethyl ether. For the deprotected copolymers swelling occurred in water and methanol.

The degradation behavior of the P((GME-*co*-IGG) C) copolymers in solution was investigated in THF. Within 21 days no decrease in molecular weight can be seen in the SEC traces (**Figure S13**). Compared to poly(1,2-glycerol carbonate) synthesized from benzyl glycidyl ether or ethoxy ethyl glycidyl ether with carbon dioxide, [53] the P((GME-*co*-IGG) C) copolymers were stable in solution, and no backbone degradation occurred, which we ascribe to the reduced stability of the resulting 5-membered cyclic carbonate structures. Nevertheless biodegradation should be possible.

Conclusion

A novel type of functional, linear aliphatic polycarbonate random copolymers from CO_2, GME, and a protected glycidyl ether derivative has been synthesized. To the best of our knowledge such poly(carbonate) structures with diol side chains have not been prepared directly from carbon dioxide and epoxides before.[13,17] The amount of glycerol side chain functionalities was adjusted by varying the epoxide comonomer composition. Acidic hydrolysis of the protection groups afforded polycarbonates with two vicinal hydroxyl groups in the glycerol unit resulting from IGG. Detailed characterization in terms of composition, thermal properties, deprotection kinetics and hydrolytic stability was performed. Studies in solution as well as in bulk revealed that rather hydrophilic materials with good hydrolytic stability were obtained. Moreover, the presence of two vicinal hydroxyl groups opens a general pathway for the attachment of any molecule with aldehyde or ketone functionality to the chain via formation of the cyclic acetal or ketal. Facile, acid catalyzed release allows for various applications, for example as drug or other biomolecule releasing agents.

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Supporting Information for: Stable, Hydroxyl-Functional Polycarbonates with Glycerol Side Chains Synthesized from CO_2 and Isopropylidene(glyceryl glycidyl ether)

Jeannette Geschwind[1,†] and Holger Frey[*1]

Experimental Section

Instrumentation.

^{1}H NMR spectra (300 MHz and 400 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC300 or a Bruker AMX400 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in DMF (containing 0.25 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column ($10^6/10^5/10^4$ g mol^{-1}), a UV (275 nm) and a RI detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service. DSC measurements were performed using a PerkinElmer DSC 8500 with PerkinElmer CLN2 in the temperature range from – 100 to 150 °C at heating rates of 10 K min^{-1} under nitrogen.

Reagents.

Solketal, epichlorohydrin (99%), sodium hydroxide as well as dimethylsulfoxide (puriss, over molecular sieve), tetrahydrofurane (puriss, over molecular sieve), and toluene (puriss, over molecular sieve) were purchased from Aldrich. Pyrogallol was recrystallized from Benzene/EtOH. Deuterated chloroform-d_1 and DMSO-d_6 were purchased from Deutero

GmbH. Carbon dioxide (99.995%) was purchased from Westfalen AG and used as received. All other solvents and reagents were purchased from Acros Organics.

Monomer Synthesis.

13g (99 mmol) Solketal was dissolved in 20 mL benzene, 20 mL of a 50% NaOH and 3,22g (10 mmol) tetrabutyl ammonium bromide (TBAB) was added. The mixture was cooled to ca. 10°C and 18,35g (200 mmol) epichlorohydrin was slowly added with a syringe. The reaction was vigorously stirred at room temperature for 48 h, diluted with ether and washed three times with water, saturated $NaHCO_3$ and NaCl, and finally dried over MgSO4. Diethyl ether and excess of epichlorohydrin was removed in vacuo and the crude product was distilled in vacuo (b.p. 90°C at 10-2 mbar, yield 51%. Purification via column chromatography (silica, diethyl ether: petroleum ether 5:3) results in higher yields (70-90%). 1H-NMR (400 MHz, $CDCl_3$, δ in ppm): 4.3 (m, 1H, CH acetal), 4.07 (m, 1H), 3.88-3.39 (m, 6H), 3.17 (m, 1H), 2.81 (t, 1H, CH_2 epoxide), 2.63 (q, 1H, CH_2 epoxide), 1.44 (s, 3H, CH_3), 1.38 (s, 3H, CH_3). 13C-NMR (97 MHz, $CDCl_3$, δ in ppm): 109.4 (quart. C acetal), 74.6 (tert. CH acetal), 74.4- 74.1 (CH_2), 66.6 (CH_2, acetal), 50.7 (CH, epoxide), 44.1 (CH_2 epoxide), 26.7 CH_3, acetal), 25.3 (CH_3, acetal).

Representative SEC results for the Poly(IGG carbonate) copolymers

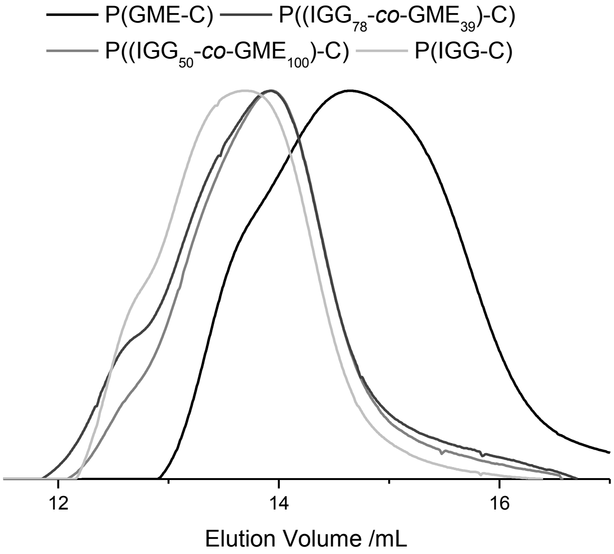

Figure S1. SEC diagrams of the synthesized Poly(IGG carbonate) copolymers

Representative ^{13}C NMR and 2 D NMR spectra of the protected and deprotected Poly(IGG carbonates)

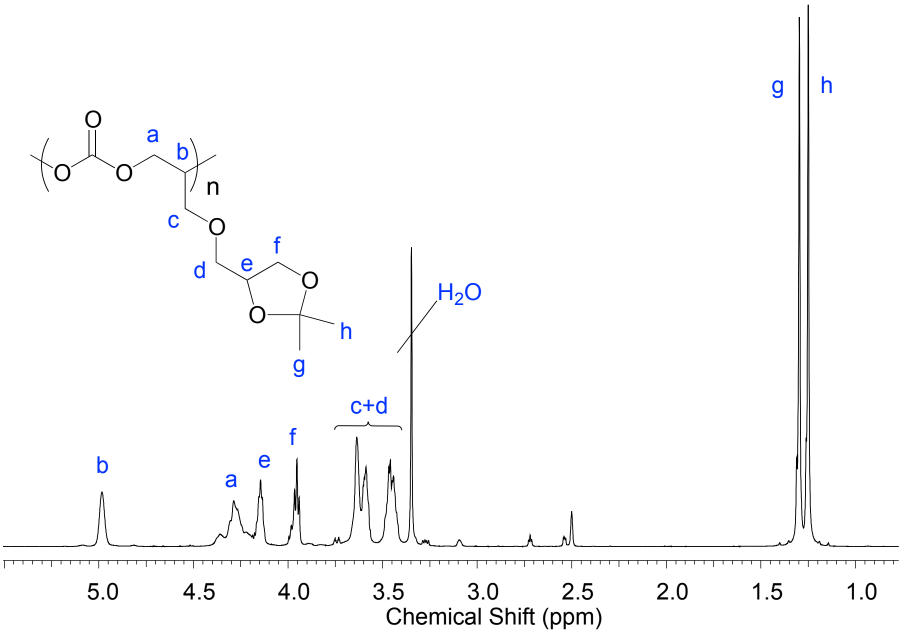

Figure S2. ^{1}H NMR spectrum of the synthesized Poly(IGG carbonate) copolymer (Table 1, sample 5).

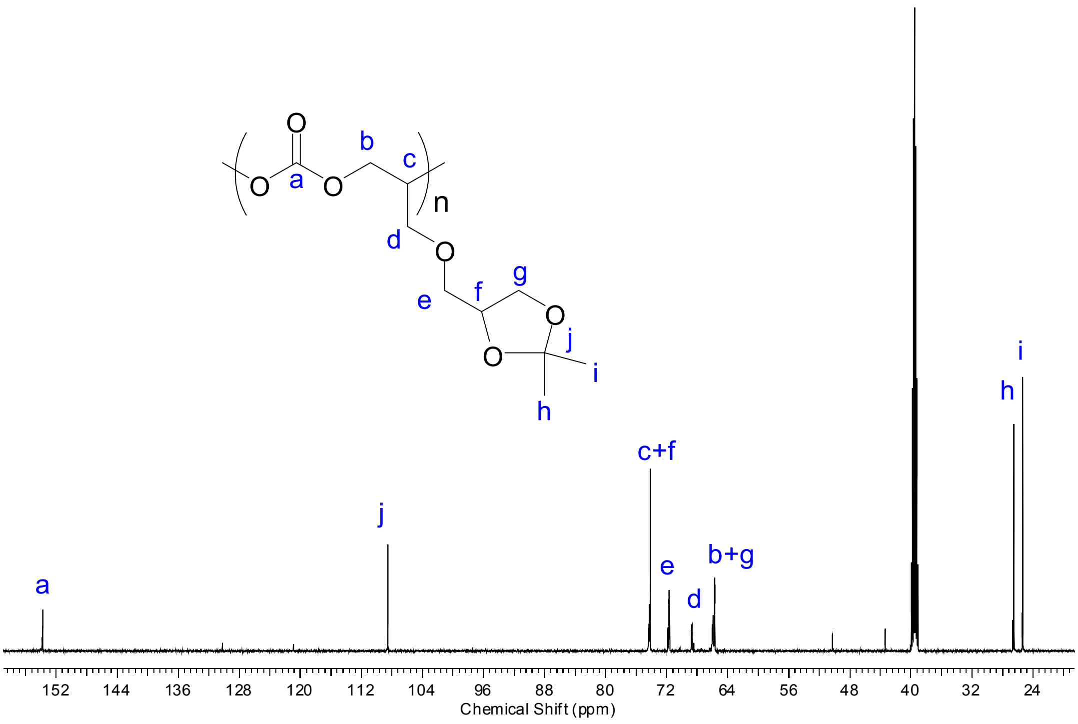

Figure S3. ^{13}C NMR spectrum of the synthesized Poly(IGG carbonate) copolymer (Table 1, sample 5).

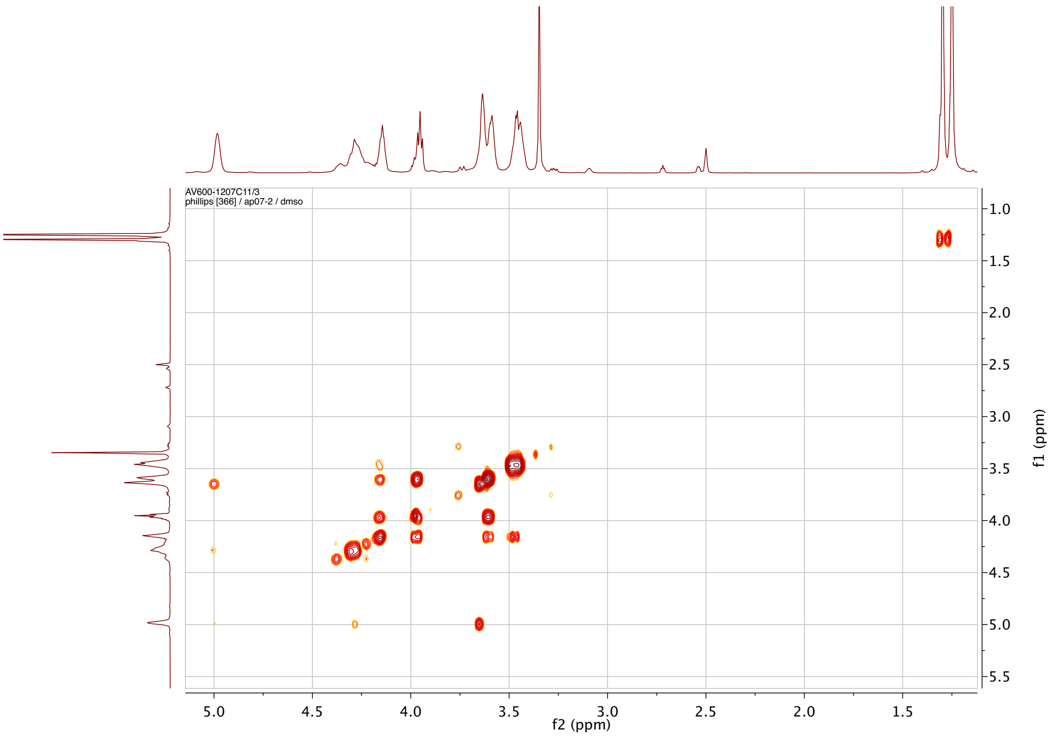

Figure S4. COSY spectrum of the synthesized Poly(IGG carbonate) copolymer (Table 1, sample 5).

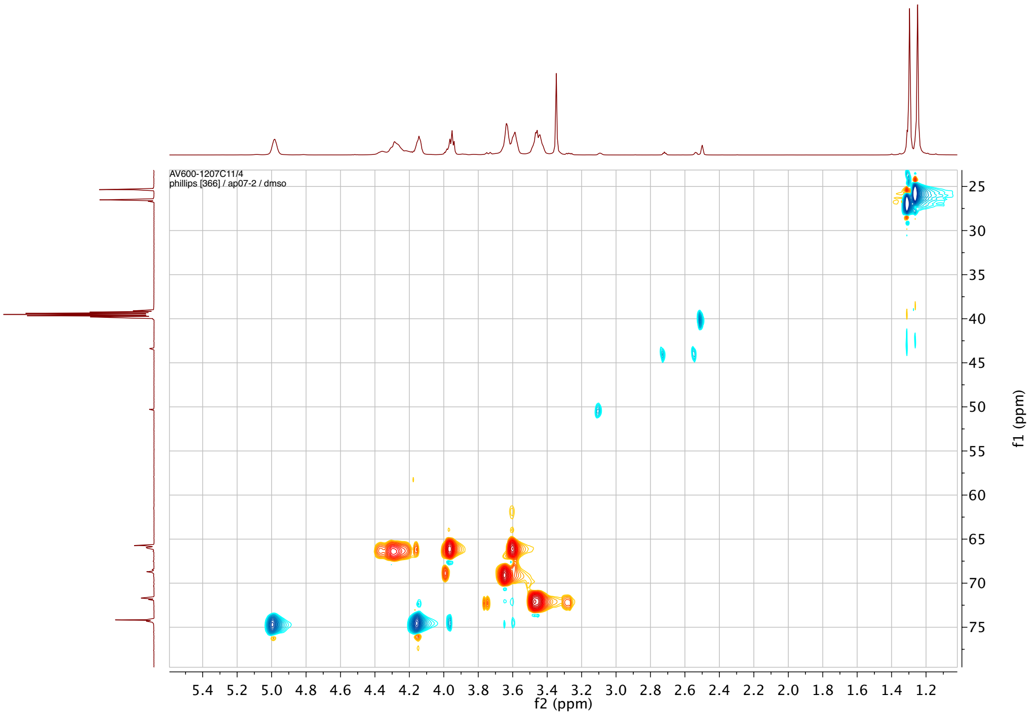

Figure S5. HSQC spectrum of the synthesized Poly(IGG carbonate) copolymer (Table 1, sample 5).

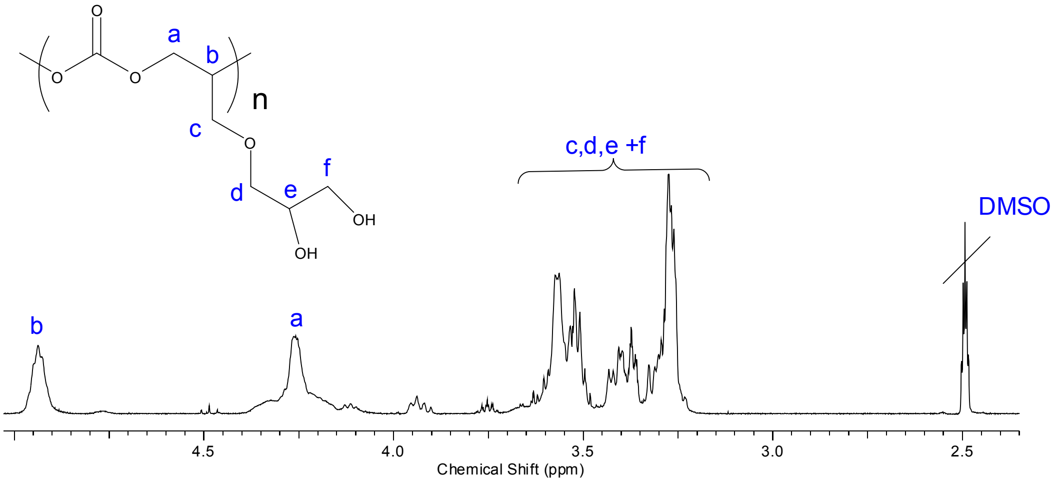

Figure S6. ^{1}H NMR spectrum of the deprotected Poly(IGG carbonate) copolymer (Table 1, sample 9).

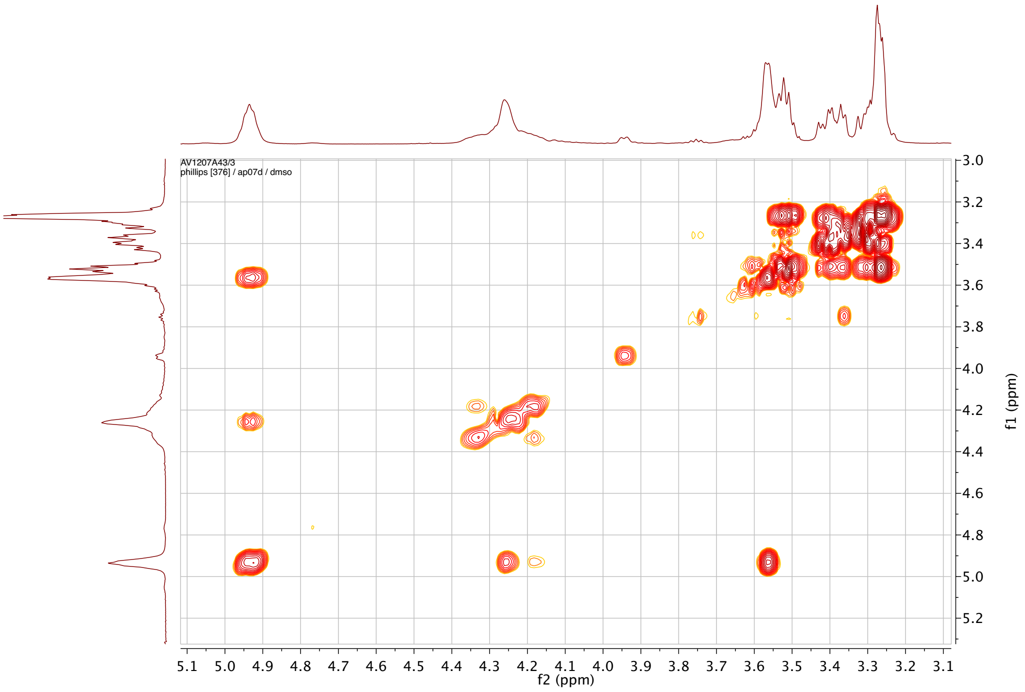

Figure S7. COSY spectrum of the deprotected Poly(IGG carbonate) copolymer (Table 1, sample 9).

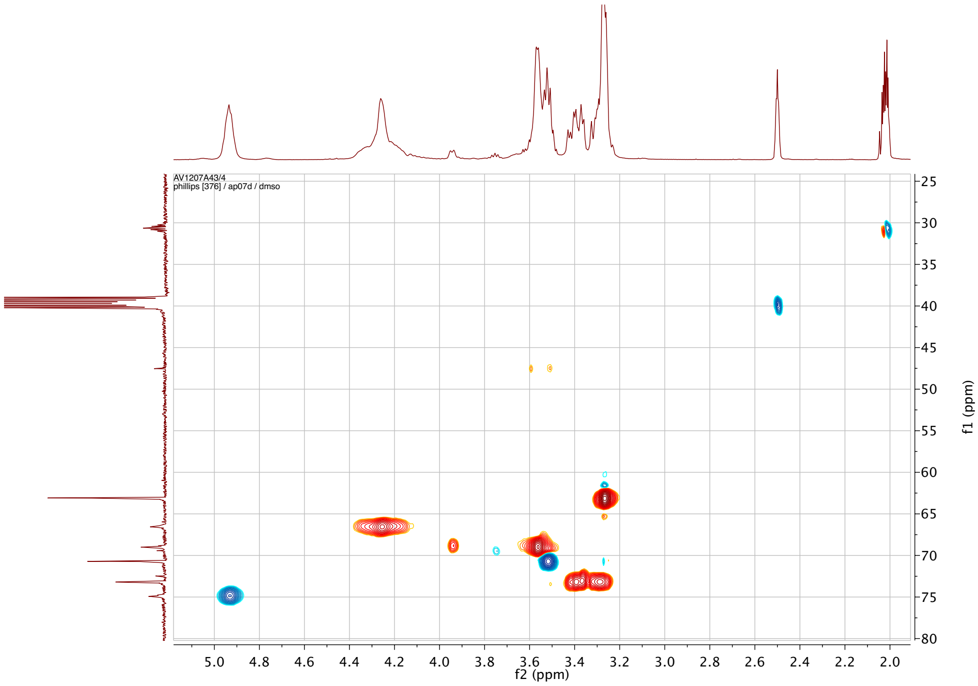

Figure S8. HSQC spectrum of the deprotected Poly(IGG carbonate) copolymer (Table 1, sample 9).

IR spectra of the resulting polymers

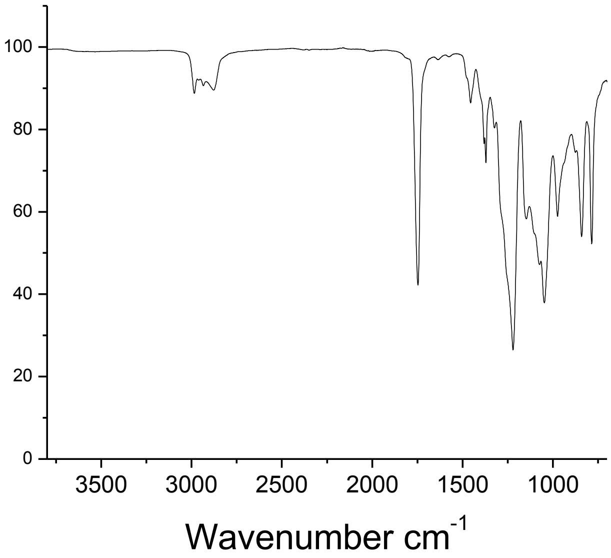

Figure S9. IR spectrum of the synthesized Poly(IGG carbonate) copolymer (Table 1, sample 5).

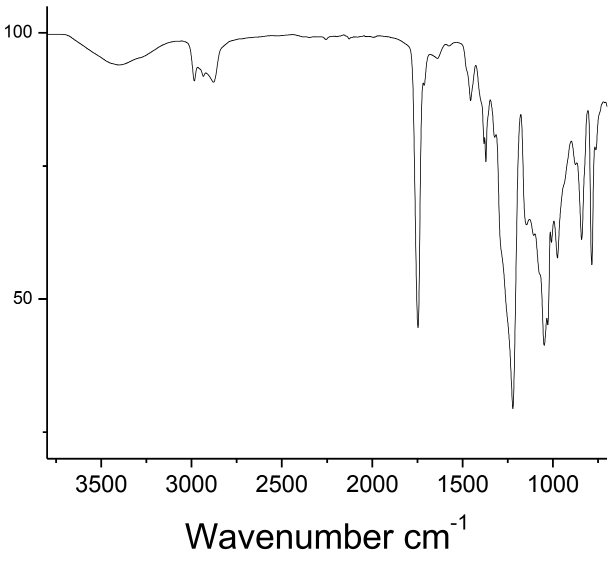

Figure S10. IR spectrum of the deprotected Poly(IGG carbonate) copolymer (Table 1, sample 9).

Deprotection Kinetics

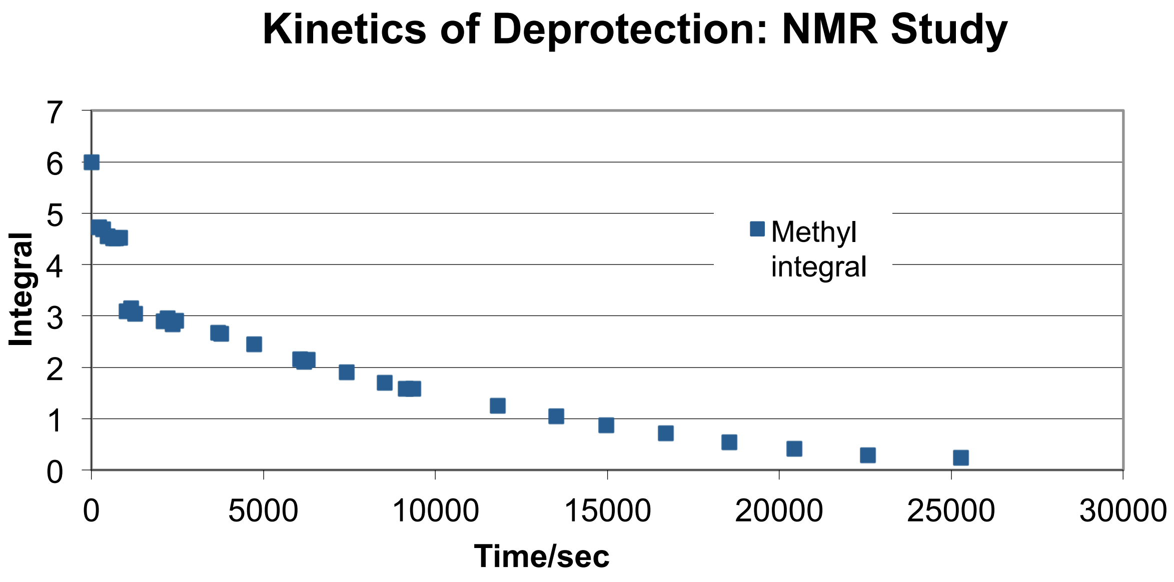

Figure S11. Deprotection Study: Kinetics of removal of acetal protection groups, as derived from NMR spectra.

DSC Results

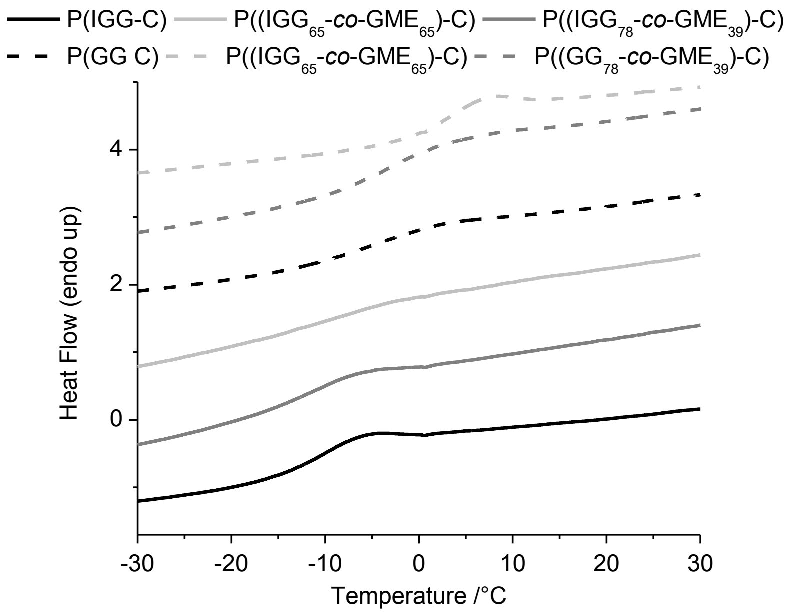

Figure S12. DSC Results of the series of functional polycarbonates

Degradation Studies

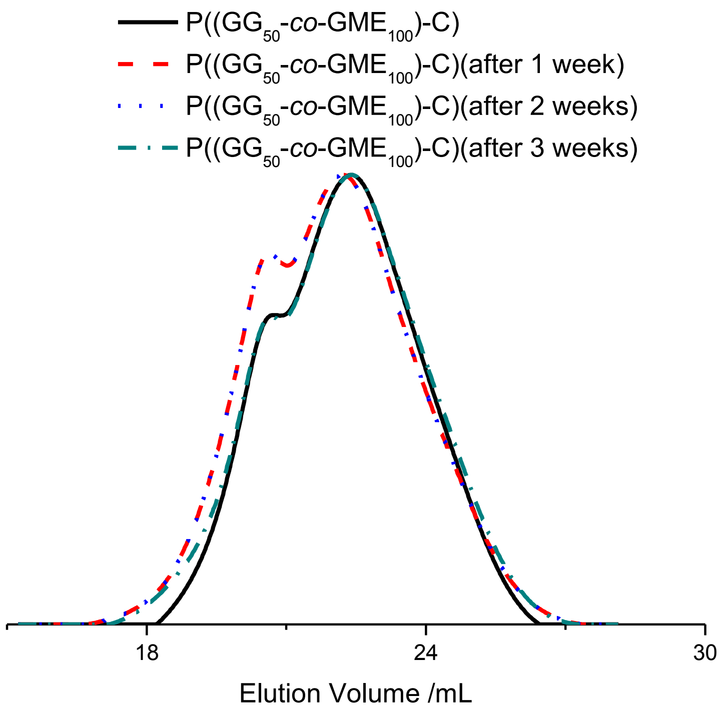

Figure S13. SEC diagrams of polycarbonate samples after different deprotection times.

3.4. Propargyl-functional Aliphatic Polycarbonates Obtained from Carbon Dioxide and Glycidyl Propargyl Ether

Jeannette Hilf[1†] **and Holger Frey**[*1]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg
10-14, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany

[†]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

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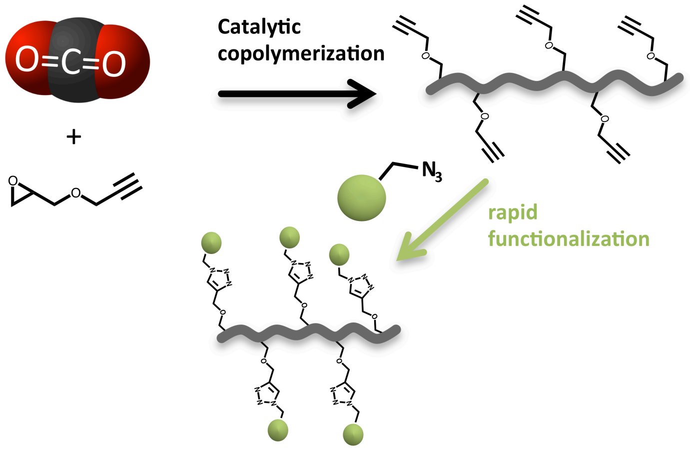


Abstract

The synthesis of propargyl-functional poly(carbonate)s with different content of glycidyl propargyl ether (GPE) units was achieved *via* the copolymerization of propargyl glycidyl ether and carbon dioxide. A new type of functional poly(carbonate) synthesized directly from CO_2 and the glycidyl ether was obtained. The resulting polymers showed moderate polydispersities in the range of 1.6-2.5 and molecular weights in the range of 7000-10 500 g/mol. The synthesized copolymers with varying number of alkyne functionalities and benzyl azide were used for the copper-catalyzed Huisgen-1,3-dipolar addition. Moreover, the presence of vicinal alkyne groups opens a general pathway to produce functional aliphatic poly(carbonate)s from a single polymer scaffold.

Introduction

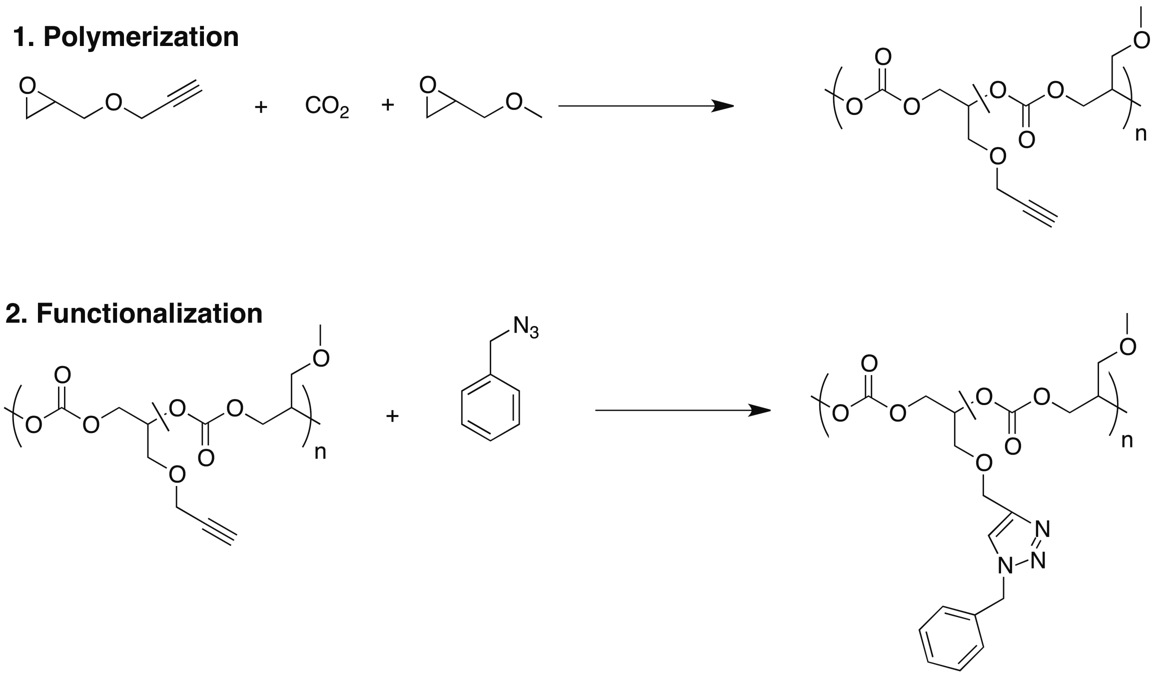
In recent years the synthesis of degradable polymers has gained significant attention due to their increasing use in biomedical applications.[1] Aliphatic poly(carbonate)s (PC) represent a promising class of biodegradable polymers due to their biocompatibility and low toxicity.[2] Usually such poly(carbonate)s are prepared either by ring-opening polymerization (ROP) of cyclic carbonate monomers[3] or by catalytic copolymerization of epoxides with carbon dioxide (CO_2).[4–7]

In the past four decades numerous catalyst systems for the CO_2/epoxide copolymerization have been developed.[8–15] Mostly cobalt or zinc based catalyst systems are used at present. Alternating copolymerization of CO_2 with epoxides to form biodegradable poly(carbonate)s is a promising reaction, since carbon dioxide is non-toxic, renewable and readily available in large quantities and high purity. However, to date, mainly propylene oxide or cyclohexene oxide have been used, and functional poly(carbonate)s have only been presented to a limited extent.[4,12,16–18,23] Despite the facile copolymerization of carbon dioxide with epoxides, glycidyl ethers as functional monomers have not received much attention until recently, which may be due to the non-suitability of most established, high efficient catalyst systems based on cobalt or zinc complexes for this class of monomers. However copolymerization is possible as shown by several groups.[19–23]

A current drawback for several applications of polycarbonates is the lack of functional groups at the poly(carbonate) backbone in the case of polycarbonates based on propylene oxide or cyclohexene oxide. Functional groups can be introduced into aliphatic polycarbonate derivatives either by the ROP of functional six-membered cyclic carbonates,[2,3,24–43] or by copolymerization of carbon dioxide with functional epoxides, which is a pathway that has been least explored to date.[19,21,44–49]

The alkyne group is a very interesting functionality, which is utilized in many organic reactions as a consequence of its versatile reactivity. Alkynes have been widely studied, especially with respect to the Huisgen 1,3-dipolar cycloaddition reaction, often designated “click” reaction.[50–55] The widespread utilization of this highly efficient reaction is due to its high specificity, near-quantitative yields, and high fidelity in the presence of most other functional groups. In contrast, examples of the modification of polycarbonates by click chemistry are rare. Dove and coworkers described the organocatalytic synthesis and post-polymerization functionalization of propargyl-functional poly(carbonate)s.[25] Other groups prepared lactide-carbonate copolymers with pendant alkynyl groups by ring-opening copolymerization of lactide and 5-methyl-5-propargyloxycarbonyl-1,3-dioxan-2-one.[30 40,56,57]

In the present work, we report poly(carbonate)s with pendant propargyl groups directly prepared from carbon dioxide and glycidyl propargyl ether (GPE) that could be conveniently functionalized by the click reaction. To the best of our knowledge, this is the first report on a controlled and variable incorporation of glycidyl propargyl ether into the PC backbone. The straightforward approach represents a general strategy for the synthesis of novel multifunctional PCs based on the copolymerization of different functional epoxides, glycidyl methyl ether (GME) and CO_2 (Scheme 1). A simple zinc-pyrogallol catalyst system was used as a catalyst for the copolymerization. For the system reported herein, the comonomer content was varied gradually from 0 to 100% and also subsequent functionalization is demonstrated. Post-polymerization functionalization of the pendant alkyne groups in the polymer backbone was shown to be highly efficient and occurs without observable polymer degradation, leading to the synthesis of a range of new functional aliphatic poly(carbonate)s.



Scheme 1. Synthesis of the poly((GPE-*co*-GME)-C) and subsequent functionalization via click chemistry.

Experimental Section

Monomer Synthesis.

Glycidyl propargyl ether (GPE) was prepared as described in the Supporting Information and glycidyl methyl ether (GME) was purchased from TCI.

Preparation of the catalyst.

The catalyst was prepared under argon atmosphere immediately before use, following a procedure described previously[20]. A solution of pyrogallol (0.47 g, 4 mmol in 10 mL of 1,4-dioxane) was slowly added to a stirred solution of $ZnEt_2$ (2 mmol in 35 mL of dioxane) at room temperature. After the addition was complete, stirring was continued until the evolution of ethane stopped.

Polymerization.

The copolymerization was carried out in dioxane in the presence of a catalytic system based on $ZnEt_2$ and pyrogallol at a molar ratio of 2:1. The catalyst solution (2 mmol) and 50 mmol epoxide was placed in a stainless steel autoclave filled with argon. CO_2 was then introduced at a pressure of ca. 20 bar. The reaction was carried out at room temperature for 72 h. The reaction was stopped by decompression of the autoclave. The resulting solution was diluted with CH_2Cl_2, washed with 10% HCl and twice with water, dried with $MgSO_4$, precipitated in cold methanol and dried in vacuum. Yields of the crude products were ca. 80%. The purified polymers are white solids, which are soluble in acetone, chlorinated, THF and aromatic solvents, and insoluble in water, lower alcohols and diethyl ether.

Results and Discussion

Synthesis and Molecular Characterization.

The synthetic strategy developed to obtain the multifunctional aliphatic polycarbonate structures is shown in **Scheme 1**. The glycidyl propargyl ether content in the copolymer was varied between 27 and 100% to adjust the number of functional groups in the resulting materials. Glycidyl methyl ether was used as a comonomer because of the structural similarity to GPE and the absence of functional groups. GPE was synthesized in one step from epichlorohydrin and propargyl alcohol in a phase transfer reaction (Supporting Information). Characterization data for the series of copolymers obtained from the copolymerization of GME and GPE are given in **Table 1**. The ratio of epoxide monomer to catalyst (50:2) was kept constant. All reactions were performed in 1,4-dioxane for 72 h at room temperature. For some catalyst systems, especially organozinc systems, the epoxide/CO_2 copolymerization is usually accompanied by a side reaction, the formation of cyclic carbonates. In this case cyclic side products were also found to a low extent, but could be completely removed by precipitation of the polymers in cold methanol.

Size exclusion chromatography (SEC) shows moderate molecular weight distributions with M_w/M_n values below 2.5 for all samples. Molecular weights were in the range of 7000 to 10500 g/mol (see also Supporting Information). In some cases bimodal molecular weight distributions were observed, which is a typical phenomenon in the copolymerization of carbon dioxide with epoxides, as already described in other works.[4,17,58]

Table 1. Characterization Data for All Copolymer Samples Prepared

#	Sample	%Carbonate linkages[a]	% GPE[b]	M_n g/mol (SEC)[c]	PDI (SEC)	T_g °C[d]
1	P(GPE-C)	>99	100	7900	2.3	-9.7
2	P((GPE$_{47}$-*co*-GME$_{12}$)-C)	>99	80	8900	1.6	-8.1
3	P((GPE$_{35}$-*co*-GME$_{15}$)-C)	>99	70	7500	2.1	-5.5
4	P((GPE$_{32}$-*co*-GME$_{17}$)-C)	>99	65	7300	2.0	-3.8
5	P((GPE$_{24}$-*co*-GME$_{24}$)-C)	>99	50	7000	2.2	-0.9
6	P((GPE$_{17}$-*co*-GME$_{39}$)-C)	>99	27	8100	1.8	1.5
7	P(GME-C)	>99	0	10 500	2.5	3.1

[a)] Determined by ^{1}H NMR spectroscopy, [b)] GPE comonomer content in mol% [c)] Determined by SEC calibrated with a PEG standard in DMF at 40 °C, [d)] Glass transition temperature obtained from DSC, Reaction conditions: 20 bar CO_2, 72h, RT

The incorporation of CO_2 into the polymers was confirmed by IR spectroscopy (**Figure 1**). Only one carbonate band at around 1755 cm^{-1}, assigned to C=O group of the linear carbonate, is detected. No bands typical for a cyclic carbonate, which appear at around 1790 cm^{-1}, were found in the IR or NMR spectra of the copolymers. Furthermore, the alkyne bands are clearly visible in the FT-IR spectrum. The –C≡C– stretch appears as a weak band at around 2100 cm^{-1}, and the terminal alkyne shows a strong, narrow band from the C–H vibration in the range of 3330-3270 cm^{-1}.

Furthermore, detailed NMR characterization permits the calculation of the ratio of comonomers incorporated in the case of the GME/GPE copolymers by determination of GPE units from the intensity of the alkyne proton signal (Figure 2). From a comparison of the composition of the monomer feed and the copolymer composition it can clearly be stated that the incorporated GPE/GME-ratio corresponds to the monomer feed, as determined by ^{1}H NMR spectroscopy. A typical spectrum of the copolymer in $CDCl_3$ is displayed in **Figure 2**.

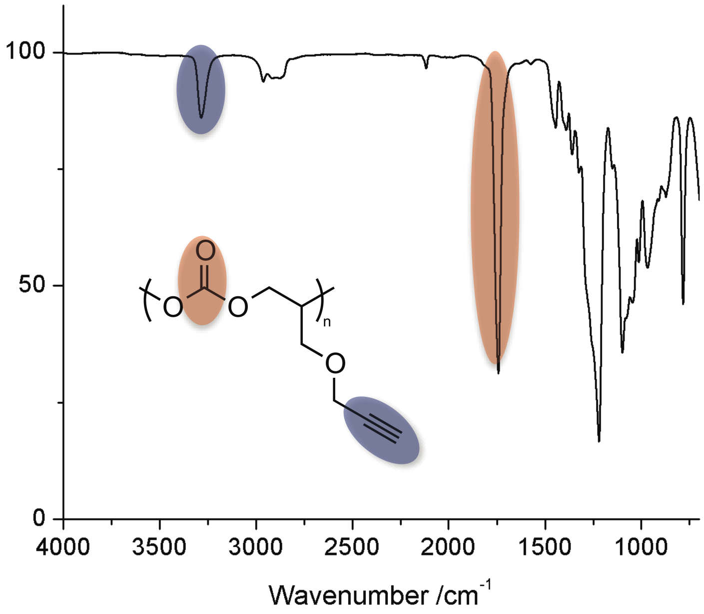


Figure 1. FT-IR Spectrum of P(GPE-C) polycarbonate (Table 1, entry 1)

The resonances d (4.19 ppm) and e (2.50 ppm) correspond to the alkine side chain, and by integration of these signals and comparison to the signals a, b and c due to the poly(carbonate) backbone (4.33, 5.05 and 3.76 ppm) the copolymer composition can be calculated. Additional ^{1}H and ^{13}C NMR spectra can be found in the Supporting Information. No GPE/GME structures with direct ether linkages, that is, without CO_2 incorporation can be detected in the ^{1}H NMR spectra.

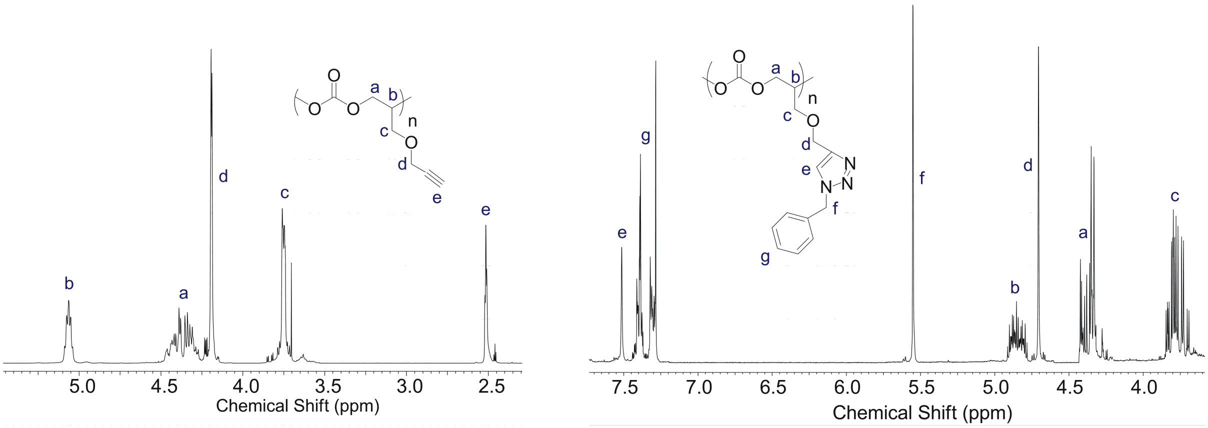


Figure 2. ^{1}H NMR spectrum of P(GPE-C) (Table 1 entry 1) before (left) and after (right) click reaction.

Characterization of the thermal properties was carried out via differential scanning calorimetry (DSC, heating 10 K/min). The results are also summarized in Table 1. These results lend further support to the random incorporation of GME and GPE in the copolymer (Figure S9). All determined glass transition temperature (T_g) values are slightly lower than the T_g of pure poly(glycidyl methyl ether carbonate) and decrease with increasing GPE/GME ratio. The T_g of the copolymers decreased from the P(GME-C) homopolymer (3.1 °C) to the value for the P(GPE-C) homopolymer (-9.7 °C). The T_g of 1.5 °C for sample 6 with a GPE content of 27% decreases slightly with increasing GPE content to -8.1 °C for 80% GPE. Compared to the T_g of poly(propylene carbonate) (35 °C), the most common material obtained from epoxide/CO_2 copolymerization, the glass transition temperature is lowered significantly. These results for the incorporation of glycidyl ethers show that these copolymers are interesting candidates for new aliphatic poly(carbonate) applications.

Functionalization via “Click”-Reaction

The functionalization of alkyne-bond carrying poly(carbonate)s generated by multi-step ring-opening procedures by copper assisted azide-alkyne “click“ reactions has been studied by several groups.[30,40,56,57] The term “click-reaction” with respect to polymer modification reactions has recently been subject of an intense discussion.[59] The general requirements of click reactions are close to complete conversion, preferably with no solvent involved, facile reaction conditions with easily available starting materials and a simple isolation/purification procedure.

Benzyl azide was chosen as a model compound, since it allows for the facile assignment of the relevant resonances in ^{1}H NMR spectroscopy. The reaction was carried out overnight in THF at room temperature, and after removal of the copper iodide with EDTA solution the successful transformation of the alkyne bond can be observed by the disappearance of the resonances at 2.5 ppm, while new resonances are detected due to the formation of the triazole structure. These due to the triazol proton at 7.49 ppm, 7.36 and 7.29 ppm for the aromatic benzyl protons and 5.52 ppm for the CH_2 unit adjacent to the aromatic ring (Figure 2).

The comparison of the triazol signals with the poly(carbonate) backbone and the initial amount of alkyne bonds allows to determine the conversion of the alkyne moieties. In all cases full conversion was obtained. This proof-of-principle functionalization study demonstrates that the attachment of small molecules to the alkyne side chains is possible and can in principle be employed for any compound bearing an azide moiety.

Conclusion

In this work, we have demonstrated the facile synthesis of multifunctional aliphatic poly(carbonate)s based on CO_2/GME/GPE copolymers with alternating incorporation of carbon dioxide and the respective epoxides. To the best of our knowledge, such aliphatic polycarbonate structures with pendant alkyne groups have not been prepared from CO_2 and epoxides to date. Polymers with 0%-100% glycidyl propargyl ether (GPE) and molecular weight between 7000 and 10 500 g/mol were obtained under mild reaction conditions (25 bar CO_2, RT, 3 d). Notably, the post-polymerization functionalization of the pendant alkyne groups in the polymer backbone via CuI was shown to be highly efficient and occurs without observable backbone degradation, enabling the synthesis of a broad range of new functional aliphatic poly(carbonate)s.

Relying on the approach reported here, the catalytic terpolymerization of glycidyl ethers and CO_2 represents an interesting and highly modular alternative to the widely used ring-opening strategy based on six membered cyclic carbonates for functional aliphatic polycarbonates, since many different functional epoxides are readily available.

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Supporting Information for: Propargyl-functional Aliphatic Polycarbonate Obtained from Carbon Dioxide and Glycidyl Propargyl Ether

Jeannette Hilf[1,†] and Holger Frey[*1]

Experimental Section

Instrumentation.

^{1}H NMR spectra (300 MHz and 400 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC300 or a Bruker AMX400 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in DMF (containing 0.25 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column ($10^6/10^5/10^4$ g mol^{-1}), a UV (275 nm) and a RI detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service. DSC measurements were performed using a PerkinElmer DSC 8500 with PerkinElmer CLN2 in the temperature range from – 100 to 150 °C at heating rates of 10 K min^{-1} under nitrogen.

Reagents.

Propargyl alcohol, epichlorohydrin (99%), sodium hydroxide as well as dimethylsulfoxide (puriss, over molecular sieve), tetrahydrofurane (puriss, over molecular sieve), and toluene (puriss, over molecular sieve) were purchased from Aldrich. Pyrogallol was recrystallized from Benzene/EtOH. Deuterated chloroform-d_1 and DMSO-d_6 were purchased from Deutero GmbH. Carbon dioxide (99.995%) was purchased from Westfalen AG and used as received. All other solvents and reagents were purchased from Acros Organics.

Monomer Synthesis.

99 mmol propargyl alcohol was dissolved in 20 mL benzene, 20 mL of a 50% NaOH and 3,22g (10 mmol) tetrabutyl ammonium bromide (TBAB) was added. The mixture was cooled to ca. 10°C and 18,35g (200 mmol) epichlorohydrin was slowly added with a syringe. The reaction was vigorously stirred at room temperature for 48 h, diluted with ether and washed three times with water, saturated $NaHCO_3$ and NaCl, and finally dried over $MgSO_4$. Diethyl ether and an excess of epichlorohydrin was removed in vacuo and the crude product was distilled in vacuo (b.p. 90°C at 10-2 mbar, yield 51%. Purification via column chromatography (silica, diethyl ether: petroleum ether 5:3) resulted in higher yields (70-90%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 4.11 (m, 2H, CH_2-triple bond), 3.7 (m, 1H, CH_2), 3.4 (m, 1H, CH_2), 3.06 (m, 1H alkine), 2.72(t, 1H, CH_2 epoxide), 2.5 (q, 1H, CH_2 epoxide), 2.4 (q, 1H, CH_2 epoxide).

Functionalization.

Alkyne functionalized P(GPE-C) (0.24 mmol), benzyl azide (0.2 mmol), CuI (0,041 mmol) and 5 mL dry THF were placed in a Schlenk tube. After three freeze pump thaw cycles 1,8-diaza[5.4.0]bicycloundec-7-ene (3.98 mmol) was added and the reaction mixture was stirred for 18 h. The resin was filtered off and the solvent was removed in vacuum. 5mL dichloromethane were added and the solution was washed with a 0.065 M EDTA solution. The organic layer was dried with anhydrous magnesium sulfate and was concentrated *in vacuo*. The polymer was precipitated in methanol, yielding a white solid which was dried under vacuum.

NMR Results

Chemical Shift (ppm)

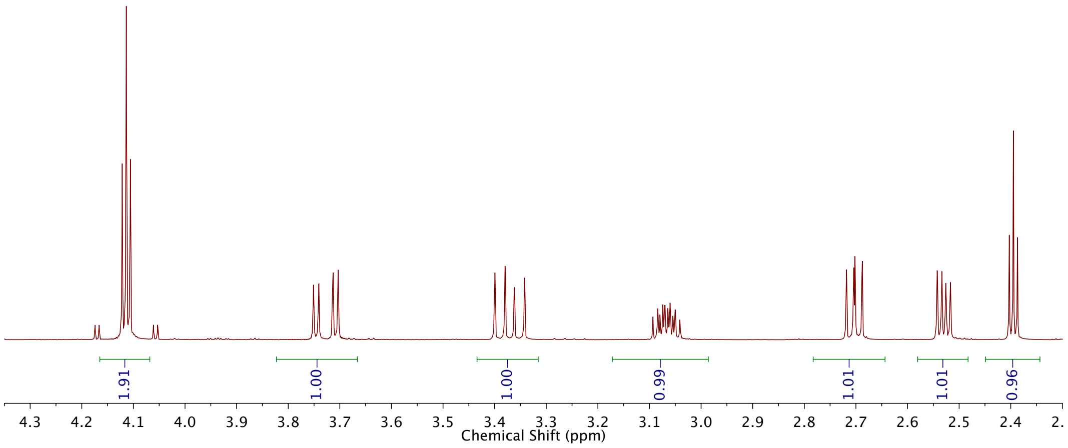

Figure S1. ^{1}H NMR spectrum of glycidyl propargyl ether (GPE) (monomer).

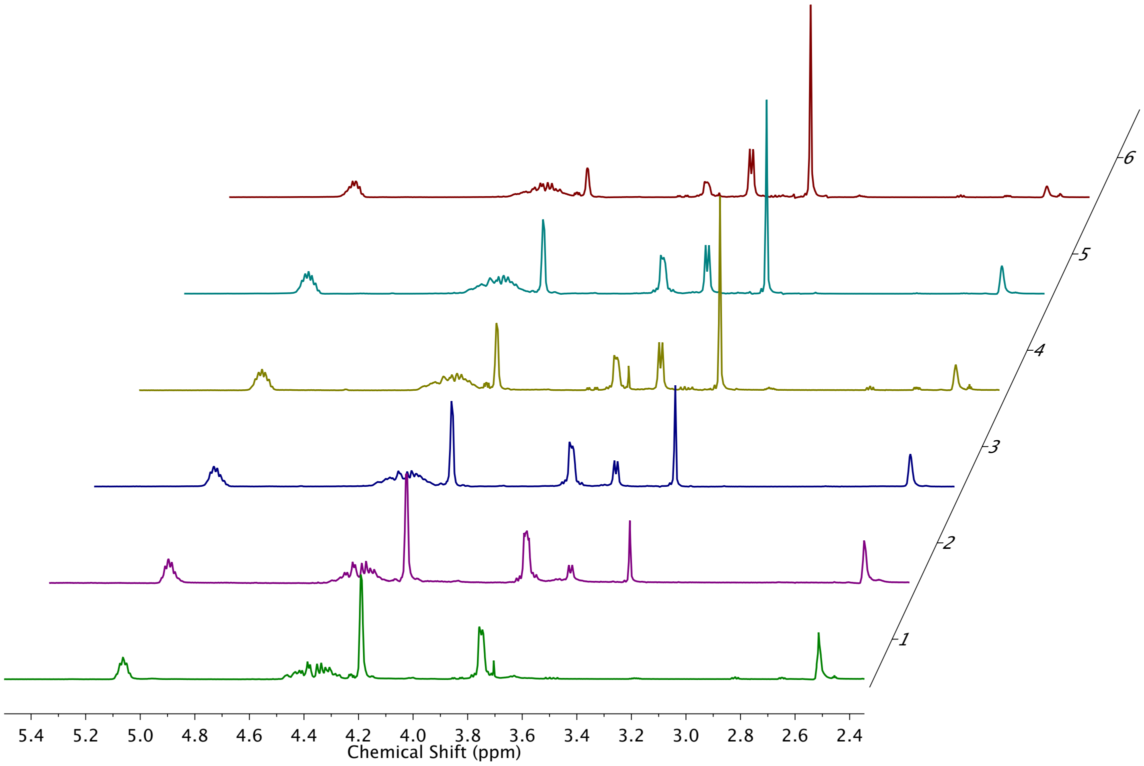

Figure S2a. ^{1}H spectra of poly((glycidyl propargyl ether-*co*-glycidyl methyl ether)carbonate) copolymers with increasing amount of glycidyl methyl ether from spectrum 1 to 6.

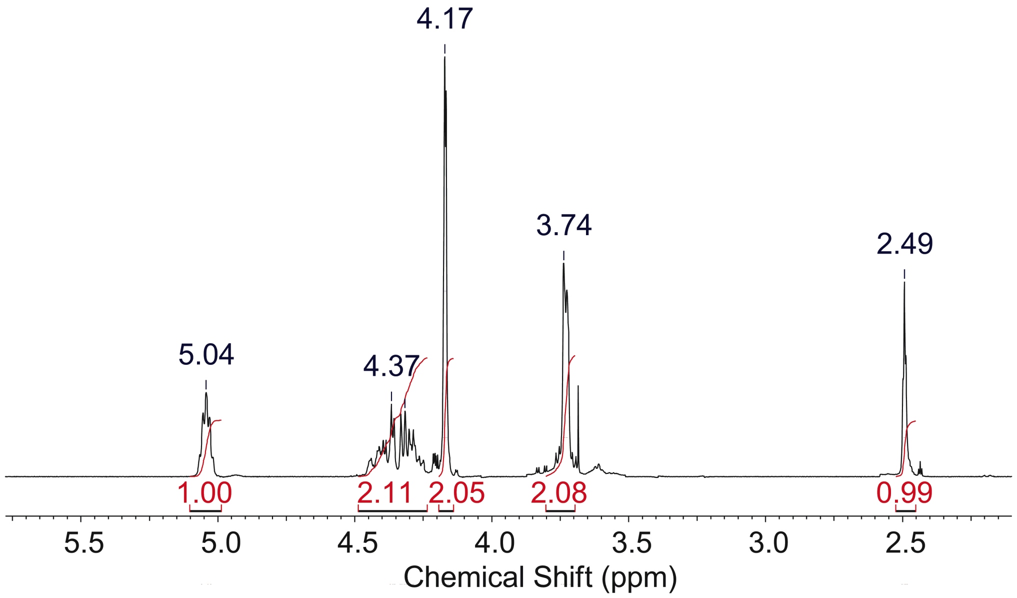

Figure S2b. ^{1}H spectrum of poly(glycidyl propargyl ether carbonate) copolymers with labels and integrals.

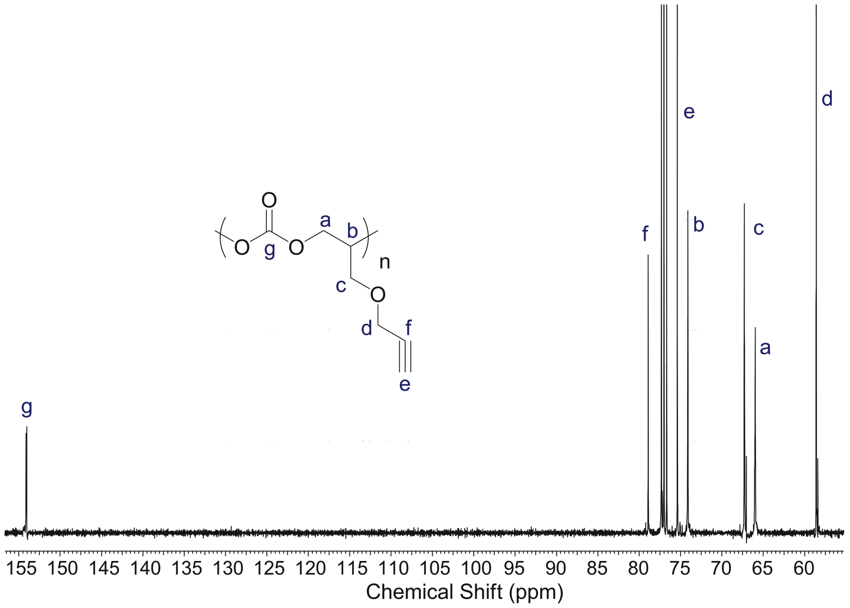

Figure S3. ^{13}C NMR spectrum of poly(glycidyl propargyl ether carbonate), Table 1, # 1.

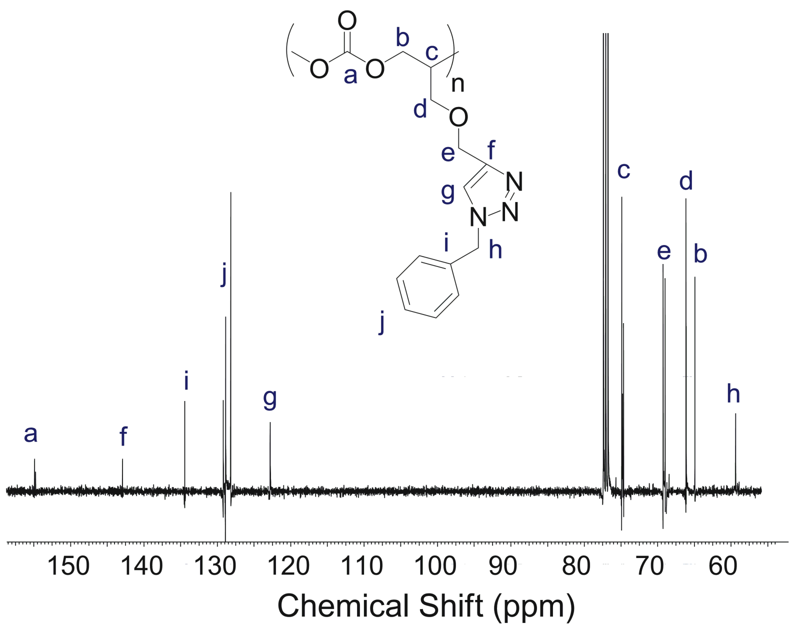

Figure S4. ^{13}C NMR spectrum of benzyl azide-functionalized poly(glycidyl propargyl ether carbonate).

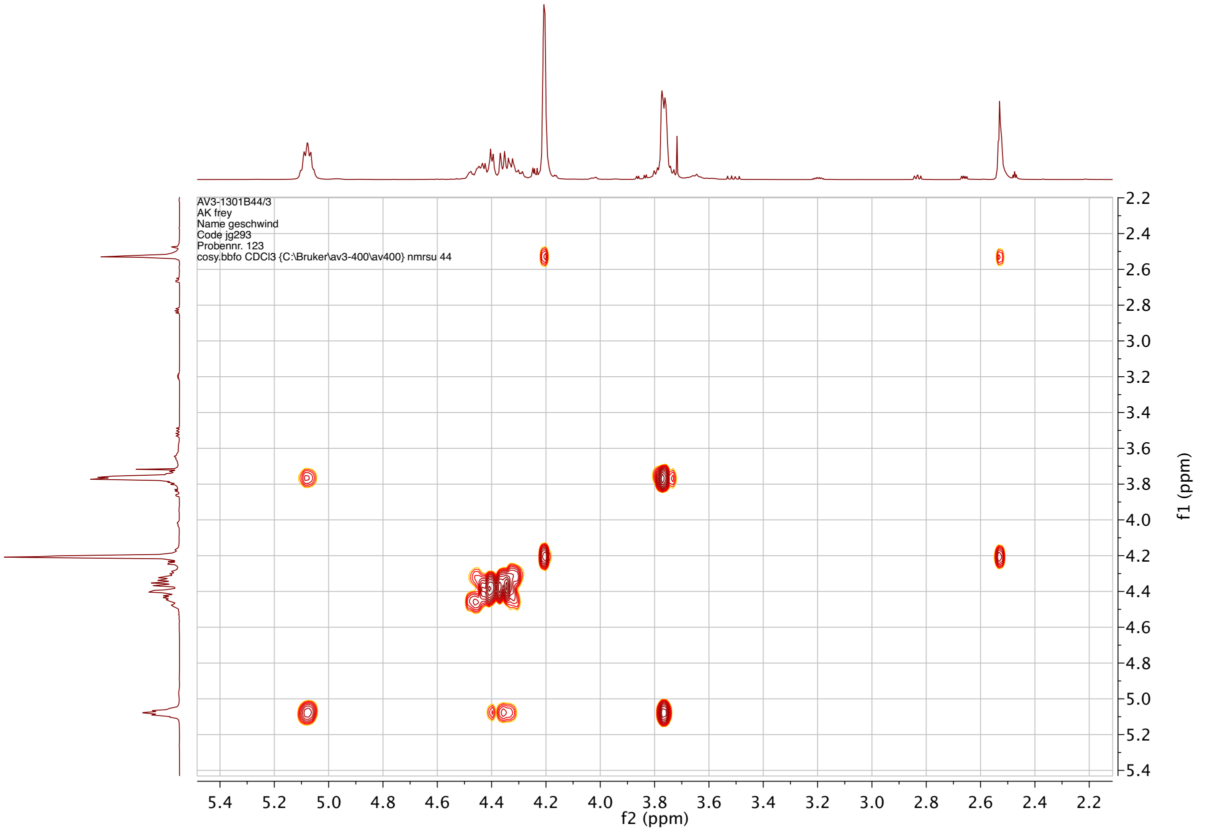

Figure S5. COSY 2D NMR spectrum of poly(glycidyl propargyl ether carbonate)

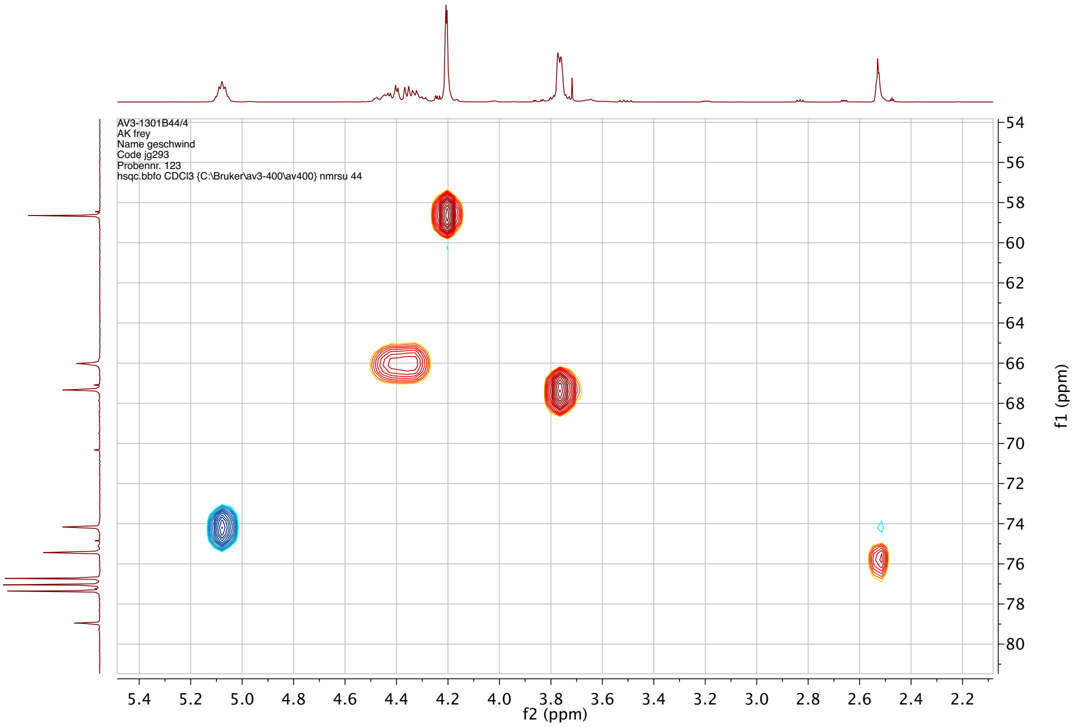

Figure S6. HSQC 2D NMR spectrum of poly(glycidyl propargyl ether carbonate).

SEC Results

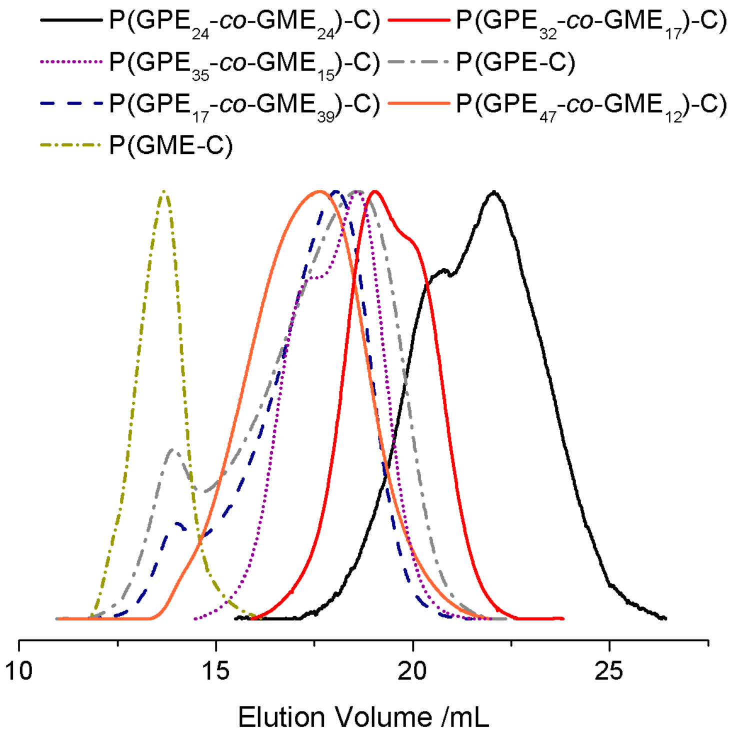

Figure S7. SEC results for all copolymers prepared.

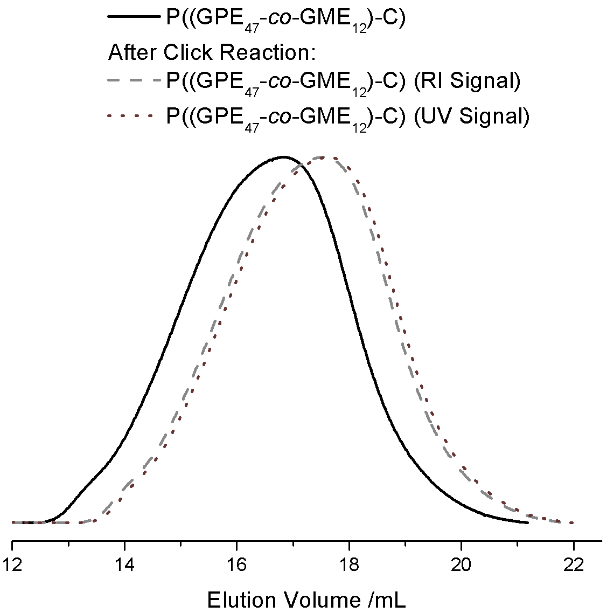

Figure S8. SEC results for benzyl azide-functionalized poly(glycidyl propargyl ether carbonate).

DSC Results

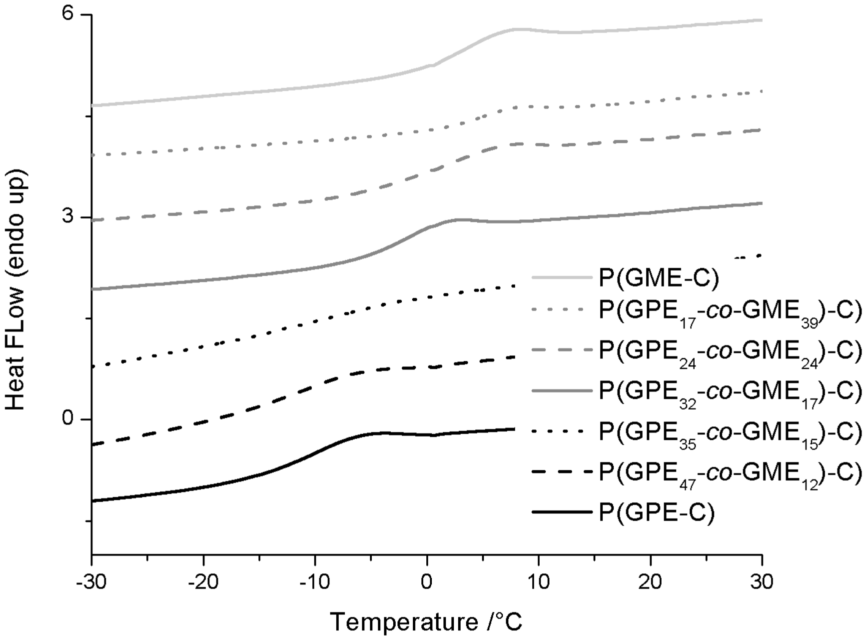

Figure S9. DSC results for all copolymers prepared.

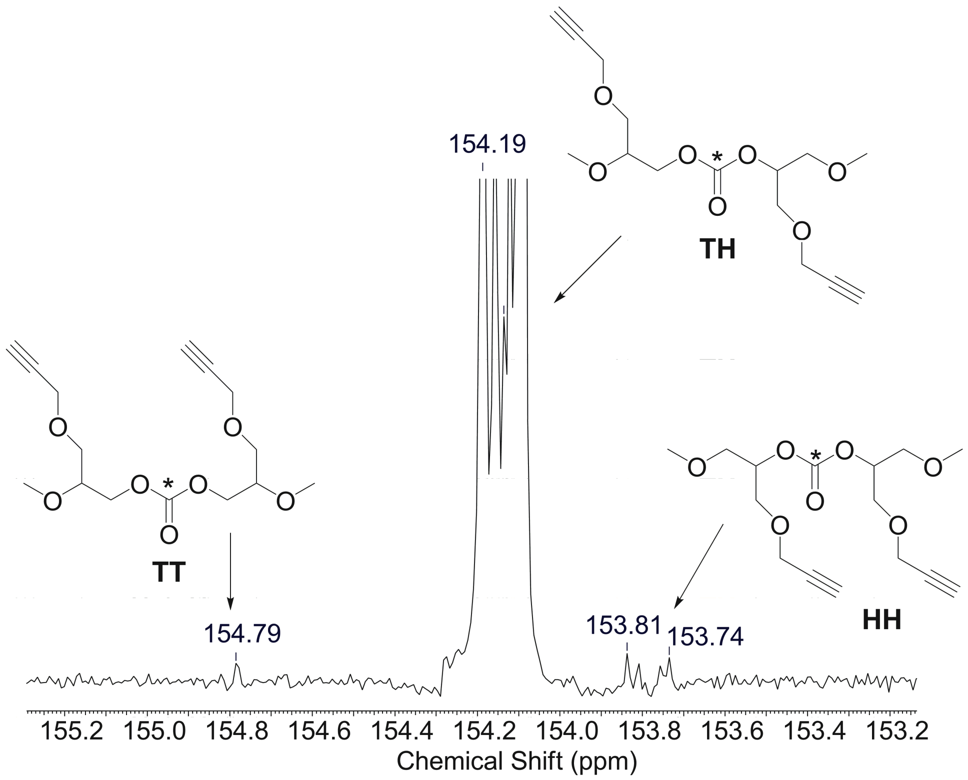

Figure S10. ^{13}C NMR spectrum of poly(glycidyl propargyl ether carbonate) in $CDCl_3$. Tail-to-tail (TT), head-to-head (HH) and the desired head-to-tail (TH) linkages are shown.

3.5. Reversible Functionalization of Aliphatic Polycarbonates Prepared from Carbon Dioxide and Furfuryl Glycidyl Ether

Jeannette Hilf [1,2], Jeffrey Poon[1], Christian Moers[1,2] and Holger Frey [1,*]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg 10-14, Johannes Gutenberg-University Mainz, D-55128 Mainz, Germany

[2]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

Keywords: Polycarbonate, CO_2, Epoxides, functional groups, Diels Alder

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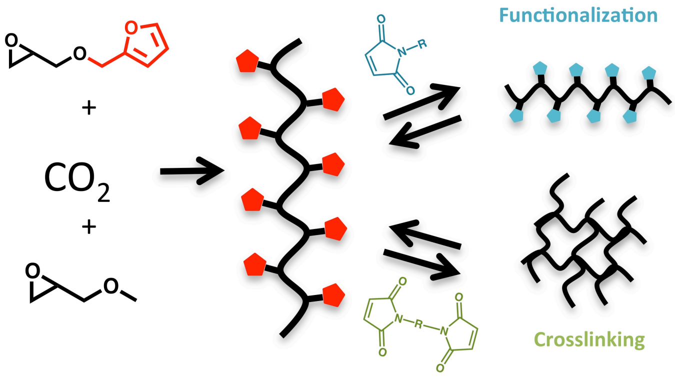


Abstract

Well-defined poly((glycidyl methyl ether)-*co*-(furfuryl glycidyl ether) carbonate) (P((GME-*co*-FGE)C)) copolymers with varying furfuryl glycidyl ether (FGE) content in the range of 26 to 100% have been prepared. The polymers have been characterized by size exclusion chromatography (SEC), ^{1}H NMR spectroscopy and differential scanning calorimetry. Most furfuryl functional samples exhibit monomodal molecular weight distributions with PDIs between 1.16 and 1.43 and molecular weights (M_n) between 3300 and 4100 g/mol. Thermal properties reflect the amorphous structure of the polymers. Functionalization and crosslinking was performed via Diels Alder chemistry, using maleimide derivatives. This transformation was thermally reversible at 110°C.

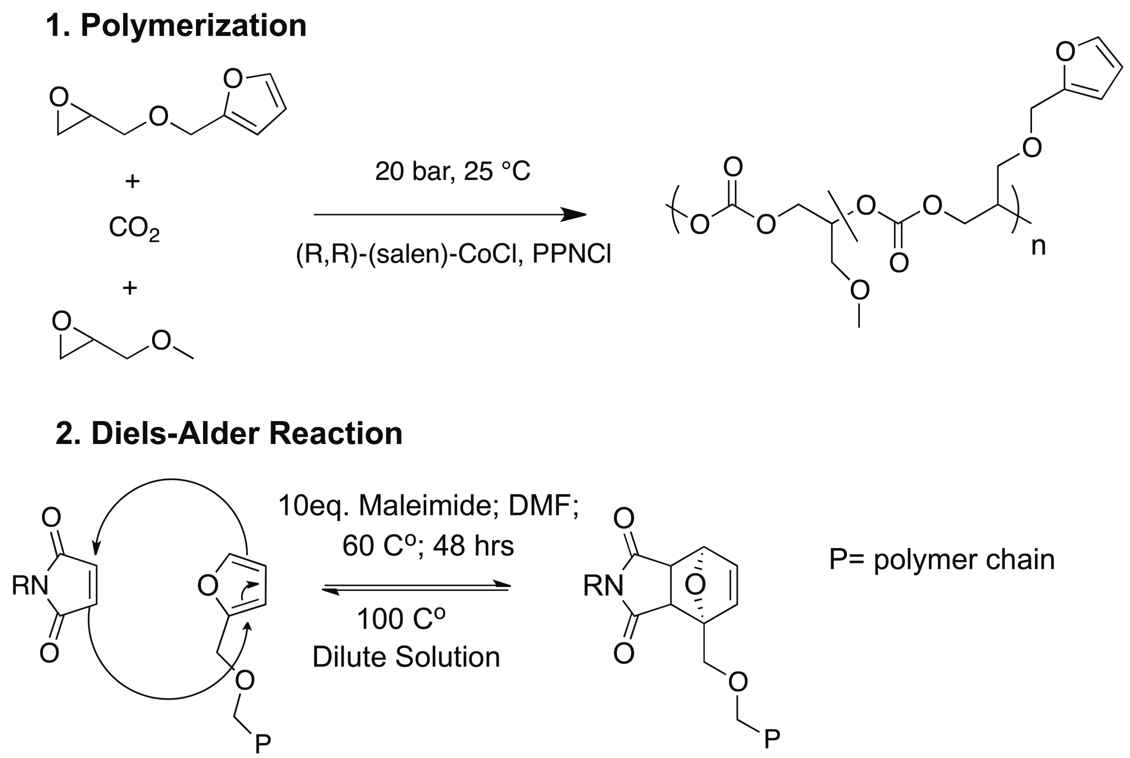
Introduction

Carbon dioxide (CO_2) is an attractive carbon source for materials synthesis with respect to resource utilization, as it is non toxic, renewable, and readily available in large quantities and high purity.[1–4] The alternating copolymerization of epoxides with CO_2 , which was first reported by Inoue and coworkers in 1960s,[5] has been considered as one of the most promising processes for its utilization. In the past four decades, a variety of zinc or cobalt based catalyst systems for this copolymerization have been developed.[4,6–11]

Mostly propylene oxide and cyclohexene oxide are used as epoxide monomers for the synthesis of novel aliphatic polycarbonates (APC). The materials are promising for applications, such as ceramic binders, adhesives, coatings and packaging materials as well as in biomedical applications, since they are potentially biodegradable into nontoxic compounds.[12] Increasing demand for more versatile biomaterials has also revived the interest in aliphatic polycarbonates for biomedical applications,[13,14] for which degradability, low glass transition temperature and elasticity of APC's, previously perceived as their major drawbacks, have turned into an advantage. However, a current detriment for several applications of such polycarbonates is their lack of functional groups along the PC backbone. Functional APCs can be prepared via two approaches, on the one hand the post-polymerization modification of a polymer scaffold containing reactive groups and on the other hand via the synthesis and polymerization of specifically designed functional monomers. They are usually synthesized by ring opening polymerization (ROP) of six membered cyclic carbonates, and the respective monomers have to be prepared in a multistep procedure.[12,15–24] An innovative new pathway for their synthesis is the preparation by copolymerization of carbon dioxide with functional epoxides. A prominent group of functional epoxides are glycidyl ethers, which have recently been used for the synthesis of several novel functional polycarbonate derivatives.[13,25,26] This strategy has been employed, e.g., for poly(1,2-glycerol carbonate) and poly(isopropylidene(glyceryl glycidyl ether carbonate) copolymers.[13,14,26,27]

An additional possibility for a (reversible) post-polymerization functionalization is created by the introduction of furfuryl groups, which can also be produced from renewable ressources.[28,29] Kavita et al. used furfuryl methacrylate as a comonomer in the ATRP of methacrylates[30] and Schubert et al. recently prepared poly(furfuryl glycidyl ether) by living anionic polymerization**.**[31] After polymerization, the furfuryl groups could be used in a subsequent Diels-Alder reaction for, e.g., cross-linking and network formation.[32] Further heating above a certain temperature induces the retro-Diels-Alder reaction, resulting in the cleavage of the network junctions. Subsequent cooling restores the network. The process was shown to be fully reversible for polyether materials.[31]

We report the synthesis of well-defined poly(furfuryl glycidyl ether carbonate) P(FGE C) homopolymers and the corresponding poly((glycidyl methyl ether)-*co*-(furfuryl glycidyl ether) carbonate) P((FGE-co-GME) C) random copolymers via copolymerization of furfuryl glycidyl ether, glycidyl methyl ether and carbon dioxide (Scheme 1). The copolymers can be functionalized and crosslinked reversibly with a variety of different maleimide derivatives using a click-like [4+2] cycloaddition transformation.[33]



Scheme 1. Synthesis of the P(FGE-*co*-GME C) and functionalization via Diels-Alder Chemistry.

Experimental Section

Synthesis of (R,R)-(salcy)-CoCl. (R,R)-(salcy)-CoCl was prepared as described by Jacobsen *et al.*[34]

Polymerization Procedure (Table 1, sample 4): The copolymerization of CO_2, glycidyl methyl ether (GME) and furfuryl glycidyl ether (FGE) was performed in a 50 mL autoclave equipped with a magnetic stirrer and a pressure indicator. A typical copolymerization was performed as follows: (R,R)-(salcy)Co(III)-Cl (18 mg, 28.8l mol), PPNCl (16 mg, 28.8l mol), GME (0.8 mL, 9 mmol), and FGE (3 mL, 22 mmol) were introduced into 100 mL autoclave under argon atmosphere. The autoclave was pressurized to 40 bar CO_2 and was left to stir at room temperature for 18 h. Subsequently, the reactor was vented and the polymerization mixture was dissolved in chloroform (5 mL), quenched with 5% HCl solution in methanol (0.2 mL) and transferred to a dialysis tube. After dialysis against chloroform for two days (MWCO 1000 g/mol) the product was precipitated into methanol (50 mL). The polymer was collected and dried *in vacuo*. Yield 95 % ^1H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) = 7.39 (CH-O furfuryl), 6.32 (CH furfuryl), 5.01 (methine polymer backbone), 4.46-4.21 (CH_2 polymer backbone and

CH_2-furfuryl), 3.65-3.58 (CH_2-OMe and CH_2-O-furfuryl) and 3.35 (CH_3)

Monomer synthesis and Diels-Alder reactions are described in the Supporting Information.

Results and Discussion

Copolymerization of epoxides and carbon dioxide represents a facile strategy for the introduction of functional groups into polycarbonate-based materials, thus enabling post-polymerization functionalization reactions.[25] Furfuryl glycidyl ether (FGE) represents a promising monomer structure for this reaction and subsequent post-polymerization functionalization via the pendant furan ring by, for example, Diels-Alder reactions. The furan/maleimide Diels-Alder reaction is regarded as a versatile click-unclick tool in macromolecular synthesis.[33] FGE was synthesized in one step from epichlorohydrin and furfuryl alcohol employing phase transfer catalysis (Supporting Information). The synthetic strategy developed to obtain the furfuryl containing aliphatic polycarbonate structures is shown in **Scheme 1**.

Table 1. Overview of the Characterization Data for All Copolymer Samples Prepared

#	Sample	%FGE (calc)	%FGE (NMR)[a]	M_n g/mol (SEC)[b]	PDI (SEC)	T_g °C[c]
1	$P(FGE\ C)_{21}$	100	100	4100	1.16	-24.7
2	$P((FGE_{16}\text{-}co\text{-}GME_{2})\ C)$	91	86	3300	1.43	-22.9
3	$P((FGE_{19}\text{-}co\text{-}GME_{5})\ C)$	80	80	4300	1.29	-21.4
4	$P((FGE_{14}\text{-}co\text{-}GME_{6})\ C)$	71	72	3500	1.24	-19.7
5	$P((FGE_{13}\text{-}co\text{-}GME_{7})\ C)$	62	65	3400	1.43	-16.7
6	$P((FGE_{10}\text{-}co\text{-}GME_{10})\ C)$	50	51	3300	1.23	-10.5
7	$P((FGE_{9}\text{-}co\text{-}GME_{12})\ C)$	40	43	3500	1.26	-6.0
8	$P((FGE_{7}\text{-}co\text{-}GME_{21})\ C)$	25	26	4100	1.31	-2.4

[a] FGE Comonomer content determined by ^1H NMR spectroscopy [b)]Determined by SEC calibrated with a PEG standard in DMF at 40 °C, [c)]Glass transition temperature (DSC)

The furfuryl glycidyl ether content in the copolymers was varied between 25 and 100% to adjust the number of functional groups in the resulting materials. Glycidyl methyl ether was used as a comonomer because of the structural similarity to FGE, enabling random copolymerization. All polymerizations were carried out under identical reaction conditions, i.e., solvent-free at room temperature and 40 bar CO_2 pressure with the common (R,R)-(salcy)CoCl catalyst and bis(triphenylphosphine(iminium chloride) (PPNCl) as a cocatalyst.[34]

Incorporation of carbon dioxide into the polymer and formation of the poly(propylene carbonate) was confirmed by IR as well as NMR spectroscopy. A single carbonate band at 1755 cm^{-1} was detected in FTIR spectra, which can be clearly assigned to the carbonyl group of the linear carbonate. It is important to mention that absence of resonances at 1790 cm^{-1} proves the crude reaction mixture to be free of cyclic carbonates. **Table 1** summarizes the results with respect to molecular weights, molecular weight distributions as well as thermal properties of the materials prepared.

All resulting copolymers were characterized by ^1H NMR spectroscopy with respect to their composition. Agreement of the FGE fraction in the copolymers with the composition of the epoxide monomer feed is confirmed by proton NMR spectroscopy by comparing the polycarbonate methine backbone signals a and b ($\delta = 5.01$), which were normalized to 1, to the furan group signals f and g at $\delta = 7.45$ and $\delta = 6.38$ ppm, respectively. All other side chain signals (c-e) can be found between $\delta = 3.29$ and 4.58 ppm (Figure 1). No FGE/GME ether structures without CO_2 incorporation can be detected in the ^1H NMR spectra. If present, a polyether backbone would generate additional resonances at around $\delta = 3.5$ ppm. ^{13}C NMR spectroscopy and 2D NMR spectroscopy also confirmed incorporation of FGE, GME and CO_2 into the copolymer and the typical carbonate resonance at $\delta = 154$ ppm can clearly be detected (Figure **S2-S4**).

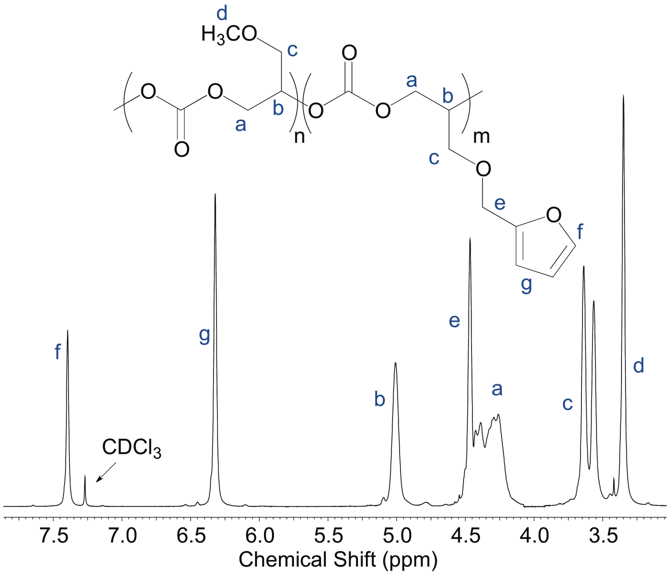


Figure 1. Typical ^{1}H NMR spectrum of a P((FGE-*co*-GME) C) copolymer (Table 1, sample 6) in CDCl$_3$.

Size exclusion chromatography (SEC) shows narrow molecular weight distributions with polydispersities below 1.43 for all samples. Molecular weights were in the range of 3300 to 4100 g/mol as expected (Figure 2 and Supporting Information). Higher molecular weights can also be obtained. In some cases bimodal molecular weight distributions were observed, which is a typical phenomenon in the copolymerization of carbon dioxide with epoxides, as already described in other works.[8,10,35]

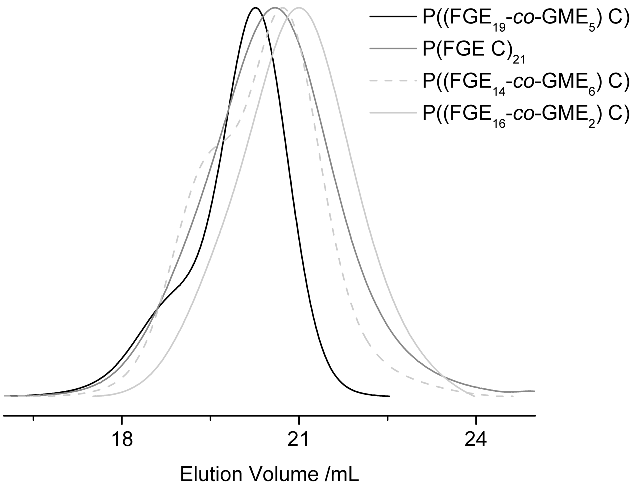


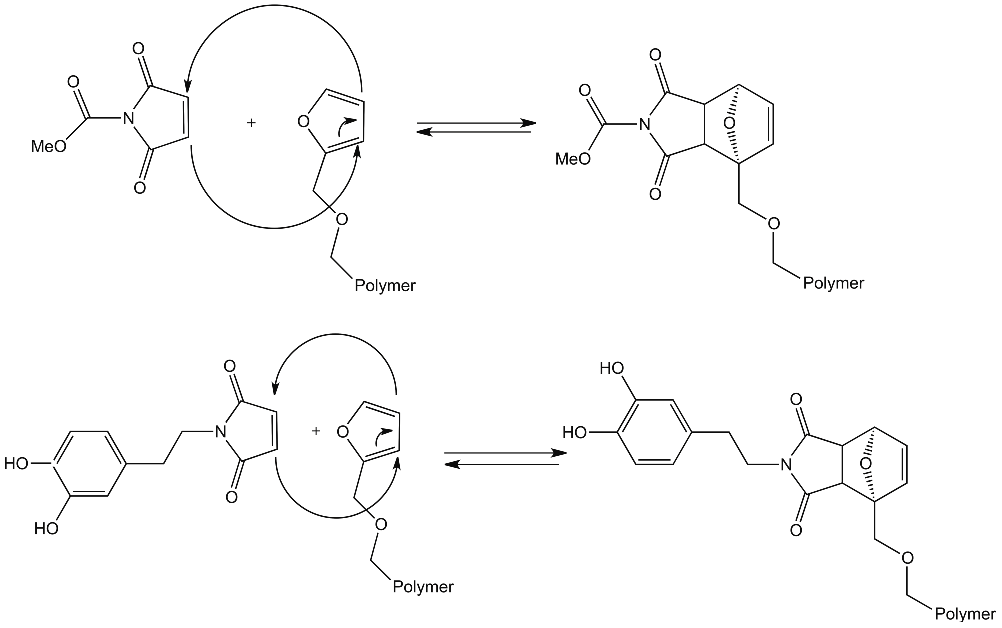
Figure 2. Representative SEC results of selected polycarbonate samples. (Table 1, Sample 1,2 and 4)

Thermal Properties.

The thermal characteristics studied by differential scanning calorimetry (DSC) are also listed in **Table 1** (DSC diagrams see Figure S15). All samples were amorphous and exhibited glass transition temperatures (T_g) between those of the two homopolymers (-24.7 °C for P(FGE C) and 1.7 °C for P(GME C)).[36] The T_g of the copolymers increases from the T_g of the P(FGE C) homopolymer (-24.7 °C) to -2.4 °C for P((FGE$_7$-*co*-GME$_{21}$) C). Generally, the T_gs of the polymers showed a slight increase with increasing GME/FGE-ratios. This result illustrates how the inherent flexibility of the polymer backbone can become manifest, if the side chains are sufficiently flexible to allow for facile internal reorientational motions, as also described in literature.[37] Furthermore, all P((FGE-*co*-GME) C) copolymers were obtained as clear, honey-like materials at room temperature that were soluble in acetone, chlorinated media, THF and aromatic solvents, and insoluble in water, lower alcohols and diethyl ether.

Diels-Alder Functionalization and Crosslinking

Scheme 2. Reversible Functionalization of P(FGE C) copolymers with various dienophiles.



Post-polymerization modification of the pending furan groups provides access to a variety of functional PCs. In recent years the transformation of furfuryl-functional polymers by Diels-Alder reactions has been studied intensively by several groups.[31,38] Utilization of this highly efficient reaction has been widespread due to the high specificity, near-quantitative yields, and near-perfect fidelity in the presence of most functional groups. Maleimide, N-(methoxycarbonyl)maleimide and 1-(3,4-dihydroxyphenyl)-1H-pyrrol-2,5-dione (dopamine maleimide) were chosen as suitable compounds (dienophiles) for modification of the multifunctional PCs. Reactions were performed (by) dissolving the relevant dienophile as well as the polymer in a minimal amount of DMF and heating it to 60 °C for 18 h. The resulting ^{1}H NMR spectra of the functionalized polymers are displayed in Figure 3 and Figure S11 and S12. Complete functionalization is obtained. The attachment of the dienophiles to the polymer backbone can also be followed by SEC characterization, as a shift to higher molecular weight after the [4+2] cycloaddition reaction is observed (Figure S9).

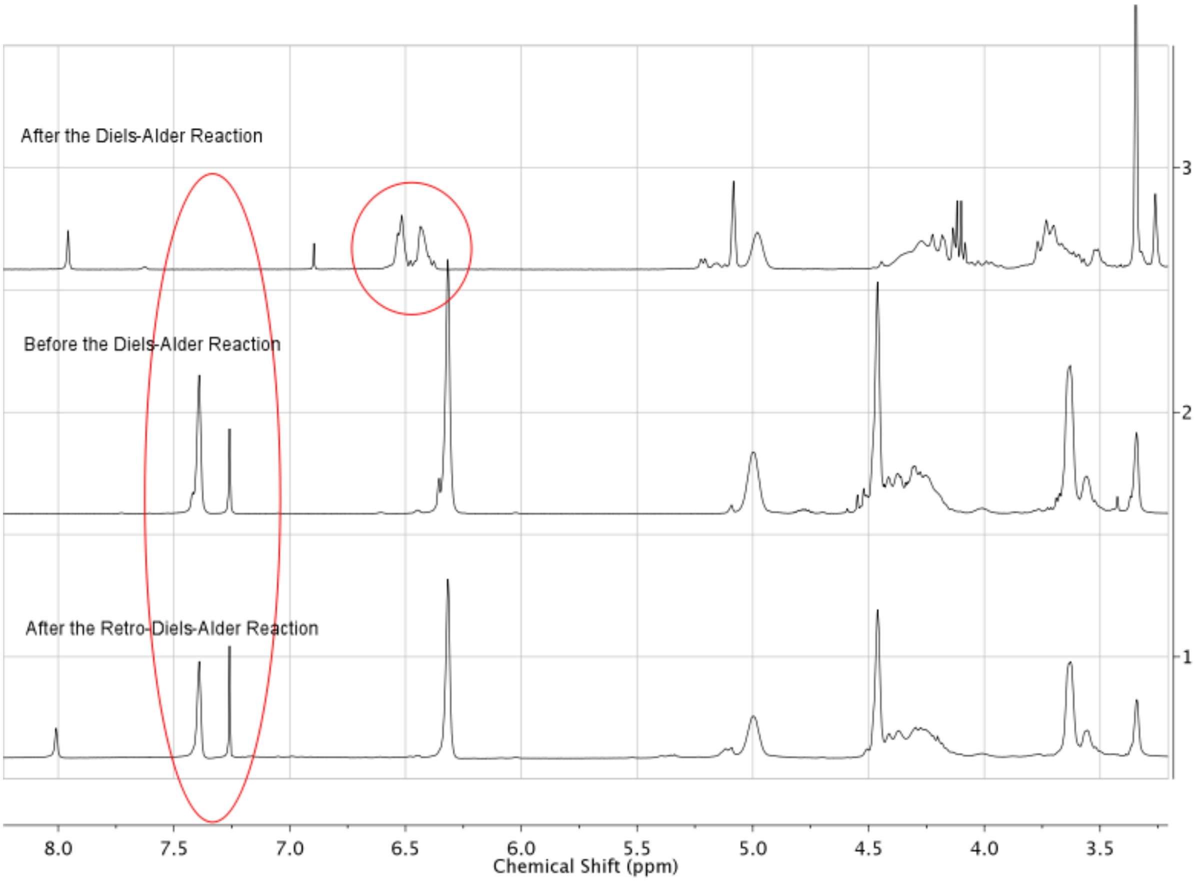


Figure 3. ^{1}H NMR spectra of the Diels-Alder reaction and retro Diels-Alder reaction with maleimide. (Table 1, sample 5)

The retro-Diels-Alder reaction was carried out in dilute DMF solution at 110 °C. After 18 h the reaction was completed without any degradation of the polycarbonate backbone, as evidenced by SEC. The cleaved dienophile was fully removed via dialysis in chloroform. ^{1}H

NMR spectroscopy reveals that the retro Diels-Alder reaction is complete, which is also demonstrated in Figure 3. Similar results were obtained for all other dienophiles.

Reversible crosslinking of the prepared polymers was achieved by a [4+2] cycloaddition reaction as well. For this purpose, P(FGE C) homopolymer (Table 1, sample 1) and a bisfunctional crosslinker, 1-1'-(methylenedi-4,1-phenylene)bismaleimide (BMA), were dissolved in DMF at a concentration of 30 mg/mL, employing a molar ratio maleimide groups/furfuryl groups of 0.8/1. The mixture was heated to 60 °C for several hours (characterization data see Supp. Inf.). After 18 h, crosslinking was complete, and the material was not soluble anymore, as an organo-gel had formed. When heating the reaction mixture to 110 °C for 2h, followed by rapid quenching in liquid nitrogen, the retro Diels-Alder reaction takes place and the polymer becomes fully soluble again (Figure S13).

Conclusions

In this work we have demonstrated the facile one step synthesis of a novel type of functional, linear aliphatic polycarbonate copolymers from the commercially available monomers CO_2, GME and furfuryl glycidyl ether. To the best of our knowledge such stable poly(carbonate) structures with furan side chains have not yet been reported directly from carbon dioxide and epoxides before. Polymers with 25-100% furfuryl glycidyl ether (FGE) and molecular weights between 3300 and 4100 g/mol were obtained under mild reaction conditions (40 bar CO_2, RT, 18 h). Again, the catalytic copolymerization of glycidyl ethers and CO_2 represents an interesting and highly modular alternative to the widely used ring-opening strategy that requires six membered cyclic carbonates to generate functional aliphatic polycarbonates.

Using the prepared polymers as a versatile platform, the furan side chains have successfully been modified *via* efficient Diels-Alder reactions enabling the introduction of novel functionalities. Hitherto not described functionalization reactions for polycarbonates resulting for example in catechol moieties have been demonstrated, that cannot be introduced directly. The transformation via Diels-Alder reaction was further shown to be fully reversible without degradation of the polycarbonate backbone.

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Supporting Information for: Reversible Functionalization of Aliphatic Polycarbonates Prepared from Carbon Dioxide and Furfuryl Glycidyl Ether

Jeannette Hilf[1,2], Jeffrey Poon,[1] Christian Moers[1,2] and Holger Frey[*1]

1. Materials and Instrumentation

Reagents. Furfuryl alcohol, epichlorohydrin (99%), sodium hydroxide as well as benzene were purchased from Aldrich. Deuterated chloroform-*d*$_1$ and DMSO-*d*$_6$ were purchased from Deutero GmbH. Carbon dioxide (99.995%) was purchased from Westfalen AG and used as received. All other solvents and reagents were purchased from Acros Organics. Dialysis tube (MWCO 1000 g/mol) were also purchased from Aldrich.

NMR experiments. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer, operated at 300 and 75.4 MHz respectively, at 21°C and the chemical shifts are given in parts per million (ppm). All spectra were referenced to residual solvent signal.

Size exclusion chromatography. For size exclusion chromatography (SEC) measurements in DMF (containing 0.25 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column ($10^6/10^5/10^4$ g mol^{-1}), a UV (275 nm) and a RI detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service.

Differential Scanning Calorimetry. Differential Scanning Calorimetry (DSC) curves were recorded with a Perkin-Elmer DSC 7 CLN2 in the temperature range from – 50 to 50 °C at heating rates of 10 K min^{-1} under nitrogen.

IR-Spectroscopy. FT-IR spectra were recorded using a Thermo Scientific iS10 FT-IR spectrometer, equipped with a diamond ATR unit.

Monomer Synthesis. 99 mmol furfuryl alcohol were dissolved in 50 mL of benzene. 50 mL of 50% aqueous NaOH solution and 3,22g (10 mmol) tetrabutyl ammonium bromide (TBAB) were added. The mixture was cooled to ca. 10 °C and 18.35 g (200 mmol) of epichlorohydrin were slowly added *via* a syringe. The reaction was vigorously stirred at room temperature for 48 h, diluted with diethyl ether and washed three times with water, saturated $NaHCO_3$ and NaCl solution, and finally dried over $MgSO_4$. Diethyl ether and excess of epichlorohydrin were removed *in vacuo* and the crude product was distilled under reduced pressure (b.p. 110°C at 10-20 mbar, yield 60%). Purification via column chromatography (silica, diethyl ether: petroleum ether 5:3) results in higher yields (70-90%). ^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 7.39 (m, 1H, CH furfuryl), 6.32 (m, 2H, CH furfuryl), 4.49 (d, 2H, C-C*H*$_2$-O), 3.75 (m, 1H, CH_2-epoxide), 3.42 (m, 1H, CH_2-epoxide), 3.13 (t, 1H, CH epoxide), 2.75 (q, 1H, CH_2 epoxide), 2.58 (q, 1H, CH_2 epoxide).

Synthesis of (R,R)-(salcy)-CoCl. (R,R)-(salcy)-CoCl was prepared as described by Jacobsen et al.[1]

1. Step: Recrystallized (R,R)-(salen)Co^{II} (6.0 g, 9.9 mmol) and *p*- toluenesulfonic acid monohydrate (2.0 g, 10.5 mmol, 1.06 equiv) were added to a 250 mL round bottomed flask charged with a Teflon stir bar. Dichloromethane (100 mL) was added to the reaction mixture and stirred vigorously for a minimum of 30 min (open to the atmosphere at room temperature). The solvent was removed by rotary evaporation and the solid was further dried under reduced pressure. The resulting solid was suspended in pentane and filtered to afford green (salen)Co–OTs as the monohydrate (7.8 g, 99% yield).

^{1}H NMR (DMSO-d$_6$, 400 MHz, δ in ppm) 1.30 (s, 18H), 1.55–1.61 (m, 2H), 1.74 (s, 18H), 1.87-1.93 (m, 2H), 1.98–2.01 (m, 2H), 2.27 (s, 3H), 3.04–3.08 (m, 2H), 3.58–3.62 (m, 2H), 7.09 (d, J=8.0 Hz, 2H), 7.43–7.47 (m, 6H), 7.81 (s, 2H).

2.Step: Methylene chloride (200 mL) was added to a 500 mL separatory funnel. Tosylate catalyst (5.0 g) was added to the funnel and agitated until the solid completely dissolved. The organic layer was rinsed with saturated aqueous NaCl (3 x 200 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The solid was suspended in pentane and filtered to afford very dark green solid (3.16 g, 75-85% yield). IR (KBr, cm^{-1}) 2954, 2924, 2912, 2866, 1596, 1524, 1462, 1390, 1361, 1337,1312, 1269, 1251, 1200, 1176, 835, 783.

^{1}H NMR (DMSO-d_6, 400 MHz, δ in ppm): 1.31 (s, 18H), 1.54–1.66 (m, 2H), 1.74 (s, 18H), 1.85–1.99 (m, 2H), 1.99–2.10 (m, 2H), 3.03–3.12 (m, 2H), 3.58–3.68 (m, 2H), 7.46 (s, 2H), 7.50 (s, 2H), 7.82 (s, 2H).

Polymerization (Table 1, sample 4): The copolymerization of CO_2, glycidyl methyl ether (GME) and furfuryl glycidyl ether (FGE) was performed in a 50 mL autoclave equipped with a magnetic stirrer and a pressure indicator. The typical copolymerization procedure was as follows: (Salen)Co(III)-Cl (18 mg, 28.8l mol), PPNCl (16 mg, 28.8l mol), GME (0.8 mL, 9 mmol), and FGE (3 mL, 22 mmol) were introduced into 50 mL autoclave under a argon atmosphere. The autoclave was pressurized to 40 bar CO_2 and was left to stir at 30 °C for 18 h. The reactor was vented at 30 °C and the polymerization mixture was dissolved in chloroform (5 mL), quenched with 5% HCl solution in methanol (0.2 mL) and transferred to a dialysis tube. After dialysis against chloroform for two days (MWCO 1000 g/mol) the product was precipitated into methanol (50 mL). The polymer was collected and dried *in vacuo*. Yield 95 % ^{1}H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) = 7.39 (CH-O furfuryl), 6.32 (CH furfuryl), 5.01 (methine polymer backbone), 4.46-4.21 (CH_2 polymer backbone and CH_2-furfuryl), 3.65-3.58 (CH_2-OMe and CH_2-O-$_F$urfuryl) and 3.35 (CH_3)

Synthesis of Thermoreversible Diels-Alder (DA) Functionalized Polymer. This procedure is described for maleimide exemplarily, but was performed in the same way for all other maleimide derivatives. 100 mg P((FGE$_{16}$-co-GME$_2$) C) (Table 1, sample 2) and 400 mg maleimide were dissolved in 3 mL DMF and heated to 60 °C for two days. Subsequently, the product was precipitated in cold methanol purify the polymer and to remove excess of maleimide. The polymer was collected and dried *in vacuo*. NMR spectra of the coupled products can be found in Figure 3.

For the Retro-Diels-Alder reaction 50 mg of the previous sample were dissolved in 10 mL DMF and heated to 110 °C for 18 h. The reaction mixture was then dialyzed against chloroform to get rid of free maleimide and DMF. Finally the solvent was removed under reduced pressure and the final product was collected and dried *in vacuo.* NMR spectroscopy indicated a complete retro Diels-Alder Reaction.

Synthesis of *N*-(Methoxycarbonyl)maleimide:[2]Maleimide (2.0 g, 20 mmol, 1.0 equiv.) was dissolved in ethyl acetate (80 mL) in a 150 mL round-bottom flask, and the solution was cooled to approximately 0 °C. A solution of N-methyl morpholine, (2.00 mL, 1.85 g, 21.0 mmol, 1.10 equiv.) in ethyl acetate (10 mL) was added dropwise over 10 min. A solution of methyl chloroformate, (2.00 mL, 2.46 g, 20.0 mmol, 1.0 equiv.) in ethyl acetate (5.0 mL) was added dropwise, and the solution was allowed to reach room temperature while stirring for 1 h. The solution was diluted with ethyl acetate (100 mL) and washed with saturated aqueous sodium bicarbonate solution, water, and saturated sodium chloride solution, successively. The organic layer was separated, dried over $MgSO_4$, and filtered.

The supernatant was concentrated under reduced pressure to yield the product as a solid (2.6 g, 81 % yield). ^{1}H-NMR (300 MHz, ppm, $CDCl_3$): 6.88 (d, 2H, J = 0.6 Hz, -CH=CH-CO), 3.97 (s, 3H, $COOCH_3$). ^{13}C-NMR (75 MHz, ppm, $CDCl_3$): 165.5 (-CH=CH-C=O), 147.9 (-N-$COOCH_3$), 145.1 (-CH=CH-C=O), 54.1 (-$NCOOCH_3$).

Synthesis of 1-(3,4-Dihydroxyphenethyl)-1H-pyrrole-2,5-dione:[3] 1. Dopamine hydrochloride (1.00 g, 5.27 mmol) in 30 mL saturated $NaHCO_3$ solution was treated at 0 °C under stirring with *N*-methoxycarbonyl maleimide (0.817 g, 5.27 mmol). After 10 min the solution was diluted with 100 mL water and stirred at room temperature for 40 min. The solution was acidified to pH 1–2 with concentrated H_2SO_4 and extracted three times with 10 mL of ethyl acetate. The combined organic layers were dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (CH_2Cl_2/ MeOH 20 : 1) to give 1 as a yellow solid. Yield: 65%. ^{1}H NMR (300 MHz, CD_3OD, d): 6.74 (s, 2H, maleimide), 6.15–6.66 (m, 3H, Ar H), 3.60–3.67 (m, 2H, CH_2NH), 2.70 (t, 3J 1⁄4 7.1 Hz, 2H, CH_2Ar); ^{13}C NMR (75 MHz, CD_3OD, d): 34.72, 40.35, 116.23, 116.94, 121.03, 130.73, 134.50, 145.01, 146.31, 172.42.

2. Representative ^{1}H NMR, ^{13}C NMR and 2 D NMR spectra of P((FGE-co-GME) C) copolymers and their functionalization.

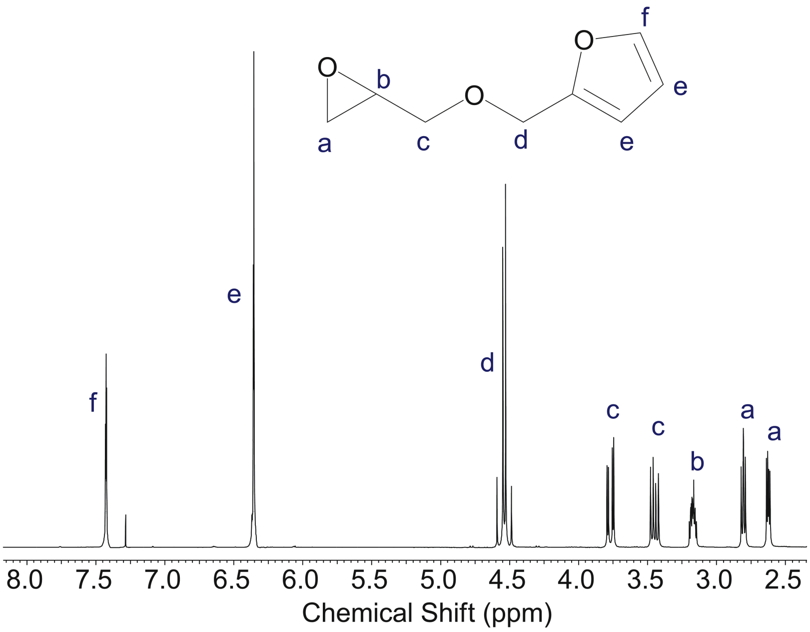

Figure S1. ^{1}H NMR spectrum of furfuryl glycidyl ether in $CDCl_3$

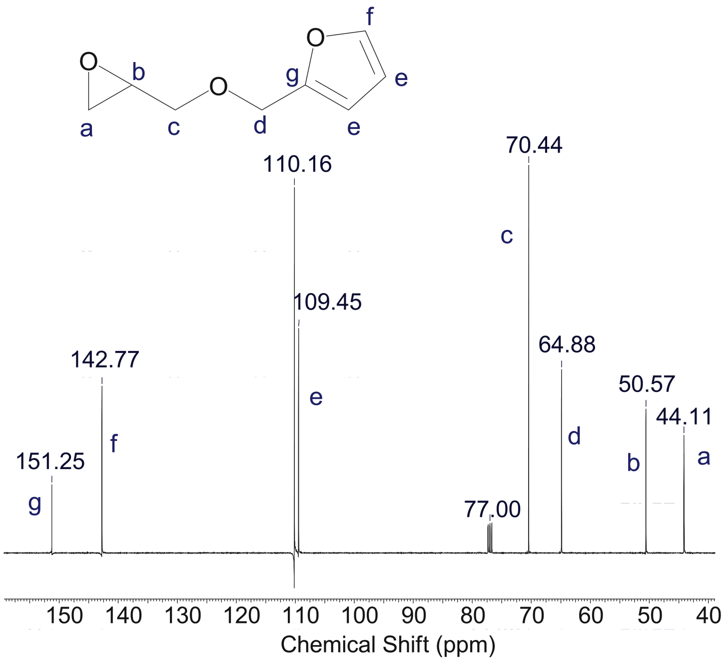

Figure S2. ^{13}C NMR spectrum of furfuryl glycidyl ether in $CDCl_3$

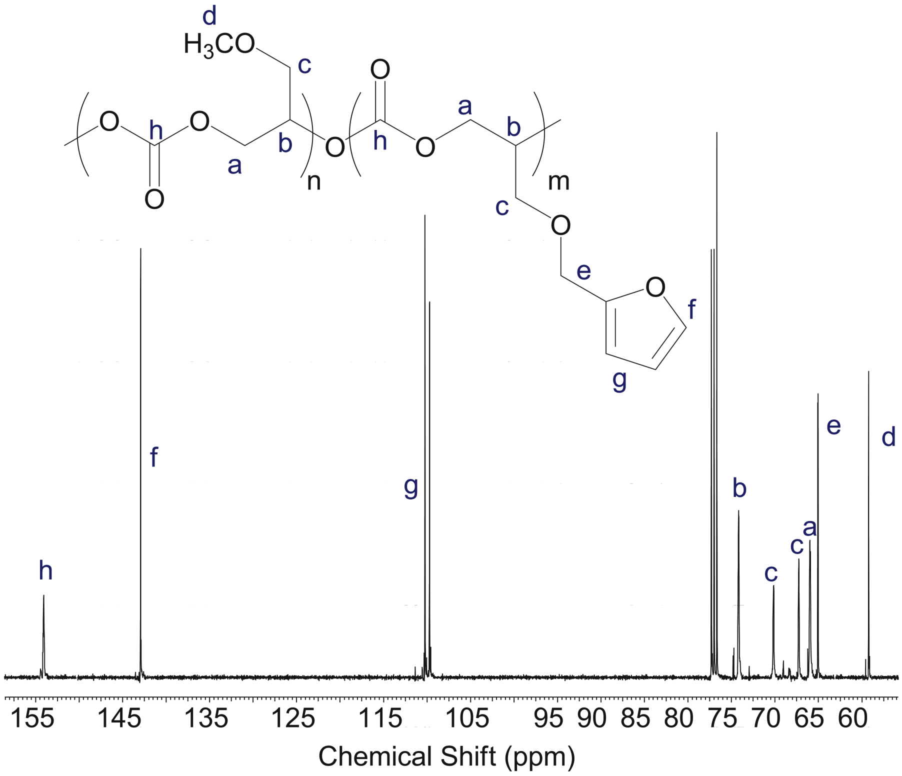

Figure S3. ^{1}H NMR spectrum of P((FGE$_{14}$-*co*-GME$_6$) C) (sample 4, Table 1) in $CDCl_3$

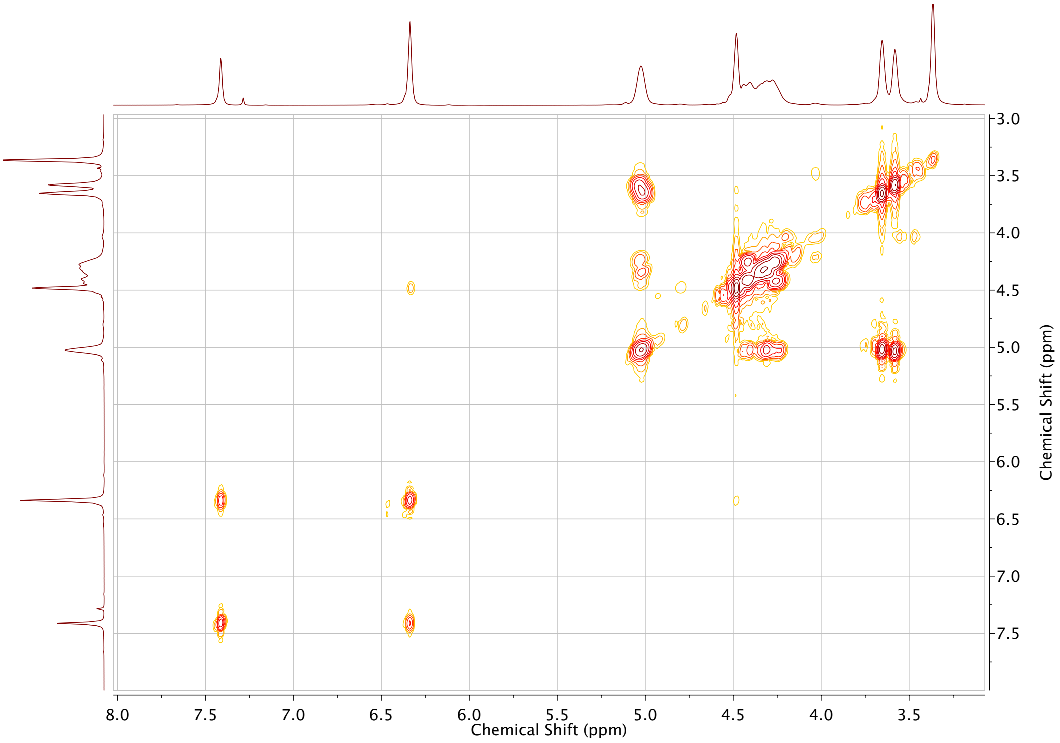

Figure S4. COSY spectrum of P((FGE$_{14}$-*co*-GME$_6$) C) (sample 4, Table 1) in $CDCl_3$

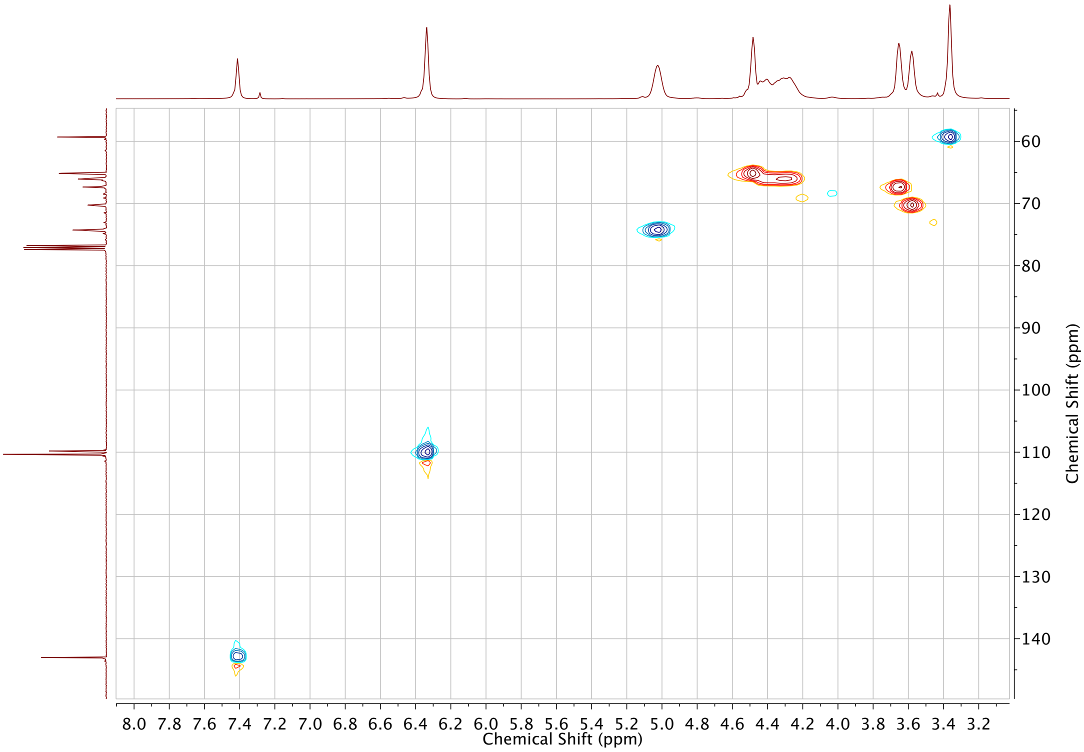

Figure S5. HSQC spectrum of P((FGE$_{14}$-*co*-GME$_6$) C) (sample 4, Table 1) in $CDCl_3$

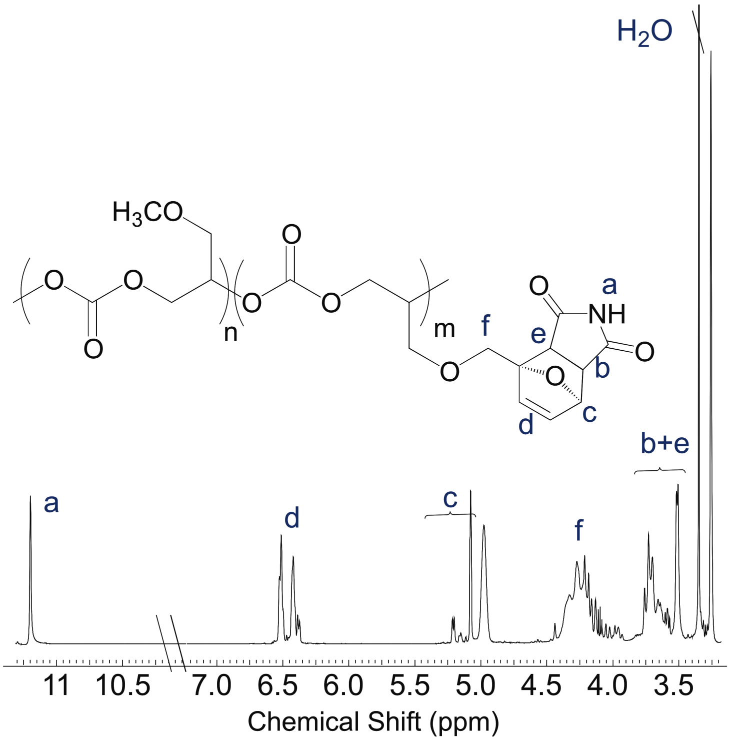

Figure S6. ^{1}H NMR spectrum of P((FGE$_{14}$-*co*-GME$_6$) C) (sample 4, Table 1) functionalized with maleimide in DMSO.

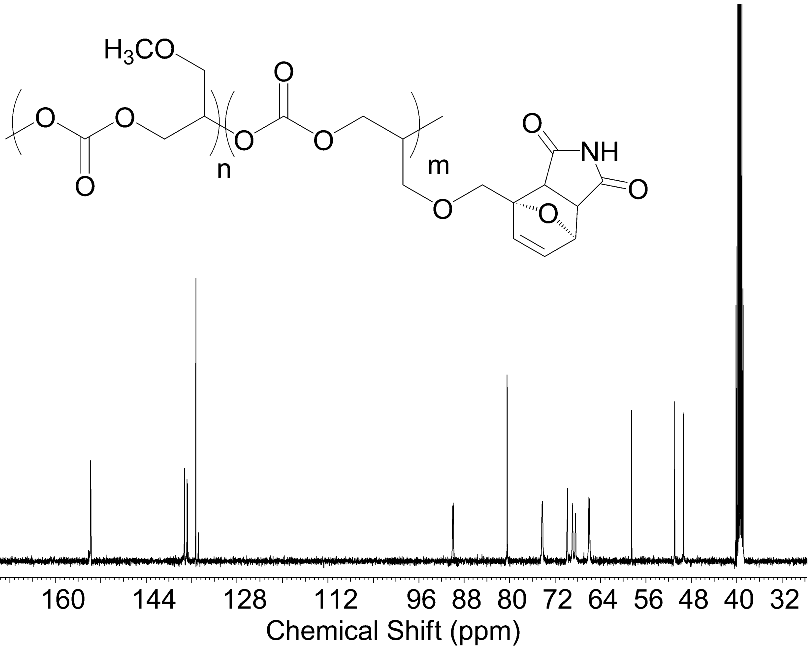

Figure S7. ^{13}C NMR spectrum of P((FGE$_{14}$-*co*-GME$_{6}$) C) (sample ?, Table 1) functionalized with maleimide in DMSO.

3. SEC results of the resulting polymers

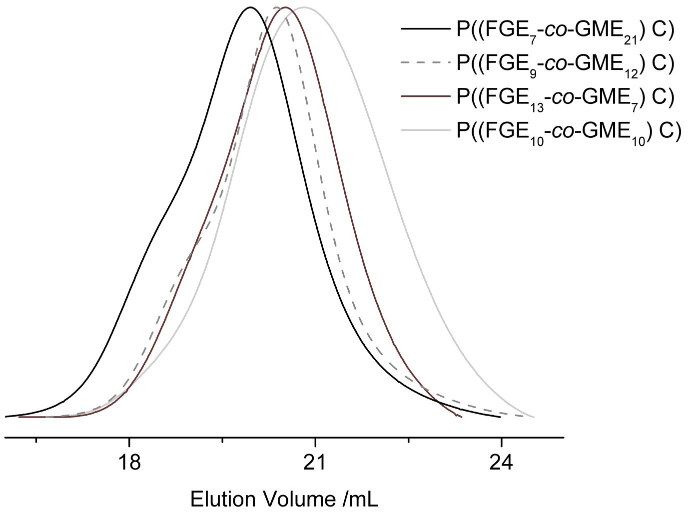

Figure S8. Representative SEC results of the selected polymers.

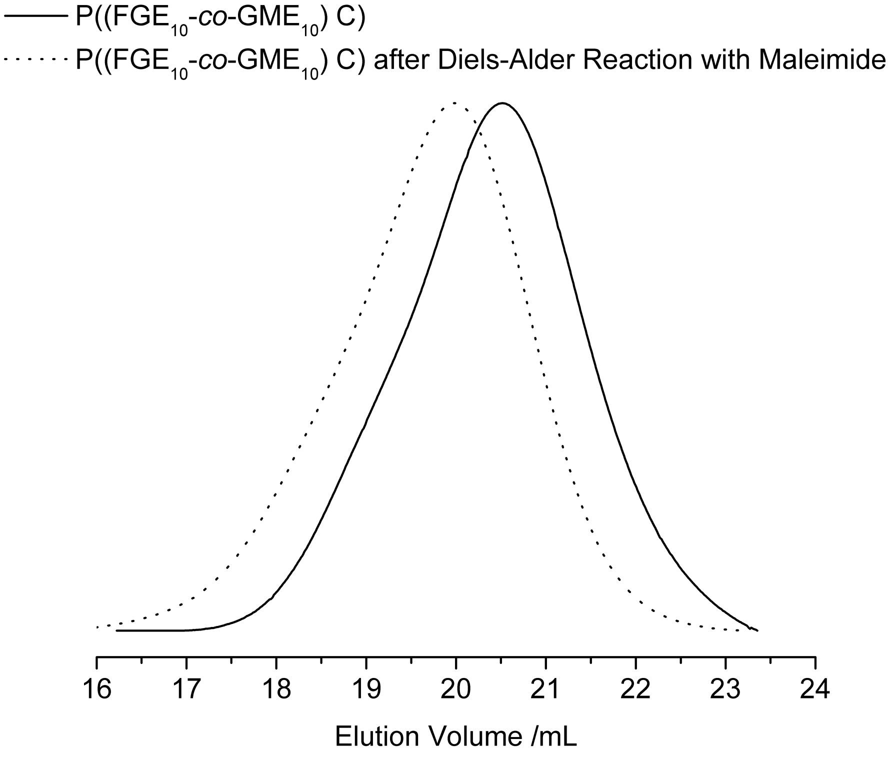

Figure S9. SEC results of the some functionalized polymers.

4. IR spectra of the resulting polymers

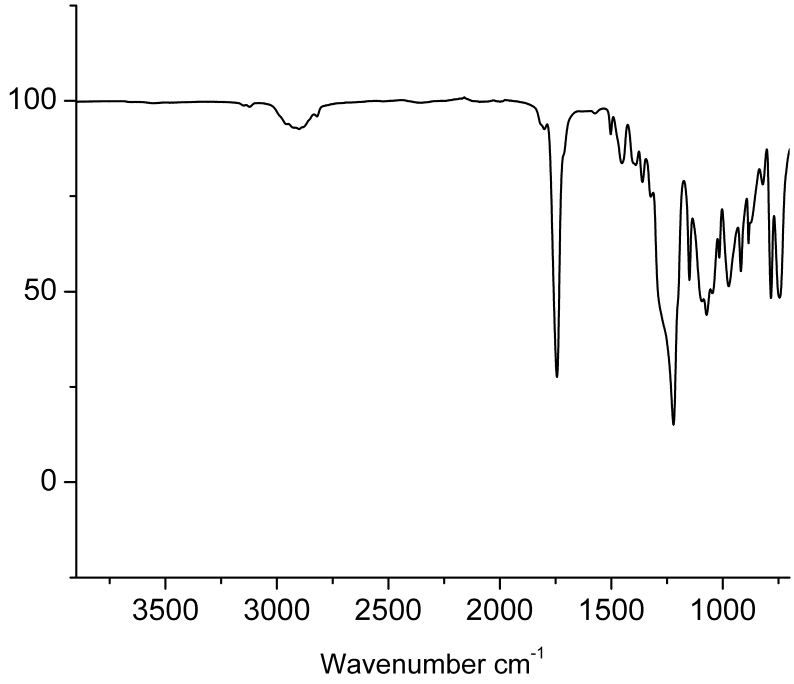

Figure S10. IR spectrum of the synthesized P(FGE C) copolymer (Table 1, sample 1).

5. Functionalization

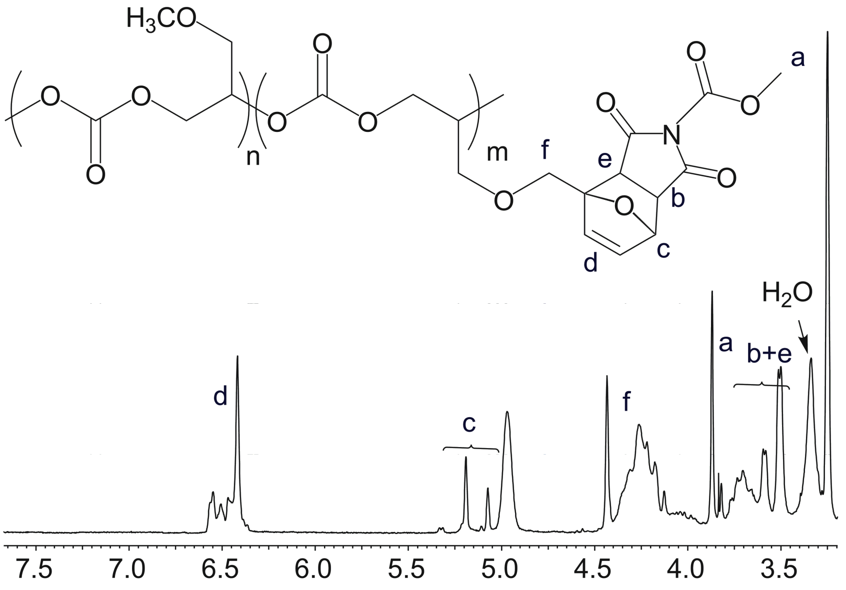

Figure S11. ^{1}H NMR spectrum of P((FGE$_{14}$-*co*-GME$_6$) C) (sample 4, Table 1) functionalized with *N*-(Methoxycarbonyl)maleimide in DMSO.

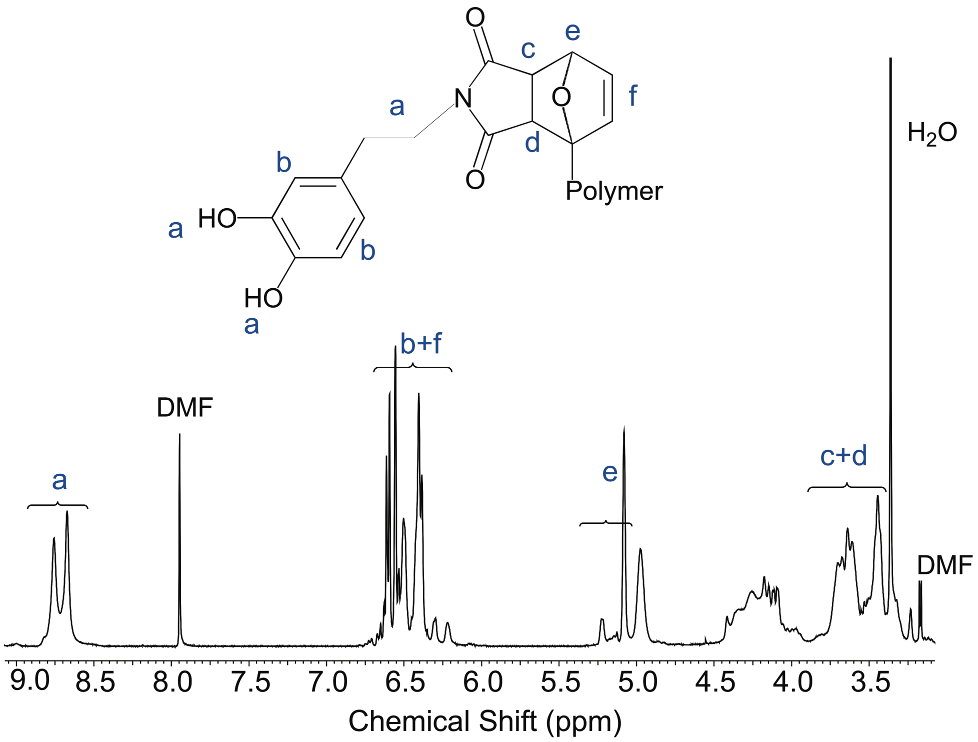

Figure S12. ^{1}H NMR spectrum of P((FGE$_{14}$-*co*-GME$_6$) C) (sample ?, Table 1) functionalized with 1-(3,4-Dihydroxyphenethyl)-1H-pyrrol-2,5-dione in DMSO.

P((FGE$_{14}$-*co*-GME$_6$) C) and crosslinker in DMF before DA Reaction
→**Liquid** solution

P((FGE$_{14}$-*co*-GME$_6$) C) and crosslinker in DMF after DA Reaction
→Polymer is **crosslinked**

P((FGE$_{14}$-*co*-GME$_6$) C) and crosslinker in DMF after Retro DA Reaction
→**Liquid** solution

Figure S13. ^{1}H NMR spectrum of P((FGE$_{14}$-*co*-GME$_6$) C) (sample 4, Table 1) functionalized with 1-1’-(methylenedi-4,1-phenylene)bismaleimide (BMA) in DMSO.

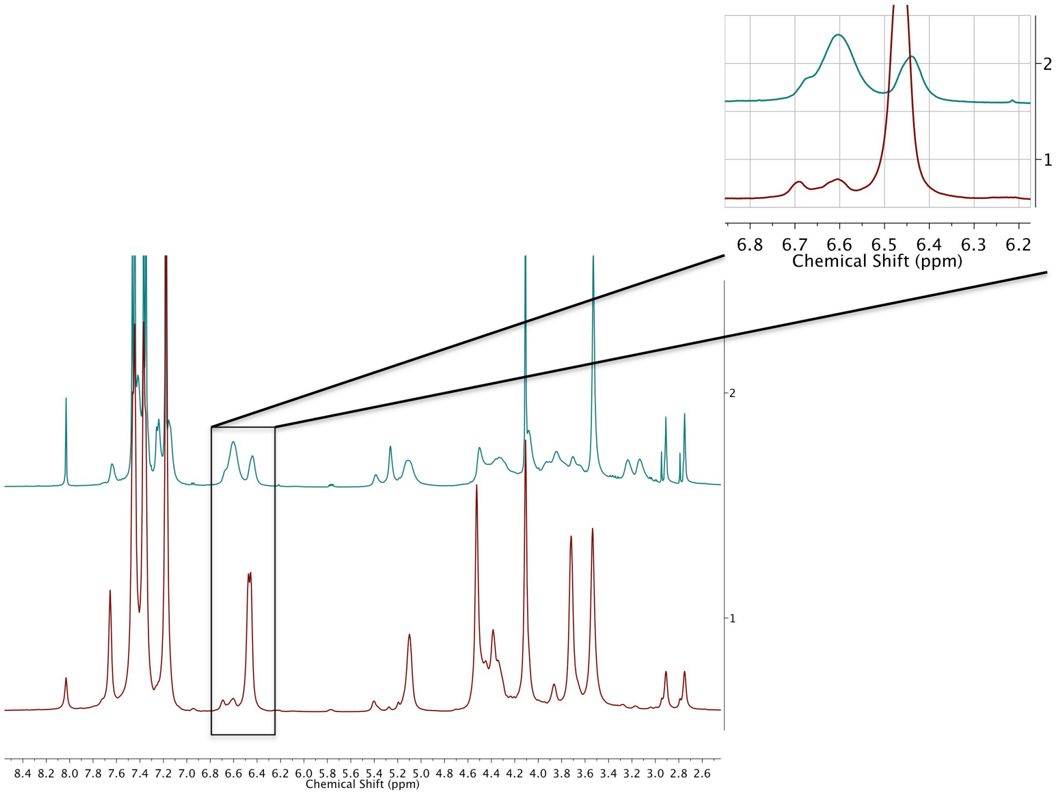

Figure S14. ^{1}H NMR spectrum of P((FGE$_{14}$-*co*-GME$_6$) C) (sample 4, Table 1) functionalized with 1-1’-(methylenedi-4,1-phenylene)bismaleimide (BMA) in DMSO.

6. DSC Results

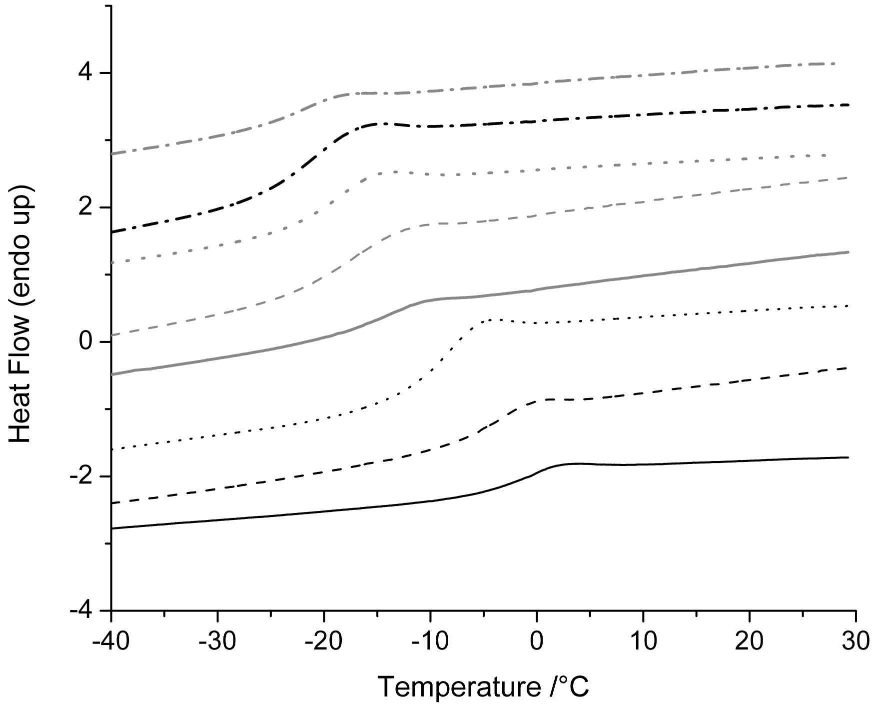

Figure S15. DSC Results of the series of functional polycarbonates

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Chapter 4: Functional Polycarbonates with Propylene Oxide-Derivatives

4.1. From CO_2-Based Multifunctional Poly(carbonate)s with Controlled Number of Functional Groups to Graft-Polymers

Jeannette Geschwind[1,†], Frederik Wurm[2] and Holger Frey[*1]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg 10-14, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany

[2]Max Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz

[†]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

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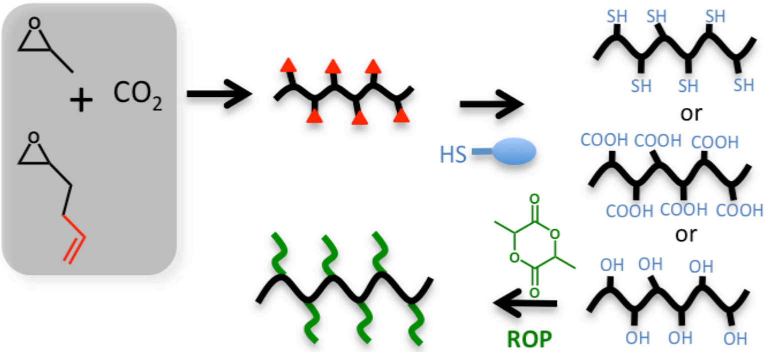


Abstract

Copolymerization of CO_2 and epoxides has been employed to generate functional polycarbonates. The introduction of reactive double bonds at a poly(propylene carbonate) (PPC) backbone has been realized by copolymerization of aliphatic alkene epoxides with propylene oxide (PO) and carbon dioxide (CO_2). A series of copolymers with random structure and varying comonomer content (3-22%) with molecular weights in the range of 22 000-34 000 g/mol has been synthesized and characterized with respect to their microstructure and thermal properties. The facile transformation of the double bonds was verified by a thiol-ene reaction, resulting in quantitative conversion of the double bonds. Polycarbonate derivatives with multiple functionalities have been prepared, providing suitable moieties for further grafting.

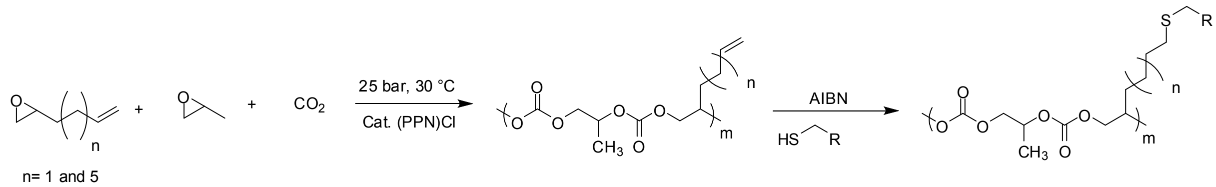
Introduction

With regard to the growing global emission of carbon dioxide, efficient conversion of CO_2 into organic materials has become a topic of intense research efforts. CO_2 as a direct building block for polycarbonates (PCs) is particularly interesting, since toxic reactants, such as phosgene may eventually be replaced. Since CO_2 is thermodynamically stable, it is difficult to apply it as a reactant directly, and the use of efficient catalysts is mandatory for its polymerization to poly(carbonates) (PC) by copolymerization with epoxides.[1-6] For this polymerization, a wide variety of catalytic systems have been developed, including dicarboxylic acid derivates of zinc,[1] double metal cyanide [2] complexes and cobalt salen complexes.[3,4–7,8] Other cobalt complexes have also been described.[9] Coates et al. reported that (R,R)-(salcy)-CoX complexes catalyze the alternating copolymerization of propylene oxide (PO) and CO_2 and that this complex exhibits unprecedented selectivity for the formation of carbonate linkages.[3] PCs are promising for applications as ceramic binders, adhesives, coatings and packaging materials as well as in biomedical applications, since they are potentially biodegradable into nontoxic compounds.[10] This feature renders PCs ideal materials for the development of drug delivery systems. In addition, PCs generally have lower degradation rates than many biopolyesters, which is advantageous especially when a relatively high stability is desired, e.g., in implants for medical application.[10–12]

A current drawback for many applications is the low number of functional groups at the PC backbone. The catalytic copolymerization of CO_2 with substituted epoxides is an ideal platform for the generation of multifunctional PCs.[4,13–15] However, only few examples dealing with the introduction of functional groups into PCs have been reported in literature to date.[4,13,16–18,38] Zhang et al. and Coates et al. reported the copolymerization of CO_2 and 4-vinyl-cyclohexene-1,2-epoxide.[20,21] In addition, the terpolymerization of CO_2, propylene oxide and various epoxides using a cobalt salen complex was described by Lee et al.[19] A functional comonomer was used by Wooley et al. and Rokicki et al. to synthesize hyperbranched PCs by a ring-opening polymerization (ROP) approach.[20,21] Furthermore functional PCs containing carboxyl groups were synthesized by Yang et al.[10], also relying on the ROP of six-membered cyclic carbonates. [22,23]

This work describes the controlled and variable incorporation of aliphatic alkene epoxides into the PC backbone. This straightforward, modular approach is a general strategy for the synthesis of novel multifunctional PCs based on the copolymerization of different functional epoxides, PO and CO_2. The established cobalt salen complex was used as the catalyst and bis(triphenylphosphine)iminium chloride (PPN) as an ionic cocatalyst. This modular platform allows for easy variation of the materials properties by simply changing the aliphatic alkene length and its content in the PPC backbone. For the system reported herein, the functional comonomer content was varied gradually from 3 to 22 %.

Scheme 1. Synthesis of the polycarbonate terpolymers and subsequent functionalization.



Subsequent further functionalization by “click-chemistry” has also been demonstrated. Such transformations have lately become extremely popular also in materials sciences.[24–27,28] The more than 100-year-old [29] and well-known free radical addition of thiols onto double bonds has also attracted increased attention as a “click” reaction in recent years.[26,27,30,31] Using this reaction type, functional groups, such as hydroxyl, carboxyl or even amine groups have been introduced [24,32], which have been used for further modification, for example as initiators for ROP of lactones to generate brush copolymers. To the best of our knowledge, to date only two groups synthesized poly(ester)/poly(carbonate) copolymers producing the poly(carbonate) block from epoxides and CO_2. Williams et. al. synthesized a triblock copolymer from lactide and telechelic poly(cyclohexene carbonate) and Zhang et al. prepared brush copolymers with poly(cyclohexene carbonate) backbone and poly(ε-caprolactone) side chains.[32,33]

Experimental Section

Materials and Instrumentation

1,2-epoxy-5-hexene (EH, 98%, Aldrich) was distilled over CaH_2 under reduced pressure prior to use. Tetrahydrofurane (THF) was dried over potassium and distilled under argon before use. Carbon dioxide (>99.99%) was used as received. 2,2'-Azo-bis(2-methylpropanenitrile) (AIBN, Sigma Aldrich) was purified by recrystallization from ethanol. Methylene chloride was dried over CaH_2 and distilled before use. L-lactide ((3S-*cis*-3,6-dimethyl-1,4-dioxane-2,5-dione) was obtained from Purac Biochem BV (Gorichem, The Netherlands) and recrystallized from toluene prior to use. *β*-Mercaptoethanol (98%, Sigma Aldrich), stannous octoate (95%, Sigma Aldrich) and other reagents were used as received.

NMR experiments.

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer, operated at 300 and 75.4 MHz and the chemical shifts are given in parts per million (ppm).

Gel permeation Chromatography.

Size exclusion chromatography (SEC) measurements were carried out in THF or $CHCl_3$ on an instrument consisting of a Waters 717 plus auto sampler, a TSP Spectra Series P 100 pump, a set of three PSS SDV columns (104/500/50 Å), RI- and UV-detectors (absorption wavelength: 254 nm or 500 nm). All SEC diagrams show the RI detector signal unless otherwise stated, and the molecular weight refer to linear polystyrene (PS) standards provided by Polymer Standards Service (PSS). Recycling SEC measurements were performed using a Japan Analytical Industry Co. Ltd. Recycling SEC with a JAIGEL-4H column.

Differential Scanning Calorimetry.

DSC curves were recorded with a Perkin-Elmer DSC 7.

IR-Spectroscopy.

FT-IR spectra were recorded on a Thermo Scientific iS10 FT-IR spectrometer, equipped with a diamond ATR unit.

Synthesis of (R,R)-(salcy)-CoOBzF$_5$

(R,R)-(salcy)CoOBzF$_5$ was prepared as described by Coates et. al.[3]

Recrystallized (R,R)-(salcy)-Co^{II} and pentafluorobenzoic acid (0.42 g, 2 mmol) were added to a 50 mL round-bottomed flask charged with a Teflon stir bar. Toluene (20 mL) was added to the reaction mixture, and it was stirred open to air at 22 °C for 12 h. The solvent was removed by rotary evaporation at 22 °C, and the solid was suspended in 200 mL of pentane and filtered. The dark green material was dried *in vacuo* and collected in quantitative yield (1.5 g). ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 1.30 (s, 18H), 1.59 (m, 2H), 1.74 (s, 18H), 1.90 (m, 2H), 2.00 (m, 2H), 3.07 (m, 2H), 3.60 (m, 2H), 7.44 (d, 4J) 2.5 Hz, 2H), 7.47 (d, 4J) 3.0 Hz, 2H), 7.81 (s, 2H).

Representative procedure for the terpolymerization of propylene oxide/1,2-epoxy-5-hexene/CO$_2$ here for P((PO$_{206}$-co-EH$_{21}$)C) (Table 1 entry 3)

A 100 mL Roth autoclave was dried under vacuum at 40 °C and moved to a glovebox. (R,R)-(salcy)-CoOBzF$_5$ (11.7 mg, 0.0143 mmol), the cocatalyst (PPN)Cl (8.2 mg, 0.014 mmol), PO (1.9 mL, 26 mmol) and 1,2-epoxy-5-hexene (0.3 mL, 2.86 mmol) were placed in a glass tube with a Teflon stir bar inside the autoclave. The autoclave was pressurized to 25 bar CO$_2$ and was left to stir at 30 °C for 2 h. The reactor was vented at 30 °C and the polymerization mixture was dissolved in chloroform (5 mL), quenched with 5% HCl solution in methanol (0.2 mL) and transferred to a dialysis tube. After dialysis against chloroform for two days (MWCO 1000 g/mol) the product was precipitated into methanol (50 mL). The polymer was collected and dried *in vacuo*. Yield 95 % ^{1}H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) = 5.73 (CH double bond), 4.99 (methane CH backbone and CH_2 double bond), 4.17 (methylene CH_2), 2.11-1.59 (side chain CH_2) and 1.30 (CH_3).

Thiol-ene coupling reaction between Poly(epoxyhexene carbonate) and different thiols

A typical procedure for the thiol-ene coupling reaction was started with the ratio of reagents double bond/β- mercaptoethanol/AIBN=1/15/0.75. Thiol-ene coupling reactions between poly(epoxyhexene carbonate) (1 g, 0.62 mmol of C=C group) and β-mercaptoethanol (0.72 g, 9.24 mmol) were conducted in a 100 mL Schlenk flask under argon atmosphere with 50 mL THF as solvent and AIBN (0.076 g, 0.46 mmol) as initiator. The reaction mixture was allowed to stir for 3 days at 60 °C. After filtration, the reaction mixture was dialysed in THF for 3 days (MWCO= 3500 g/mol). The product was then precipitated in toluene and dried *in vacuo*. For thiol-ene reactions with thioacetic acid and thio glycolic acid the reaction was carried out the same way.

Reaction with mercaptoethanol:

^{1}H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) = 4.98 (methane CH backbone), 4.17 (methylene -CH_2-), 3.69 (-$C\underline{H}_2$-OH), 2.67 (-$C\underline{H}_2$-CH_2-OH), 2.51 (-CH_2-S-CH_2-CH_2-OH), 1.91-1.48 (side chain -CH_2-) and 1.30 (-CH_3).

Reaction with thioacetic acid:

^{1}H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) = 4.99 (methane CH backbone), 4.17 (methylene -CH_2-), 2.79 (-CH_2-SH), 2.31 (-CO-CH_3), 1.67-1.43 (side chain -CH_2-) and 1.30 (-CH_3).

Deprotection of thioacetic acid functionalized copolymers:

200 mg of the thioacetic-acid functionalized copolymer was dissolved in 10 mL dry THF, then Na-methoxide (1.05 eq for one protecting group) and acetic acid (1.1 eq for one

protecting group) were added. After 10 seconds the resulting polymer was precipitated in cold diethyl ether, dried and washed with cold diethyl ether again.

Reaction with thio glycolic acid:

^{1}H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) = 4.98 (methane CH backbone), 4.17 (methylene CH_2), 3.24 ($-S-C\underline{H}_2-COOH$), 2.68 ($-CH_2-C\underline{H}_2-S-$), 1.65-1.48 (side chain CH_2) and 1.30 (CH_3).

Synthesis of graft copolymers by "grafting from" method.

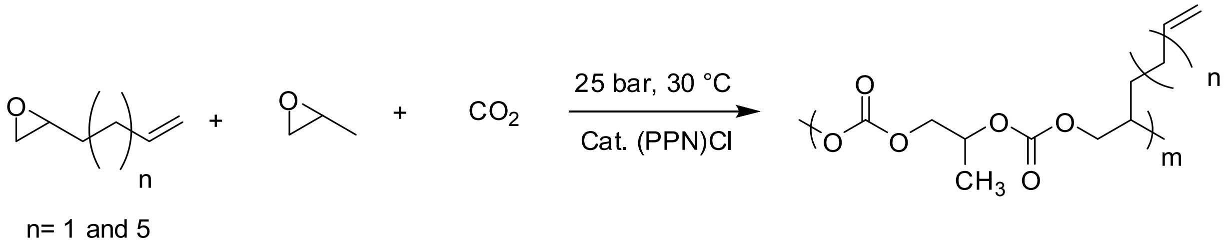
The "grafting-from" strategy was employed to synthesize polymer brushes via ring-opening polymerization of L-lactide using Poly(epoxyhexene carbonate)-OH as macroinitiator. The procedure is exemplified for one backbone polymer and was carried out in analogous manner for all other polymers prepared. The backbone polymer P(EH carbonate)-OH (150 mg with 0.028 mol OH groups) was dried under vacuum for at least 4 h in a Schlenk tube. L-lactide (80 mg 0.56 mol) was added and the mixture was dissolved in 5 ml dry toluene. The mixture was heated to 90°C under argon atmosphere. Subsequently the required amount of $Sn(Oct)_2$ catalyst as a 10 vol.% solution in toluene was injected into the vial. Stirring was continued for 24 h and at the end of the reaction the mixture was allowed to cool. The solvent was removed in vacuum, the product precipitated in cold methanol and dried *in vacuo* and collected in quantitative yield. By changing the [lactide]/[OH] feeding ratios, P(epoxyhexene carbonate)-g-PLLA with various DPn were synthesized.

^{1}H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) = 5.15 (poly(lactide) CH), 4.98 (methane CH backbone), 4.17 (methylene $-CH_2-$), 2.67 ($-C\underline{H}_2-CH_2-O-$), 2.51 ($-CH_2-S-CH_2-CH_2-OH$), 1.91-1.48 (side chain $-CH_2-$ and poly(lactide) $-CH_3$) and 1.30 ($-CH_3$).

Results and Discussion

Multifunctional polycarbonates have been prepared by terpolymerization of CO_2, PO and 1,2-epoxy-5-hexene (EH) and 1,2-epoxy-9-decene (ED) with various feed ratios of the two epoxides (Scheme 1) in order to vary the degree of functionalization of the PPC backbone. By using epoxides with different spacer length, thermal and mechanical properties can be influenced (Scheme 2).

Scheme 2: Synthesis of the polycarbonate terpolymers



All polymerizations were carried out under identical reaction conditions, i.e. 30 °C and 25 bar CO_2 pressure. The catalyst was efficiently removed from the polymer solution after polymerization via exhaustive dialysis in $CHCl_3$ for two days resulting in a colorless polymer. Cyclic carbonate side products were not observed, which can be shown by the IR spectra of the crude reaction mixture (Figure S1).

Table 1. Copolymerization of 1,2-epoxy-5-hexene or 1,2 epoxy-9-decene, propylene oxide and CO_2 using (R,R)-(salcy)CoOBzF$_5$ as a catalyst and (PPN)Cl as a cocatalyst[a]

#	**Monomer/cat /cocat**	**Polymer**	**% EH**	**M_n (g/mol)[b]**	**M_w/ M_n[b]**	**% Carbonate linkages[c]**	**T_g /°C**
1	2000:1:1	P((PO$_{300}$-*co*-EH$_9$)C)	3	32 000	1.38	> 99	29
2	2000:1:1	P((PO$_{194}$-*co*-EH$_{18}$)C)	8	22 000	1.34	> 99	22
3	2000:1:1	P((PO$_{206}$-*co*-EH$_{21}$)C)	10	24 000	1.24	> 99	19
4	2000:1:1	P((PO$_{245}$-*co*-EH$_{32}$)C)	13	28 000	1.26	> 99	16
5	2000:1:1	P((PO$_{180}$-*co*-EH$_{40}$)C)	22	24 000	1.21	> 99	10
6	2000:1:1	P((PO$_{69}$-*co*-EH$_{21}$)C)	30	10 000	1.17	50	-
7	2000:1:1	P((PO-co-EH)C)	50	-	-	-	-
8	2000:1:1	P((PO-*co*-ED)C)	5	28 000	1.28	> 99	18
9	2000:1:1	P((PO-*co*-ED)C)	10	21 000	1.32	> 99	11

[a] Polymerization conditions: 30 °C, 2h, 25 bar CO_2, [b] Determined by SEC calibrated with polystyrene standard in $CHCl_3$ at 40 °C, [c] Carbonate bond linkages in the polymer chain determined by ^1H NMR spectroscopy.

Most polymers showed monomodal molecular weight distributions in SEC with rather low polydispersity (PDI) values (1.21-1.38) and apparent molecular weights between 22 000 and 32000 g/mol (Table 1, Figure 1). Some copolymers showed bimodal distributions after work-up, which is a typical phenomenon in the copolymerization of CO_2 and epoxides when using binary catalyst systems. This is due to two reactive catalyst species and possible initiation by traces of water (Figure S2).[2,5] After separation of both peaks with a recycling SEC, detailed characterization by ^{1}H and ^{13}C NMR spectroscopy of the separated products confirmed that the PO/EH/CO_2 ratio is identical for both distributions, i.e. initiation methods (Figure S3), indicating that no homopolymerization of both epoxides takes place.

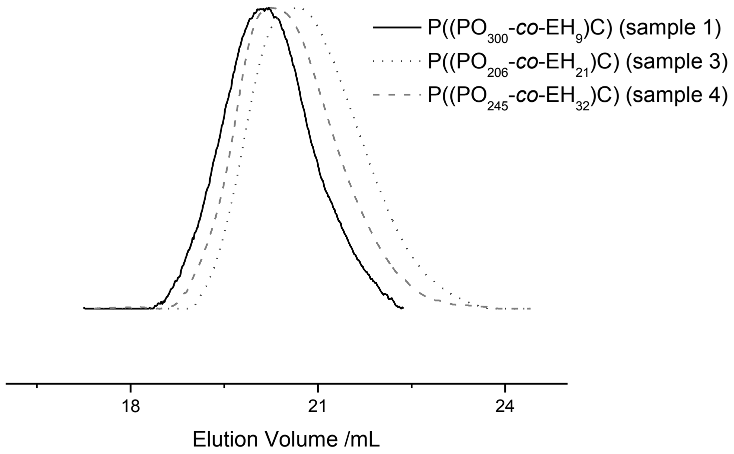


Figure 1. SEC data for some PO/epoxyhexene/CO_2 terpolymers showing monomodal distributions ($CHCl_3$, RI signal).

The contents of both epoxy monomers have been varied in a systematic manner from 3% to 22% to generate a functionalized PPC. In this range the typical poly(propylene carbonate) properties can still be found. Table 1 summarizes the results for the series of functional copolymers that were prepared in this manner with molecular weights, PDIs and glass transitions temperatures (T_gs). Unexpectedly, for higher EH/PO or ED/PO ratios (> 25%; entry 6) under the chosen reaction conditions no strictly alternating CO_2/epoxide copolymers were obtained, and an increased amount of ether linkages occurred (Figure S6). For ratios >50% no polymerization was observed (Table 1). We are further exploring this unexpected limitation of the terpolymerization at present.

After 2 h reaction time, full conversion of the epoxides was proven by ^{1}H NMR spectroscopy from the crude mixture. Figure 2 shows the ^{1}H NMR of a purified sample with EH as a comonomer. The resonances at δ 5.7 ppm are assigned to the CH group (signal e) of the double bond, which was used to calculate the molar ratio of the comonomers incorporated in the polymers, while the signal at δ 1.6-2.1 ppm corresponds to the side chain CH_2 (signal d) groups. The signals at δ 5.0 and 4.2 ppm can be assigned to the resonances of the methine (signal b) and methylene units (signal a) of the carbonate unit. No epoxide homopolymer, i.e., ether linkages, were detected in the ^1H NMR spectra. Ether bonds would result in additional signals between δ 3-4 ppm. This observation evidences a strictly alternating placement of PO or the respective functional epoxide (EH or ED) with CO_2 (^1H NMR for the P((PO-*co*-1,2-epoxy-9-decene)C) polymers is shown in Figure S4).

^{13}C NMR spectroscopy also confirmed the incorporation of EH or ED, PO and CO_2 into the copolymer, and the carbonate resonance at δ 154 ppm can clearly be detected. Once more no polyether signals were observed (Figure S5), confirming polycarbonate formation.

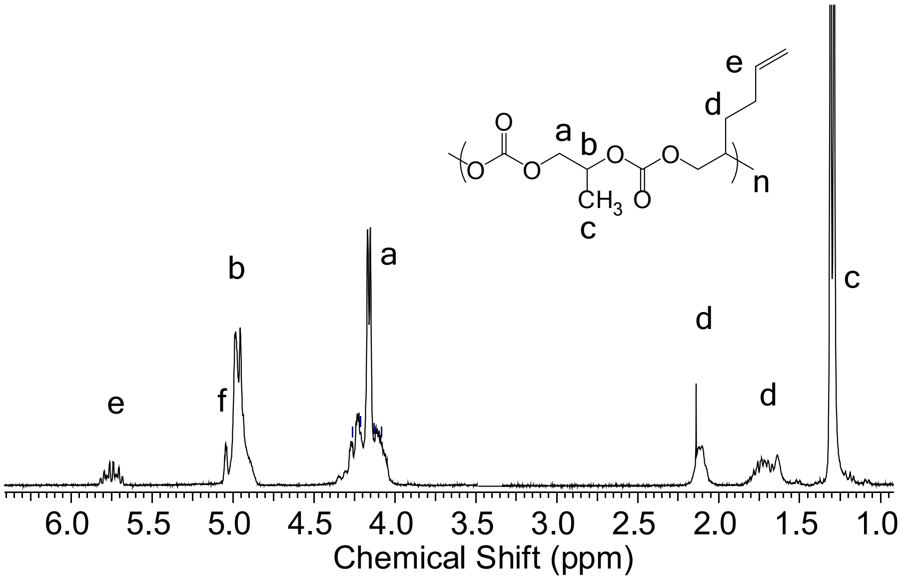


Figure 2: Representative ^1H NMR spectrum (300 MHz, $CDCl_3$) of P((PO_{206}-*co*-EH_{21})C) (Table 1 entry 3) in $CDCl_3$.

In addition to the NMR data, the incorporation of CO_2 into the polymer can be confirmed by IR spectroscopy (Figure S1). Only one carbonate band at 1738 cm $^{-1}$, which can be assigned to the C=O group of the linear carbonate, is detected. No bands for a cyclic carbonate, which appear at around 1790 cm^{-1}, were found in the IR (or NMR) spectra of the non-purified copolymers.

Characterization of the thermal properties of the series of functional polycarbonates was carried out via DSC (heating rate 10 K/min). The results lend further support to random incorporation of PO and EH as well as ED (Figure S8 & Table 1). All determined T_gs of the copolymers are slightly lower than the T_g of pure PPC and decrease with increasing EH/PO or ED/PO-ratio. With 3% EH comonomer incorporation the T_g drops from 35°C to 29 °C, which further decreases to 12°C for sample 5 (with 22% EH incorporated). These results render the herein presented copolymers interesting candidates for poly(propylene carbonate) (PPC) applications, since they possess similar processing properties as PPC, but offer additional options for modification and crosslinking. Increasing the EH or ED comonomer content would further decrease the glass transition temperature and the resulting polymers would show considerably different thermal properties compared to PPC.

Post-polymerization modification of the functionalized polycarbonates

Post-polymerization modification of the pending double bonds gives access to a variety of functional PCs. The functionalization of double-bond carrying polymers by thiol-ene reactions has been studied intensively by several groups.[24] The utilization of this highly efficient reaction has been widespread due to the high specificity, near-quantitative yields, and near-perfect fidelity in the presence of most functional groups.[34,35] Mercaptoethanol, thioacetic acid and thioglycolic acid were chosen as suitable compounds for the modification of the multifunctional PCs (Scheme 3). The results are summarized in Table 2. Furthermore the resulting hydroxyl groups were used as initiators for poly(lactide) grafting, resulting in graft copolymers with variable number of arms.

The reactions were performed using azodiisobutyronitrile (AIBN) as an initiator in predried THF at 60°C for three days. In order to avoid the possible cross-linking reaction caused by radical coupling, an excess amount (10 eq) of thiol was added.

Scheme 3. Synthesis of different functional polycarbonates using thiol-ene couplings.

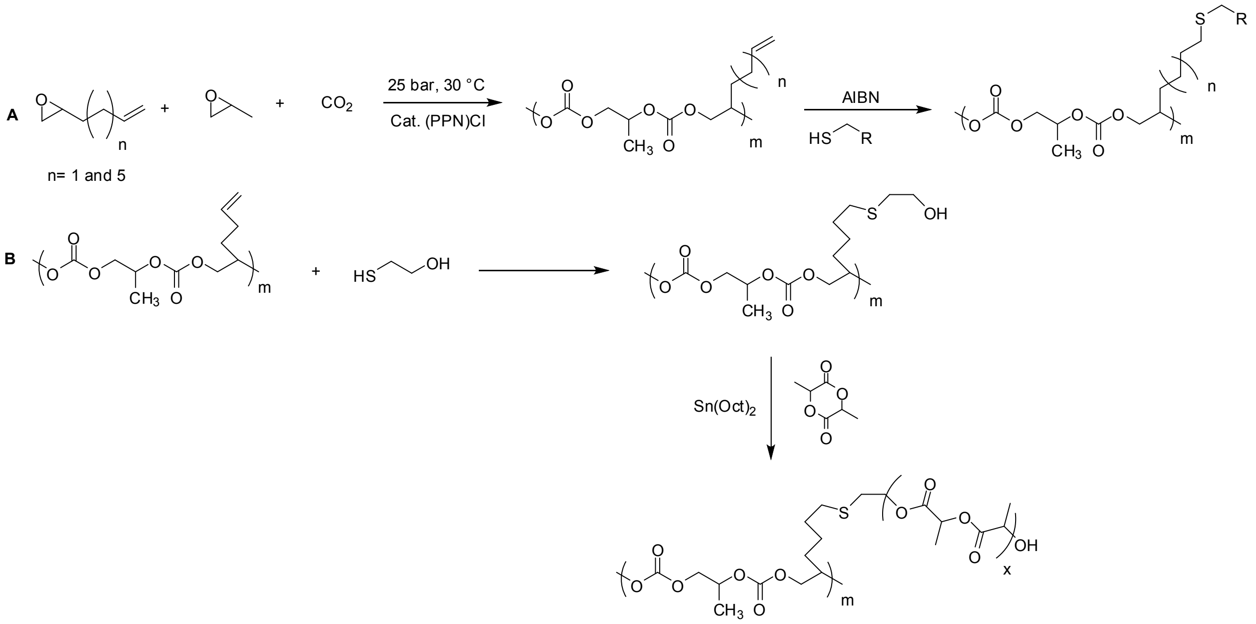
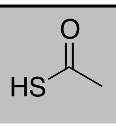
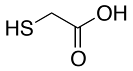
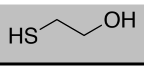


Table 2. Multifunctional poly(carbonate) derivatives derived from random precursor P((PO-*co*-EH) C) copolymers.

#	Precursor Polymer	R-SH	M_n (g/mol)^a	PDI^a	M_n (g/mol)^b	PDI^b	Yield /%	Conversion /%^{c}
A	P((PO$_{194}$-*co*-EH$_{18}$)C)		22 000	1.34	8900	1.65	80	> 99
B	P((PO$_{194}$-*co*-EH$_{18}$)C)		22 000	1.34	18 500	1.30	92	> 99
C	P((PO$_{194}$-*co*-EH$_{18}$)C)		22 000	1.34	17 200	1.26	88	> 99

[a], Data for precursor P((PO-*co*-EH)C) copolymers determined by SEC-RI in $CHCl_3$. [b] Data for functionalized P((PO-*co*-EH)C) copolymers determined by SEC-RI in $CHCl_3$. [c] Determined by ^1H NMR Spectroscopy

One of our objectives was to generate polycarbonates with multiple thiol groups. This was achieved by the reaction of the alkene-functional PCs with thioacetic acid and subsequent deprotection of the thioester under basic conditions. After the thiol-ene click reaction and dialysis, the excess of thio acetic acid was removed, and ^1H NMR evidenced the targeted functionalization, as the methyl signal of the attached thio acetic acid is clearly visible at δ = 2.3 ppm. The methylene resonance next to newly created sulfur bond can be discerned at δ

= 2.84 ppm. Selective deprotection is not facile in this case, since basic treatment can also cleave the polycarbonate backbone, which is undesired. However, following the deprotection via ^{1}H NMR spectroscopy permits to determine the reaction time that preserves the backbone, but cleaves the protective group. The deprotection can be monitored by disappearance of the methyl peak at 2.3 ppm; details of the selective procedure are given in the experimental section of this work.

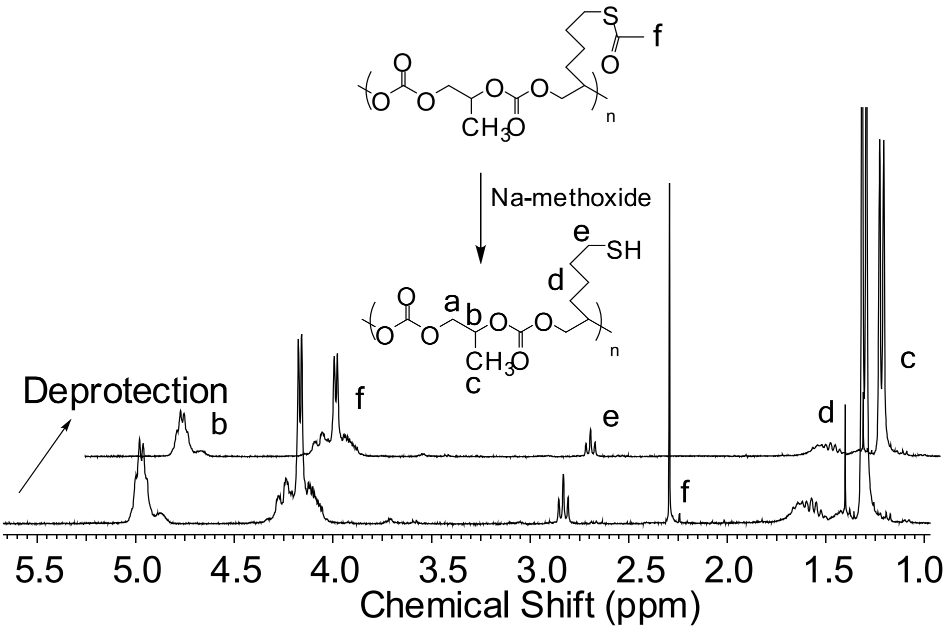


Figure 3. Thiol-ene coupling of thioacetic acid to the double bond (bottom) and deprotection with sodium methoxide (top) (in $CDCl_3$, 300 MHz).

Carboxyl groups have also been introduced, using the thiol-ene click reaction with thio glycolic acid. The reaction was carried out in THF at 60 °C for 3 days, followed by removing excess thio glycolic acid and remaining AIBN by dialysis in chloroform. Figure 4 shows the ^{1}H NMR spectrum of a carboxyl functionalized poly(carbonate) (based on sample 2, Table 1). Even with multiple carboxyl groups, the copolymers did not become soluble in water at a range of pH values, maybe due to the limited number of carboxyl groups at the PC backbone, as described in a previous section.

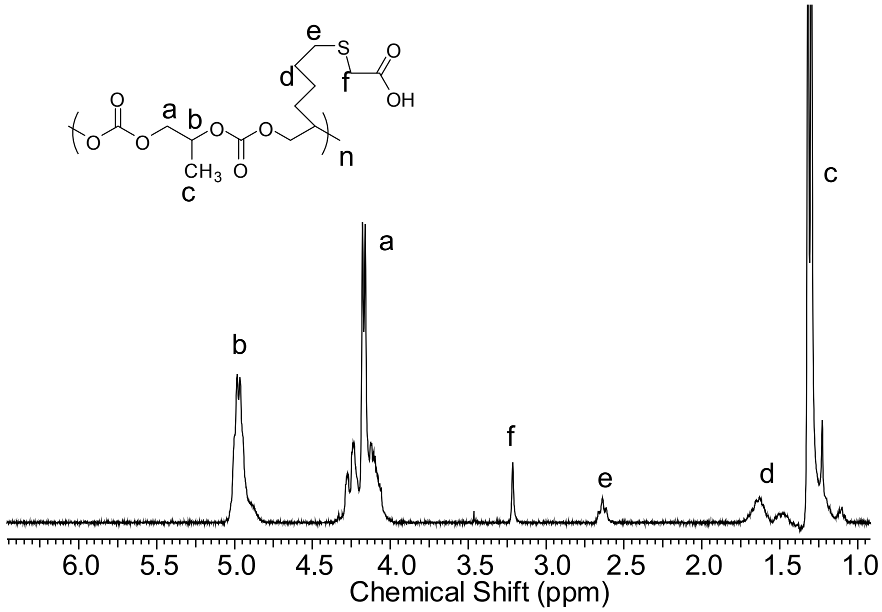


Figure 4. ^{1}H NMR spectrum of a carboxyl-functionalized polycarbonate P((PO$_{194}$-*co*-EH$_{18}$)C) with variable number of carboxyl groups (in CDCl$_3$, 300 MHz).

In order to obtain fully degradable and well-defined graft copolymers, well-defined linear CO$_2$/epoxide copolymers bearing 4 and 18 hydroxyl groups, respectively, were synthesized and used as a macroinitiator for lactide polymerization.

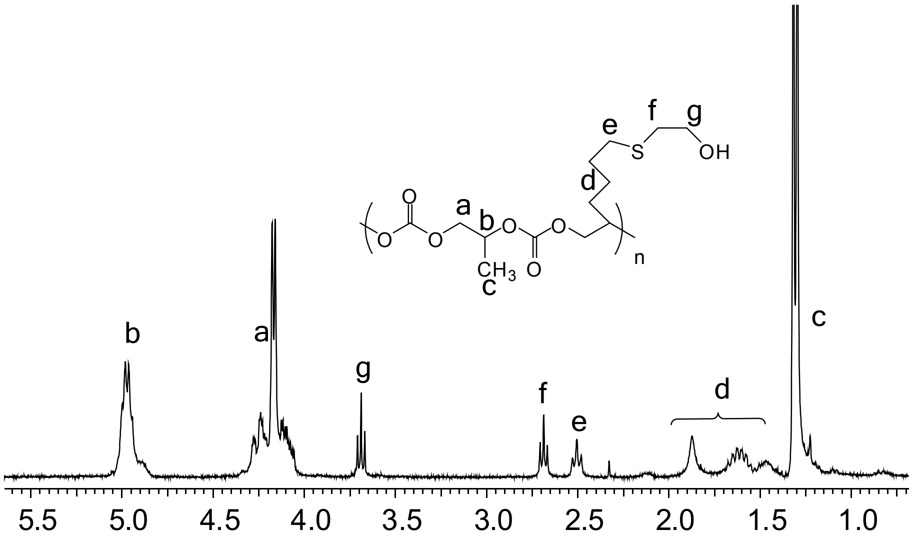


Figure 5. ^{1}H NMR spectrum of a hydroxyl functionalized poly(carbonate) via thiol-ene click chemistry with mercapto-ethanol (in CDCl$_3$, 300 MHz).

A straightforward three step protocol: alternating copolymerization of CO$_2$ and the respective epoxide (i), thiol-ene click reaction (ii) and the ROP of dilactide (iii) was followed (cf. Scheme 3). Different side chain lengths (from DP$_n$= 20 to DP$_n$= 50) were synthesized and the resulting polymers were characterized both with ^{1}H NMR and IR spectroscopy as well as differential scanning calorimetry. Depending on the side chain length, different thermal properties with respect to glass transition temperature and melting behavior were expected.

Table 3. Results for the graft copolymer samples.

#	Sample	# OH groups	M_n ^{a}/g/mol	PDI	PLLA length/side chain ^{b}	T_g /°C^c	T_m /°C
A	**P((PO_{300}-*co*-EH_4)C)**	**4**	**14 800**	**1.38**	**0**	**34**	**-**
B	P((PO_{300}-*co*-EH_4)C)-*g*-$(PLLA_{21})_4$	4	13 600	1.81	21	12	-
C	P((PO_{300}-*co*-EH_4)C)-*g*-$(PLLA_{32})_4$	4	16 200	1.65	32	18	-
D	P((PO_{300}-*co*-EH_4)C)-*g*-$(PLLA_{39})_4$	4	17 200	1.83	39	24	-
E	**P((PO_{194}-co-EH_{18})C)**	**18**	**17 200**	**1.26**	**0**	**32**	**-**
F	P((PO_{194}-*co*-EH_{18})C)-*g*-$(PLLA_{19})_{18}$	18	35 300	1.29	19	40	110
G	P((PO_{194}-*co*-EH_{18})C)-*g*-$(PLLA_{31})_{18}$	18	44 200	1.30	31	40	136
H	P((PO_{194}-*co*-EH_{18})C)-*g*-$(PLLA_{43})_{18}$	18	57 800	1.29	43	41	146
I	P((PO_{194}-*co*-EH_{18})C)-*g*-$(PLLA_{49})_{18}$	18	69 200	1.25	49	47	150

^{a} Determined by SEC calibrated with polystyrene standard in $CHCl_3$ at 40 °C, ^{b} Determined by inverse gated ^{13}C NMR spectroscopy, ^{c} Determined by DSC measurements.

The grafting reaction was carried out in toluene at 90 °C, using $Sn(Oct)_2$ as a catalyst. After 24 h, the reaction was terminated by cooling the mixture to room temperature, removing toluene under reduced pressure and precipitation of the crude product in cold methanol. The resulting samples were obtained as white powders. All materials have been characterized by NMR spectroscopy, SEC and DSC, as summarized in Table 3. In Figure 6 the ^{1}H NMR spectrum of samples F,H and I is shown as a typical example. In addition to the polycarbonate backbone signals (d = 4.98, 4.17 and 1.30 ppm), the resonances for poly(L-lactide) are observed (d = 5.17 and 1.57 ppm). Due to signal overlap, the lactide side chain length could not be determined by ^{1}H NMR, however, this was achieved by ^{13}C NMR spectroscopy. One important issue that can be resolved by ^{1}H NMR spectroscopy is, whether the lactide monomer is fully consumed during the reaction. The signals of the lactide monomer shift downfield during polymerization and disappear with complete conversion. As expected, with increasing poly(lactide)/poly(carbonate) ratio also the signal ratio in the NMR increases. For sample I with 18 side chains and a degree of polymerization of nearly 50, the backbone signals can hardly be seen.

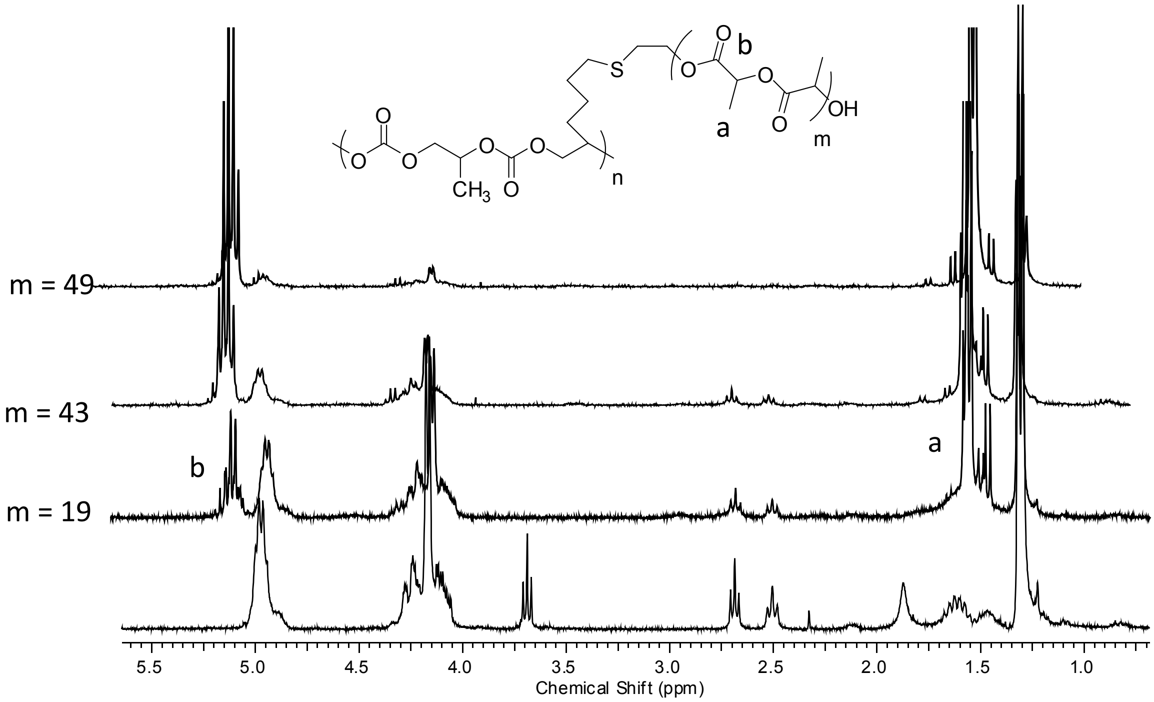


Figure 6. ^{1}H NMR spectra of poly(epoxyhexene carbonate)-*g*-PLLA$_m$, m = 0, 19, 43 and 49 ($CDCl_3$). The resonances at δ = 2.5 and δ = 2.7 ppm can be assigned to the methylene protons next to the sulfur atom and the peak at δ = 3.7 can be assigned to the methylene proton of CH-OH group, disappears after the ROP of L-lactide.

For all graft polymer samples the poly(lactide) side chain degree of polymerization was calculated from Inverse Gated (IG) ^{13}C NMR spectra by integration of the lactide chain end-group signal. The results are summarized in Table 3. Further, size exclusion chromatography shows an increase of molecular weights after grafting (Figure 7). Moreover, it was found that the polydispersities are lowered with increasing degree of polymerization of polylactide. This is in agreement with theory that shows that coupling of polydisperse arms onto a multifunctional core produces a graft polymer with reduced polydispersity.[36]

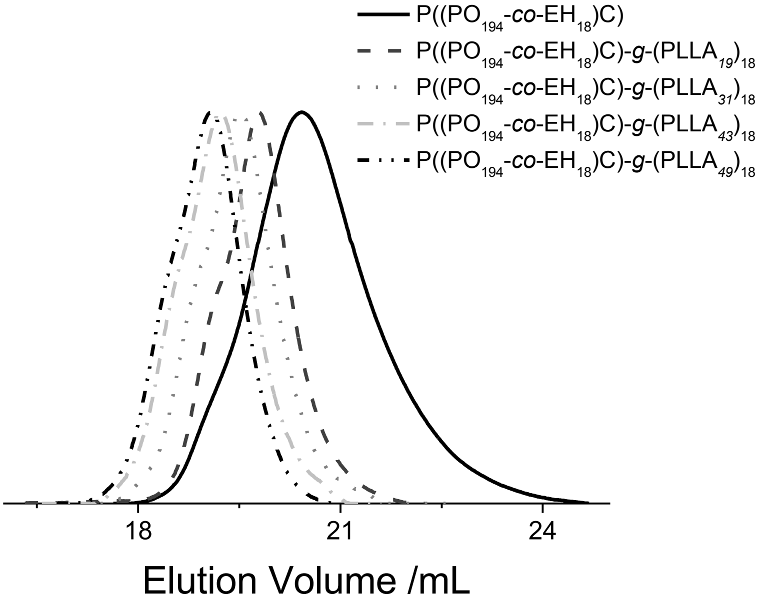


Figure 7. SEC traces for graft copolymer samples F-I with increasing molecular weight with increasing degree of polymerization of polylactide ($CHCl_3$, RI signal).

The thermal behavior of the prepared graft-copolymers has been investigated by differential scanning calorimetry (DSC). The results of the second heating scan, i.e., glass transition temperatures (T_g) and melting points of all L-lactide graft-copolymers are summarized in Table 3. In all cases only one glass transition temperature and melting point were detected. This further confirms - in combination with the monomodal SEC curves of the polycarbonate/PLLA copolymers - that no homopolymer mixtures were generated.

In general, glass transition temperatures and melting points increase with increasing amount of polylactide side chains and with the side chain degree of polymerization.[37] No melting point was observed for samples B, C and D containing only four poly(lactide) side chains. However, the glass transition temperature for these samples increases with increasing poly(lactide) content. In the samples B-D no melting was observed, because the poly(lactide)/poly(carbonate) ratio is so low that the dominating influence for the behavior of the samples is the amorphous backbone polycarbonate copolymer and not the crystalline side chains.

In general, all glass transition temperatures are still lower than those of the PLLA homopolymers, once again supporting copolymer formation. For samples F-I also an increase of glass transitions is observed, and a melting point can be found. The melting temperature shifts to a higher values with increasing poly(lactide)/poly(carbonate) ratio. Compared to the PLLA homopolymer (T_m= 170-180 °C), all copolymers show lower T_m. This can be explained i) by the PC backbone affecting crystallization and ii) by the molecular architecture of the copolymers.

In summary, by variation of the PC backbone terpolymer composition and functionality, the graft density can be varied, depending on the amount of 1,2-epoxy-5-hexene incorporated. In this work it could be shown that the distance between two neighboring side chains influences the crystallization and thereby also the degradation rate of the side chains, which is related to the degree of crystallization, as recently stated by Zhang et al. for other, structurally related systems.[32] With only four side chains no crystallization was observed at all, whereas polycarbonates with an average of 18 PLLA side chains showed clear melting peaks.

Conclusions

In this work we have demonstrated the facile synthesis of multifunctional PCs based on CO_2/PO/EH and CO_2/PO/ED terpolymers with alternating incorporation of carbon dioxide and the respective epoxides directly from CO_2. Polymers with 3-22% EH and molecular weights between 22 000 and 34000 g/mol were obtained under mild reaction conditions (25 bar CO_2, 30°C, 2h). An interesting finding is also that the (R,R)-(salcy)-CoOBzF$_5$/(PPN)Cl catalyst system developed by Coates et al.[3] can be employed to the copolymerization of functional epoxides. Epoxides containing double bonds and different spacer lengths (1,2-epoxy-5-hexene and 1,2-epoxy-9-decene) have been polymerized in this work. Clearly, the catalytic terpolymerization of alkenyl epoxides and CO_2 represents an interesting and highly modular alternative to the widely used ring-opening strategy that requires six membered cyclic carbonates to generate functional aliphatic polycarbonates.

The double bonds have been successfully functionalized through the efficient thiol-ene reaction. Hitherto not described functionalization reactions for polycarbonates resulting in thiol and carboxyl moieties have been demonstrated. Based on hydroxyl- functional polycarbonates, graft copolymers with well-defined structure and variable grafting density have been synthesized through the “grafting from” method. These materials with PLLA side chains should be fully degradable. Thermal properties are controlled by the number and degree of polymerization of the side chains. The polycarbonate-based graft polymer architectures may be interesting for processing PLA, since they can be processed at lower temperatures than their linear counterparts, due to their lower melting temperature and reduced melt viscosity and are therefore promising for biomedical purposes.

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Supporting Information for: From CO_2-Based Multifunctional Poly(carbonate)s with Controlled Number of Functional Groups to Graft-Polymers

Jeannette Geschwind[1,†], Frederik Wurm[2] and Holger Frey[*1]

IR spectrum of a typical terpolymers

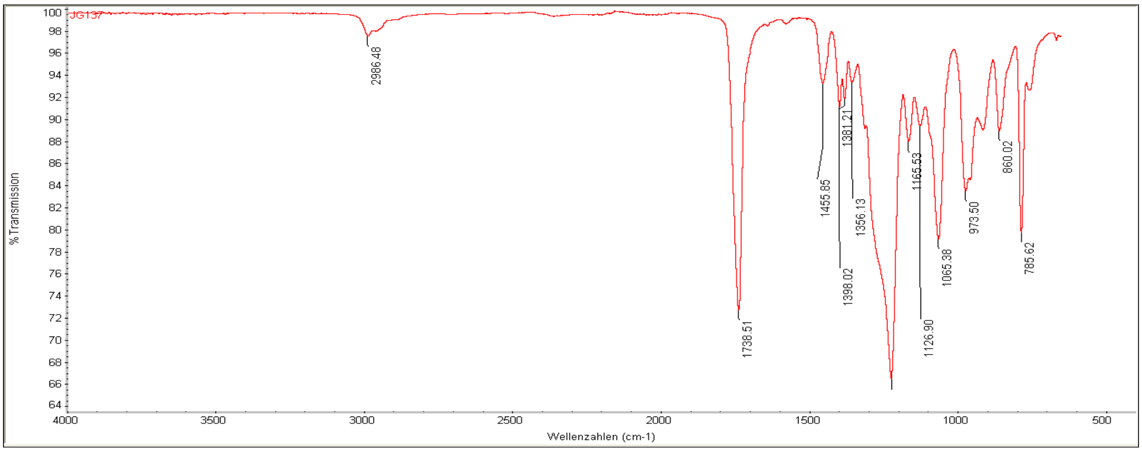


Figure S1. IR spectrum of a functional poly(carbonate) copolymer.

SEC data for the terpolymers and functionalized terpolymers

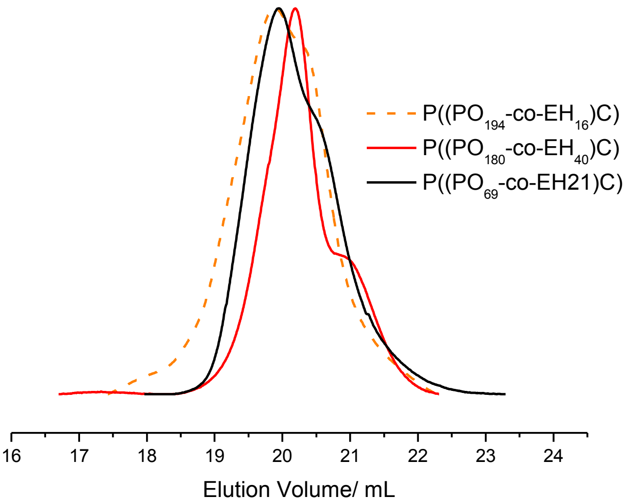
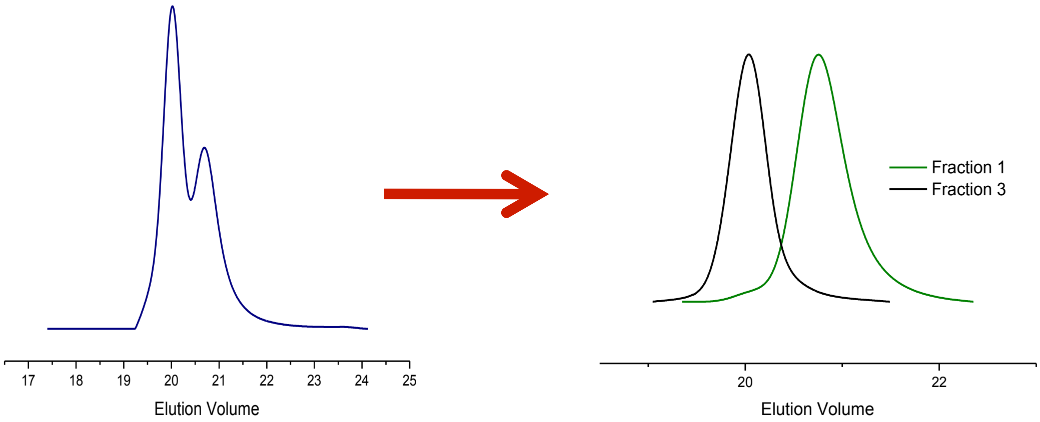


Figure S2. SEC data for the PO/EH/CO$_2$ terpolymers with bimodal distributions.



	Sample	**M$_n$**	**PDI**
1	Fraction 1	33 400	1.04
2	Fraction 3	18 700	1.06
	P((PO$_{245}$-*co*-EH$_{32}$)C)	28 000	1.26

Figure S3. SEC data for the separation of both peaks using a recycling SEC.

Representative ^{1}H and ^{13}C NMR spectra of the terpolymers and functionalized terpolymers

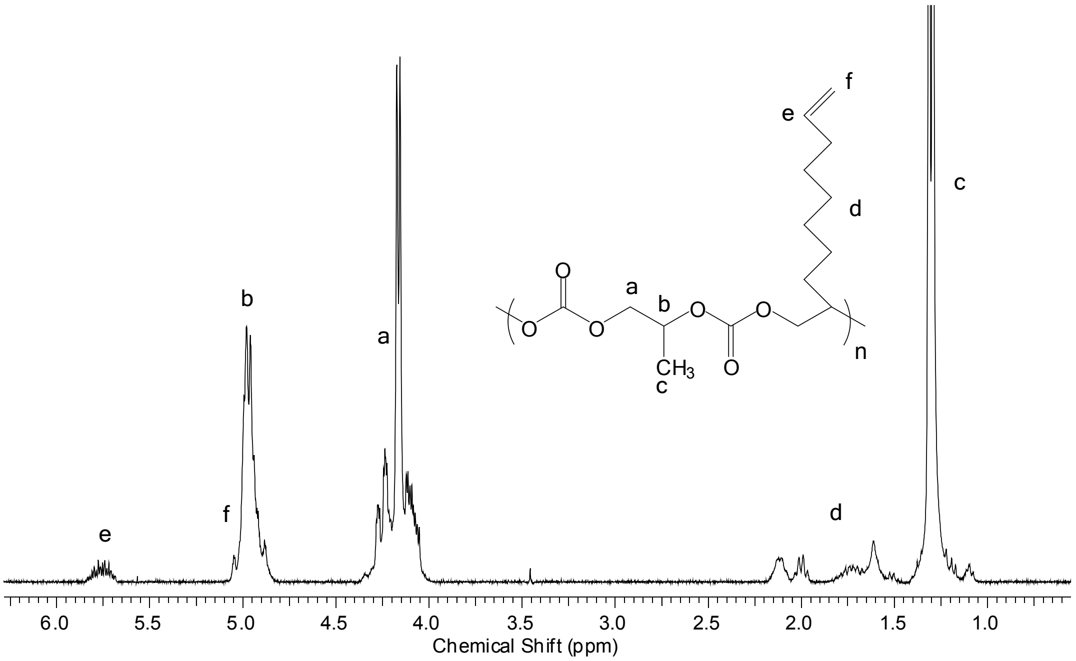


Figure S4. ^{1}H NMR (300 MHz) spectrum of a representative sample of P((PO-*co*-ED) C) in $CDCl_3$.

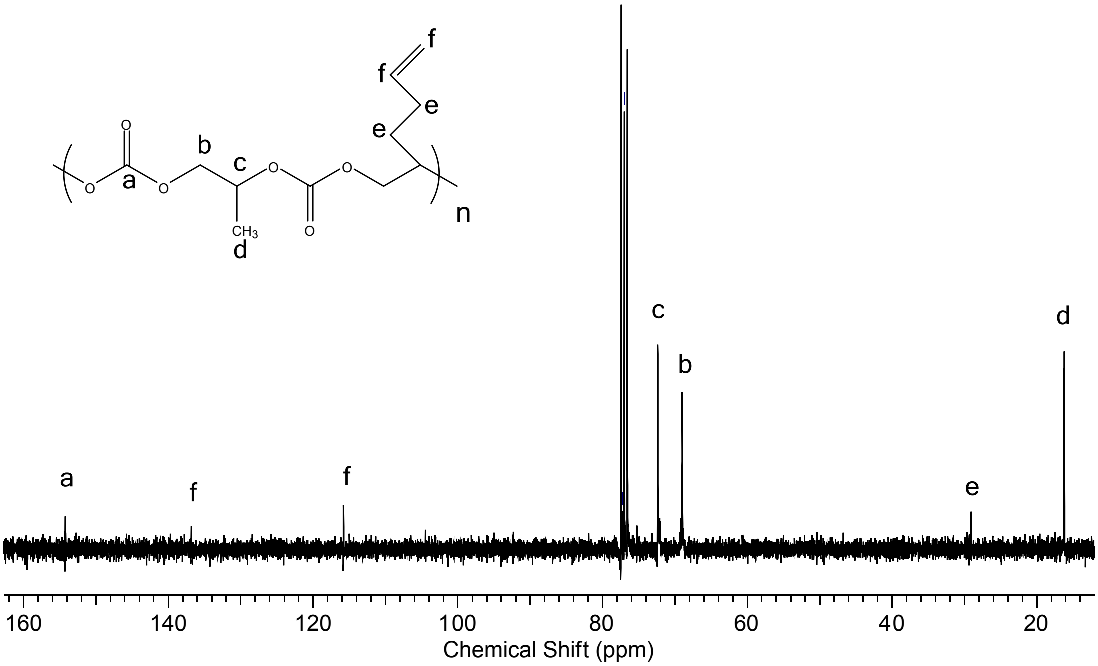


Figure S5. ^{13}C NMR (75.4 MHz) spectrum of a representative sample of P((PO-*co*-EH) C) in $CDCl_3$.

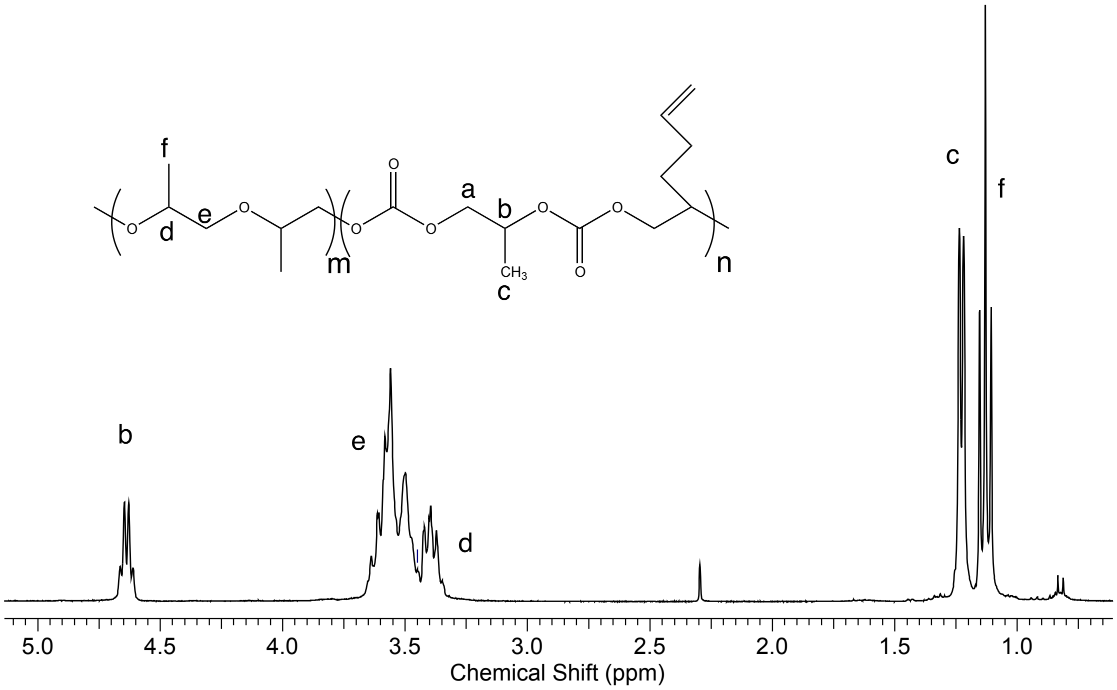


Figure S6. ^{1}H NMR spectrum of a typical sample with more than 30 % 1,2-epoxy-5-hexen in $CDCl_3$. Ether bonds are observed in this case (Table 1, sample 7).

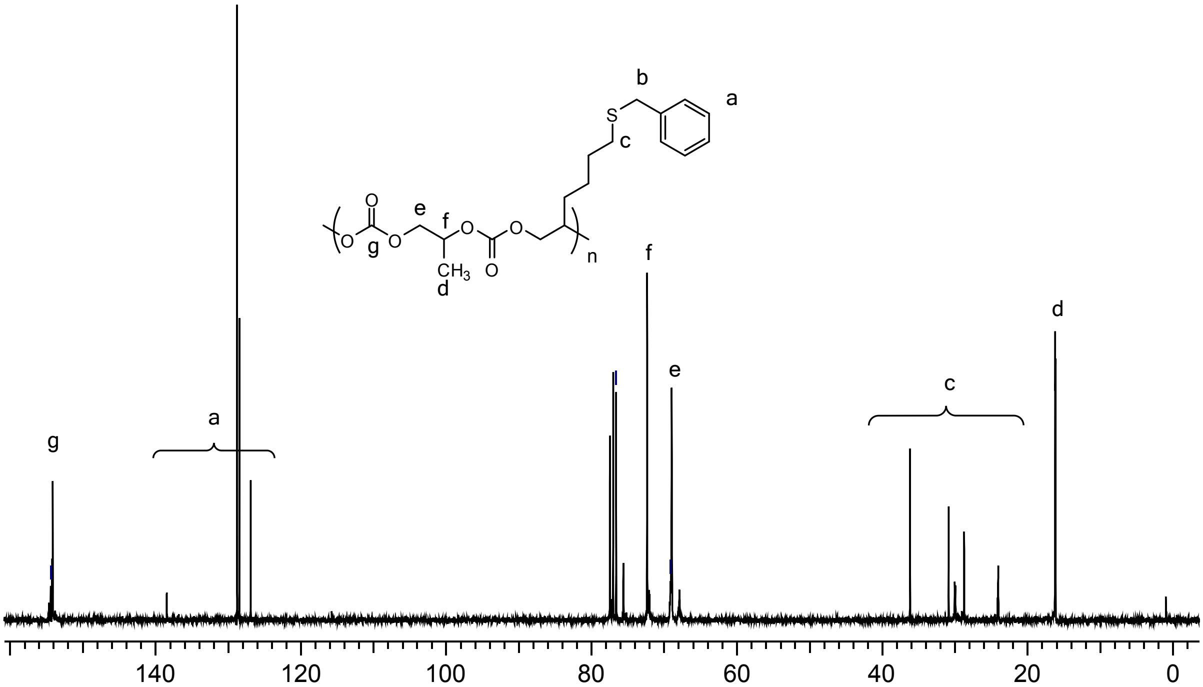


Figure S7. ^{1}H NMR spectrum of a representative sample of a functionalized P((PO-*co*-EH)) in $CDCl_3$.

Representative DSC data of the terpolymers

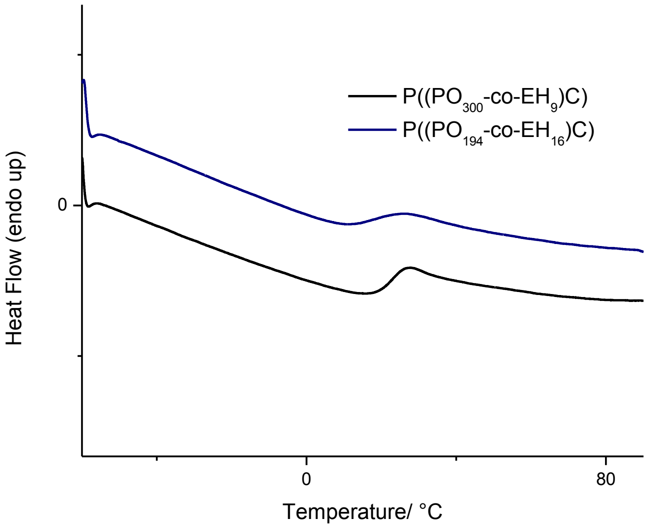


Figure S8. Representative DSC plots of the resulting terpolymers.

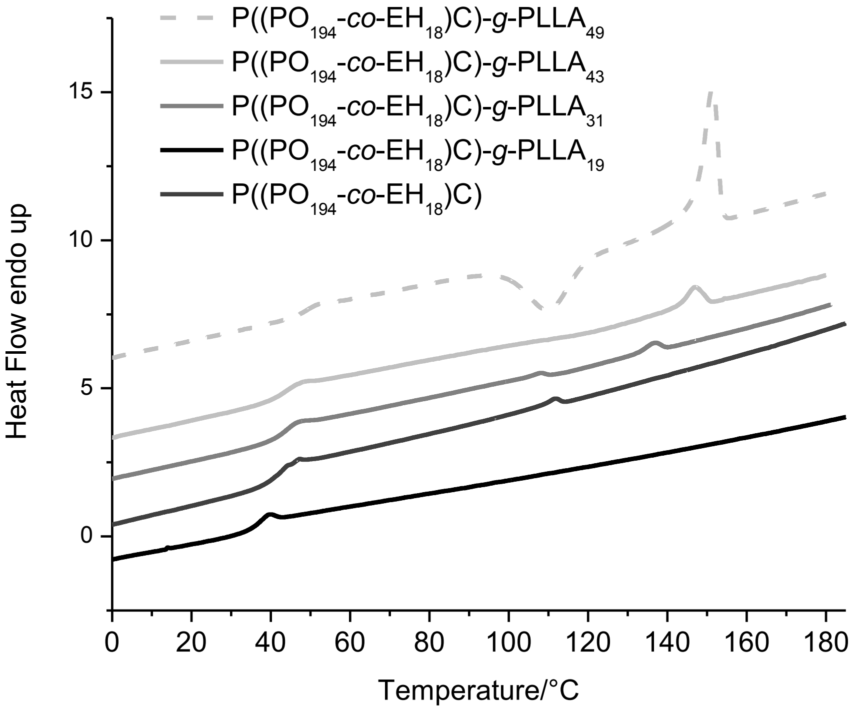


Figure S9. Representative DSC plots of some graft/copolymers (examples) with PLLA grafts.

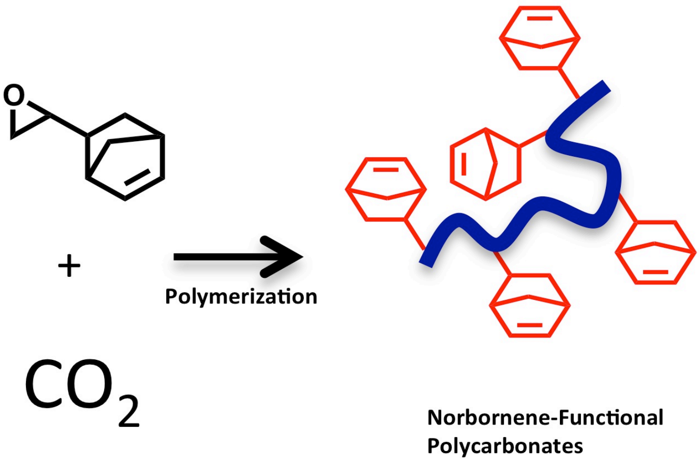
4.2. Branched Polycarbonates from CO_2 and a Bifunctional Epoxide via ROMP

Jeannette Hilf[1†] and Holger Frey[*1]

Institute of Organic Chemistry, Organic and Macromolecular Chemistry, Duesbergweg
10-14, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany

[†]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

To be submitted



Abstract

The catalytic copolymerization of CO_2 with appropriately substituted epoxides is an ideal platform for the generation of multifunctional PCs. The introduction of norbornene groups at a poly(propylene carbonate) (PPC) backbone has been realized by copolymerization of the novel 2-bicyclo[2.2.1]hept-5-ene-2-yl oxirane (BHO) with propylene oxide (PO) and carbon dioxide (CO_2). A series of copolymers with random structure and varying BHO comonomer content (5-30%) with molecular weights in the range of M_n 3600-12300 g/mol has been synthesized and characterized with respect to their microstructure and thermal properties. In a second step, Metathesis polymerization with Grubbs 1 catalyst was used for crosslinking and long chain branching of the resulting norbornene functional poly(carbonates) and no additional monomer was added.

Introduction

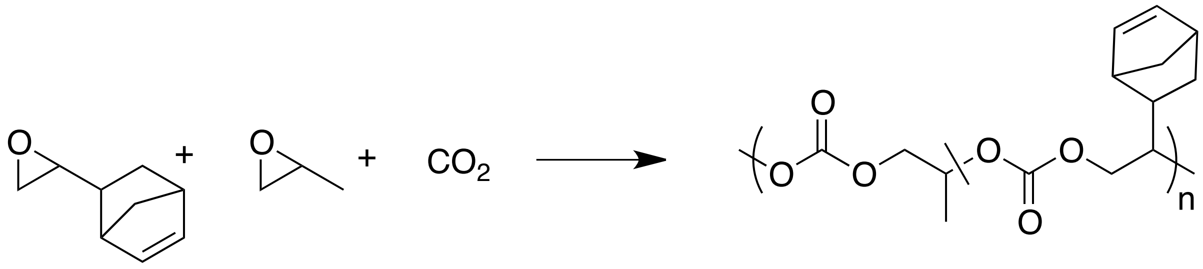
Aliphatic poly(carbonate)s (APCs) are widely known biodegradable polymers that have been introduced as integral components of medical devices, drug delivery and for tissue engineering.[1,2] Furthermore APCs have been proposed as alternative materials for degradable films both for packaging, and rigid plastic applications. There are three major polymerization techniques for the synthesis of APCs:[3] (1) polycondensation of aliphatic diols with dialkyl carbonate;[4,5] (2) ring opening polymerization (ROP) of cyclic carbonate monomers;[2,6,7] (3) copolymerization of carbon dioxide (CO_2) with epoxides.[8–11] CO_2 is one of the most abundant and renewable carbon resources, and the selective transformation of epoxides and CO_2 into degradable poly(carbonate)s is a promising sustainable route to APCs. Catalysts for this copolymerization have been improved in activity and tolerance of functional groups ever since the first report on poly(propylene carbonate) (PPC) from the alternating copolymerization of CO_2 and PO with a diethyl zinc/water catalyst prepared by Inoue in 1969.[12] Especially the groups of Darensbourg, Coates, Rieger and Williams presented a variety of highly active heterogeneous and homogeneous cobalt and zinc based catalysts for this type of copolymerization.[8,13–16] However, in most works published to date, propylene oxide or cyclohexene oxide are used as epoxide monomers.

To introduce functional groups at the polymer backbone, epoxides containing functional groups or glycidyl ethers can be used.[11,17,18] This has been shown for example for poly(carbonate) copolymers with tailored number of hydroxyl groups from benzyl glycidyl ether and carbon dioxide[19,20] as well as for propargyl-functional aliphatic polycarbonate obtained from carbon dioxide and glycidyl propargyl ether.[21]

Furthermore, other epoxides can also be used. [22] For example, Coates and coworkers synthesized multiple block copolymers via sequential addition of functionalized cyclohexene oxides with a high degree of control over the block length.[23,24]

Additionally, the norbornene group is a very interesting functionality, which can be used in many organic reactions due to its versatile reactivity. Dove and coworkers demonstrated the synthesis of norbornene-functional polycarbonates by ring-opening polymerization and the utilization for various post-polymerization reactions, like thiol-ene radical additions and Diels Alder reactions.[25]

To expand the scope of functional polycarbonates synthesized by the direct copolymerization of epoxides with carbon dioxide, we prepared norbornene-containing aliphatic polycarbonates from propylene oxide, 2-bicyclo[2.2.1]hept-5-ene-2-yl oxirane (BHO) and CO_2. An established cobalt salen complex was used as the catalyst and bis(triphenylphosphine)iminium chloride (PPNCl) as an ionic cocatalyst. This straightforward, modular approach is a general strategy for the synthesis of novel multifunctional PCs based on the copolymerization of different functional epoxides, PO and CO_2. Poly(propylene carbonate) is a polymer of increasing interest due to its utilization of CO_2 as a carbon resource and its particular materials properties.[10,26] However applications are still fairly limited due to its low glass transition temperature of about 40 °C, leading to cold flow at ambient temperature.[27] Introduction of crosslinks can improve the dimensional stability of poly(propylene carbonate) and therefore improve the thermal stability.[28] With the incorporation of pendant norbornene groups the polymer can be crosslinked, using metathesis polymerization and depending on the concentration of the reaction mixture, long chain branching occurs.



Scheme 1. Synthesis of the P((BHO-*co*-PO) C) copolymers from propylene oxide and 2-bicyclo[2.2.1]hept-5-ene-2-yl oxirane.

Experimental Section

Monomer and Catalyst Synthesis.

2-Bicyclo[2.2.1]hept-5-ene-2-yl oxirane was prepared as described in the Supporting Information and (R,R)-(salcy)$CoOBzF_5$ was prepared as described by Coates et. al.[15]

Representative procedure for the copolymerization of propylene oxide/2-Bicyclo[2.2.1]hept-5-ene-2-yl Oxirane /CO_2 here for P((BHO_8-*co*-PO_{38})-C) (Table 1 entry 5).

A 100 mL Roth autoclave was dried under vacuum at 40 °C and moved to a glovebox. (R,R)-(salcy)-$CoOBzF_5$ (11.7 mg, 0.0143 mmol), the cocatalyst (PPNCl) (8.2 mg, 0.014 mmol), PO (1.9 mL, 26 mmol) and 2-bicyclo[2.2.1]hept-5-ene-2-yl-oxirane (0.3 mL, 2.86 mmol) were placed in a glass tube with a Teflon stir bar inside the autoclave. The autoclave was pressurized to 25 bar CO_2 and was left to stir at 30 °C for 2 h. The reactor was vented at 30 °C, and the polymerization mixture was dissolved in chloroform (5 mL), quenched with 5% HCl solution in methanol (0.2 mL) and transferred to a dialysis tube. After dialysis against chloroform for two days (MWCO 1000 g/mol) the product was precipitated into methanol (50 mL). The polymer was collected and dried *in vacuo*. Yield 95 % ^1H NMR ($CDCl_3$-d_1, 300 MHz): δ (ppm) 6.09 (double bond), 5.00 (methine polymer backbone), 4.18 (CH_2 polymer backbone), 2.87-2.68 and 1.66-1.57 (norbornene side chain) and 1.32 (CH_3).

Representative procedure for the metathesis reaction of P((BHO8-co-PO38)-C) (Table 1 entry 5) with Grubbs 1 catalyst.

100 mg of P((BHO_8-*co*-PO_{38})-C) were dissolved in 100 ml dry and oxygen free CH_2Cl_2. 3 mg Grubbs 1 catalyst was added under argon and the reaction mixture was stirred for 18 h at

room temperature. The reaction was quenched with 1 ml ethyl vinyl ether and the solvent was removed under reduced pressure.

Additional reactions are described in the Supporting Information.

Results and Discussion

A. Synthesis and Molecular Characterization.

The synthetic strategy developed for the multifunctional aliphatic polycarbonate structures is shown in Scheme 1. The norbornene-functional epoxide monomer (2-bicyclo[2.2.1]hept-5-ene-2-yl oxirane) (BHO) was prepared in one step.[29] 5-Norbornene-2-carbaldehyde (a diastereomeric mixture of endo/exo) was employed as a starting material, and its reaction with S,S-dimethylthioylide, prepared by treatment of trimethylsulfonium iodide with potassium *tert*-butoxide, was performed. The reaction proceeded smoothly at room temperature to give the desired norbornene monomer BHO as a colorless liquid in 90% yield. Due to the presence of two chiral centers, BHO was obtained as a mixture of 4 diastereomers.[30] The ^{1}H NMR spectrum of the diastereomeric mixture of BHO confirmed the presence of C-C double bond and oxirane moiety in the molecule (Figure S1 and S2).

Table 1. Characterization Data for All Copolymer Samples Prepared

#	Sample	%Carbonate linkages[a]	% BHO[b]	M_n (g/mol) (SEC)[c]	PDI (SEC)	T_g °C[d]
1	P((BHO$_6$-*co*-PO$_{109}$)-C)	>99	5	12 300	1.4	24.5
2	P((BHO$_8$-*co*-PO$_{70}$)-C)	>99	10	8600	1.3	21.1
3	P((BHO$_7$-*co*-PO$_{53}$)-C)	>99	12	6800	1.2	20.0
4	P((BHO$_6$-*co*-PO$_{32}$)-C)	>99	15	4300	1.2	19.1
5	P((BHO$_8$-*co*-PO$_{38}$)-C)	>99	18	5500	1.2	17.4
6	P((BHO$_{14}$-*co*-PO$_{42}$)-C)	>99	25	6900	1.3	10.5
7	P((BHO$_9$-*co*-PO$_{19}$)-C)	>99	30	3600	1.2	5.3

Reaction conditions: 40 bar CO_2, 2h, 30°C [a)]Determined by ^{1}H NMR spectroscopy, [b)] BHO comonomer content in mol% [c)]Determined by SEC calibrated with a PEG standard in DMF at 40 °C, [d)]Glass transition temperature obtained from DSC.

All polymerizations were carried out under identical reaction conditions, i.e., room temperature and 50 bar CO_2 pressure with a (R,R)-(salcy)CoOBzF_5 catalyst and bis(triphenylphosphine(iminium chloride) (PPNCl) as a cocatalyst without any solvent. The catalyst was removed by precipitation in cold methanol as well as by dialysis in chloroform for two days.

Table 1 summarizes the results for the series of copolymers prepared in this study. The BHO comonomer content has been varied in a systematic manner from 0-30%. Unexpectedly, for higher BHO/PO ratios (> 30%) under the chosen reaction conditions no polymerization was observed. We are further exploring this unexpected limitation of the terpolymerization at present. From a comparison of the composition of the monomer feed and the copolymer composition characterized by ^{1}H NMR, it can clearly be stated that the monomer feed corresponds to the incorporated BHO/PO-ratio. Agreement of the BHO fraction in the copolymers with the composition of the epoxide monomer feed is confirmed by proton NMR from the comparison of the polycarbonate backbone signals b and a (δ = 5.00 and δ = 4.18 ppm), which were set to 1 and 2, with the double bond signal h at δ = 6.09 ppm. All other side chain signals (c-f) can be found between δ = 2.87-1.32 ppm.

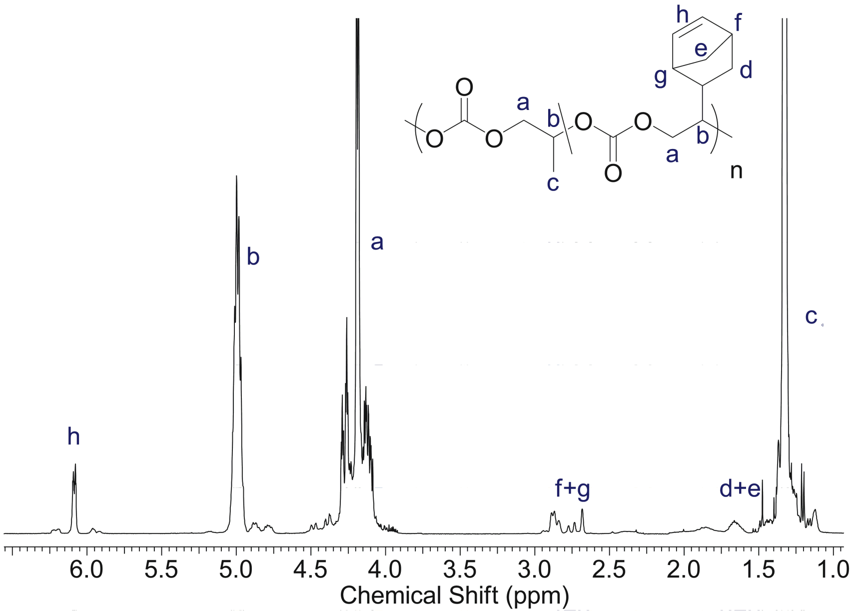


Figure 1: Typical ^{1}H NMR spectra of a norbornene functionalized copolymer (Table 1, sample **5**).

No BHO/PO structures without CO_2 incorporation, i.e., ether linkages, can be detected from the ^{1}H NMR spectra of the copolymers (Figure 1). A polyether backbone would generate additional resonances at $\delta = 3.5$ ppm. ^{13}C NMR spectroscopy also confirmed incorporation of BHO, PO and CO_2 into the copolymer and the typical carbonate resonance at $\delta = 154$ ppm can clearly be detected (**Figure S3**).

In addition to the NMR data, the incorporation of CO_2 into the polymer can be confirmed by IR spectroscopy (Figure S5). Only one carbonate band at 1738 cm $^{-1}$, which can be assigned to the C=O group of the linear carbonate, is detected. No bands typical for a cyclic carbonate, which are commonly observed at around 1790 cm^{-1}, were found in the IR spectra of the non-purified copolymers.

Molecular weights were in the range of 3600 to 12 300, and polydispersities were generally between 1.2 and 1.4 (samples 1-7). The resulting SEC traces are given in **Figure 2**. The molecular weight could not be calculated from ^{1}H NMR spectra, because no separate end group signals were detected. In some cases bimodal molecular weight distributions were observed, which is a typical phenomenon in the copolymerization of carbon dioxide with epoxides and has already been described in detail in other works.[15,31,32] However, the number average molecular weight of the samples decreases with increasing concentration of BHO. This is most probably related to a lower rate of insertion of the monomers affected by coordination of BHO to the catalyst and to its steric hindrance.

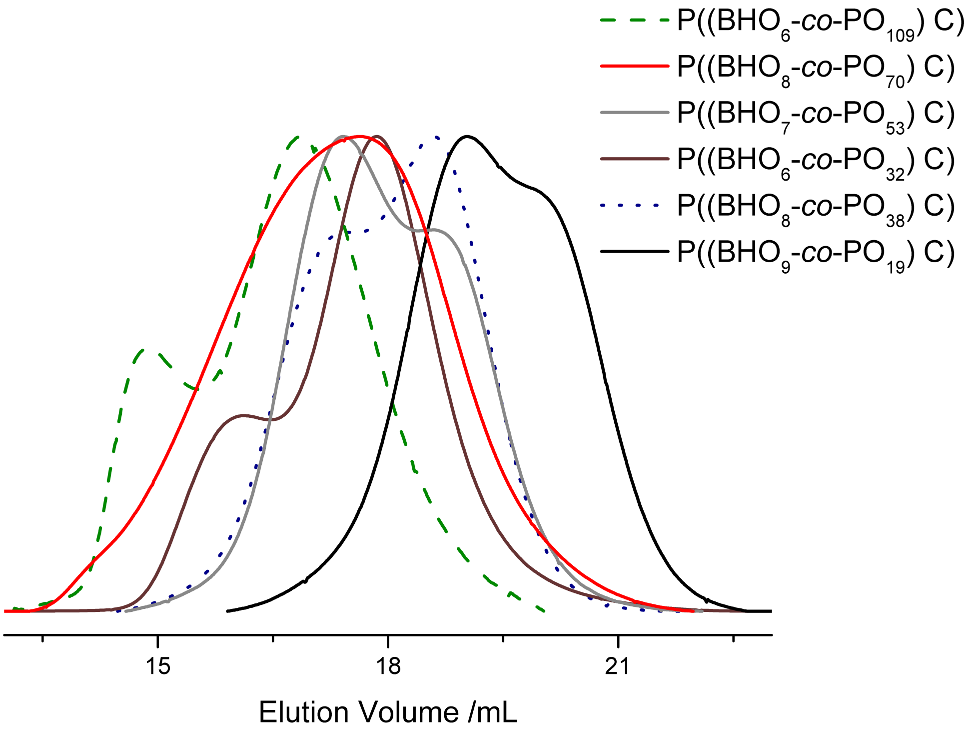


Figure 2. Representative SEC results for the selected polymers.

B. Thermal properties of the copolymers

All polycarbonate copolymers were clear, rubberlike materials and showed good solubility in chloroform, THF, DMSO and toluene at room temperature.

The thermal characteristics have been studied with differential scanning calorimetry (DSC) and are also given in **Table 1** (see also **Figure S5)**. The results lend further support to random incorporation of PO and BHO. All determined T_gs of the copolymers are slightly lower than the T_g of the PPC homopolymer and decrease with increasing BHO/PO ratio. At 5% BHO comonomer incorporation the T_g drops from 35°C to 24 °C, which further decreases to 5°C for sample 7 (with 30% BHO incorporated). These results render the herein presented copolymers interesting candidates for typical poly(propylene carbonate) (PPC) applications, since they possess similar processing properties as PPC, but offer additional options for modification and crosslinking.

C. Crosslinking and long-chain branching

Metathesis polymerization of the pendant norbornene groups was employed both for crosslinking and long-chain branching of the norbornene-functionalized polycarbonates. The reaction was carried out using the Grubbs 1 catalyst in CH_2Cl_2 for 18 hours with quantitative conversion. Depending on the concentration of the norbornene-functional polymer in the reaction mixture complete or partial crosslinking, resulting in long-chain branching, was obtained. Concentrations exceeding 30 mg polymer per mL solvent lead to insoluble, crosslinked materials, independent of the fraction of norbornene units incorporated along the polymer backbone. An organogel with dichloromethane was obtained, and the dry was polymer was insoluble in any solvent. (Figure S6) For highly diluted solutions below 1 mg/ml no reaction occurred and no intramolecular crosslinking was found.

Table 2. Characterization Data for long-chain branched polycarbonates obtained after metathesis reaction.

#	Sample	Concentration (g/ml)[a]	M_n (g/mol)[b]	PDI[b]	[η] (cm^3/g)[c]	α[c]	K[c]
A	P((BHO_{14}-*co*-PO_{42})-C)-1	5	65 600	2.21	10.86	0.22	0.87
B	P((BHO_{14}-*co*-PO_{42})-C)-2	10	81 500	2.59	16.56	0.39	0.14
C	P((BHO_{14}-*co*-PO_{42})-C)-3	25	133 000	2.43	21.66	0.32	0.37

[a])Concentration of the polymer solution during the reaction, [b)])Determined by SEC calibrated with a PS standard in THF at 40 °C, [c)]Determined by SEC calibrated with a PS standard in THF at 40 °C using a VISKOTEK H502 Differential Viscometer.

Solution concentrations between 5-25 mg/ml afforded long-chain branched polymers. **Table 2** summarizes the results for the series of samples obtained after metathesis reaction. ^1H NMR spectroscopy reveals that the norbornene side chain signals at δ = 6.09 ppm and δ = 2.87-1.32 ppm disappeared for all samples, and the typical signal for poly(norbornene) appeared (Figure S7 and S8). This confirms the conversion of the norbornene side groups through metathesis reactions and the formation of a partially cross-linked new polymer. The polycarbonate backbone on the other side is stable during the reaction as can also be seen in Figure S8.

The molecular weight of the samples increased with increasing concentration from 65 600 to 133 000 g/mol. The P((BHO_{14}-co-PO_{42})-C) starting material only had a molecular weight of 6900 g/mol before the metathesis polymerization. However the PDIs are still moderate in view of the subsequent metathesis transformation applied (2.21-2.59). (Figure 3).

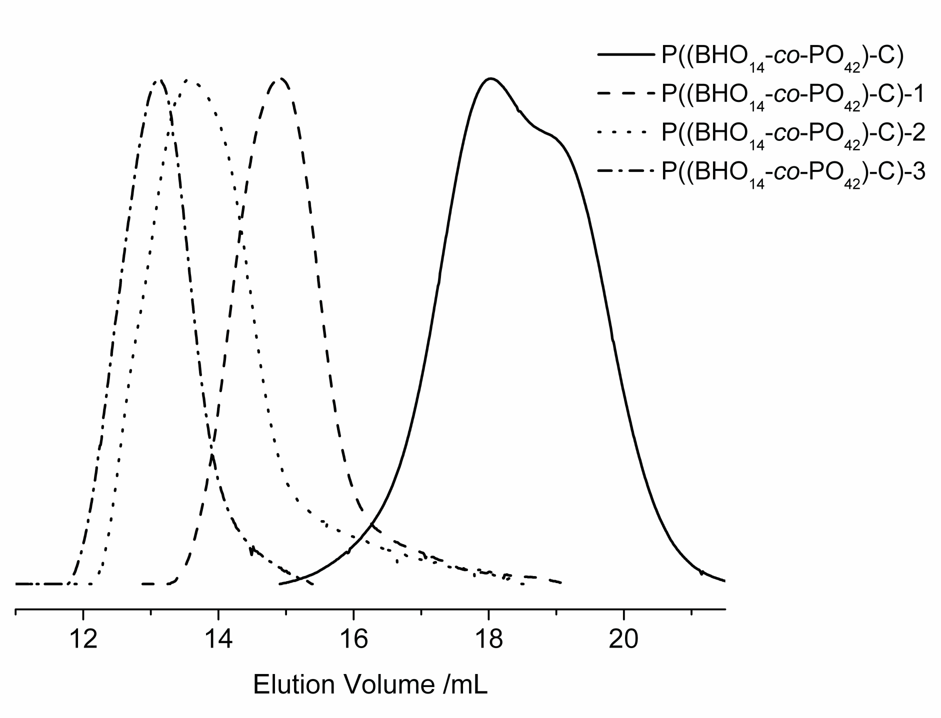


Figure 3. SEC Results of the long-chain branched polycarbonates in DMF with a PS standard. (Table 2, sample A-C)

To verify the branched character of the obtained samples the intrinsic viscosity [η] as well as the Mark-Houwink coefficients (α) were determined by size exclusion chromatography, using a VISCOTEK H502 differential viscometer and a polystyrene standard. The overall intrinsic viscosities for all samples are low in comparison to linear PPC despite the high molecular weights[31] and reflect the branched structure of the copolymers prepared. The lowest intrinsic viscosity (10.86 cm^3/g) was obtained for sample A with the lowest molecular weight, sample B and C showed higher values that can be attributed to increasing molecular weight (16.56 and 21.66 cm^3/g), which agrees well with expectation, since the intrinsic viscosity depends both on molecular weight and the extent of branching. The Mark-Houwink coefficients also give information concerning the molecular architecture and they can be calculated from the intrinsic viscosity via the Mark-Houwink Equation. Compared to linear polycarbonates the α parameters for all materials obtained after metathesis reaction are very low (<0.4) and on the order of magnitude known for hyperbranched polymers, indicating a compact structure.[33]

Conclusion

Norbornene-functionalized poly(propylene carbonate)s have been synthesized via terpolymerization of CO_2, propylene oxide and 2-bicyclo[2.2.1]hept-5-ene-2-yl oxirane as a bifunctional monomer, mediated by a cobalt salen complex and PPNCl as a cocatalyst. Polymers with 5-30% BHO and molecular weight between 3600 and 12,300 g/mol were obtained under solvent-free and mild reaction conditions (25 bar CO_2, 30 °C, 2h). The composition, thermal properties and subsequent metathesis transformation behavior of the synthesized polymers have been studied in detail. Crosslinking or long chain branching was performed using metathesis oligomerization. Poly(propylene carbonate) copolymers with rather high apparent molecular weights were generated by this route. Determination of the intrinsic viscosity as well as the α-parameter revealed that highly branched polymers with low intrinsic viscosities in the range of 10.86 to 21.66 cm^3/g were obtained. Depending on the concentration branching or crosslinking occurred. To the best of our knowledge, this approach, based on orthogonal polymerization techniques, represents the first example of a synthetic pathway for branched polycarbonates prepared directly from CO_2.

Clearly, the catalytic terpolymerization of bifunctional epoxides and carbon dioxide represents an interesting and highly modular alternative to the widely used ring-opening strategy that requires specifically designed six-membered cyclic carbonates to generate functional aliphatic polycarbonates.

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Supporting Information for: Branched Polycarbonates from CO_2 and a Bifunctional Epoxide via ROMP

Jeannette Hilf[1,†] and Holger Frey[*1]

1. Experimental Section

Instrumentation. ^1H NMR spectra (300 MHz and 400 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC300 or a Bruker AMX400 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent. For SEC measurements in DMF (containing 0.25 g/L of lithium bromide as an additive) an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column ($10^6/10^5/10^4$ g mol^{-1}), a UV (275 nm) and a RI detector. Calibration was carried out using poly(ethylene oxide) standards provided by Polymer Standards Service. DSC measurements were performed using a PerkinElmer DSC 8500 with PerkinElmer CLN2 in the temperature range from – 100 to 150 °C at heating rates of 10 K min^{-1} under nitrogen.

Reagents. (R,R)-(salcy)-Co^{II} and pentafluorobenzoic acid were obtained from Sigma Aldrich and used as received. 5-norbornene-2-carbaldehyde was purchased from Acros and used as recieved. 2-Bicyclo[2.2.1]hept-5-ene-2-yl-oxirane was distilled over CaH_2 under reduced pressure prior to use. Carbon dioxide (>99.99%) was used as received. All other reagents were purchased from Aldrich or Acros used as received.

Synthesis of 2-Bicyclo[2.2.1]hept-5-ene-2-yl-oxirane (BHO):

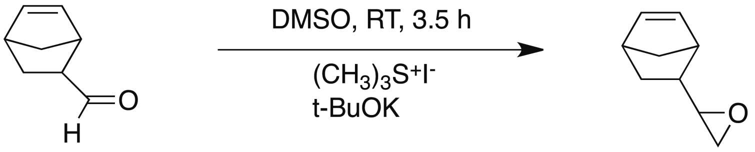

Figure S1. Reaction Scheme for the synthesis of 2-Bicyclo[2.2.1]hept-5-ene-2-yl Oxirane.

A solution of 5-norbornene-2-carbardehyde (35.6 mL, 0.30 mol) in DMSO (40 mL) was added to a DMSO solution (400 mL) of trimethylsulfonium iodide (79.6 g, 0.39 mol) under N_2

flow. To the resulting solution, potassium t-butoxide (39.2 g, 0.35 mol) was quickly added at room temperature. The solution was stirred at room temperature for 3.5 h and then poured into ice water (600 mL) and the mixture was stirred for 10 min. Diethyl ether (300 mL) was added to the mixture to extract the product. The organic layer was separated and washed by aqueous solution of NaCl twice, dried over $MgSO_4$, filtrated, and concentrated under reduced pressure. The residue was distilled in vacuo (12.7 mmHg, 71–72 °C) to obtain the monomer as a colorless liquid (33.2 g, 0.24 mol, 81% yield). ^{1}H-NMR (400 MHz, $CDCl_3$, δ in ppm): 6.22–5.98 (m, 2H, vinyl), 3.06–2.42 (m, 5H, -O-CH_2-, -O-CH-, 1-CH, 2-CH), 1.96–0.75 (m, 5H, 3-CH_2, 4-CH, 7-CH_2); ^{13}C-NMR ($CDCl_3$, δ in ppm): (mixture of 4 diastereomers) 137.64, 137.33, 137.30, 136.82, 136.15, 135.98, 132.71, 132.15, 55.71, 55.68, 55.65, 54.70, 49.64, 49.35, 47.16, 46.97, 46.63, 46.27, 45.98, 45.26, 45.19, 45.09, 44.82, 44.77, 42.47, 42.23, 42.20, 42.04, 41.98, 41.61, 41.47, 40.66, 29.77, 29.05, 28.69, and 28.42.

Synthesis of (R,R)-(salcy)-CoOBzF$_5$:

(R,R)-(salcy)CoOBzF$_5$ was prepared as described by Coates et. al.[15] Recrystallized (R,R)-(salcy)-Co^{II} and pentafluorobenzoic acid (0.42 g, 2 mmol) were added to a 50 mL round-bottomed flask charged with a Teflon stir bar. Toluene (20 mL) was added to the reaction mixture, and it was stirred open to air at 22 °C for 12 h. The solvent was removed by rotary evaporation at 22 °C, and the solid was suspended in 200 mL of pentane and filtered. The dark green material was dried *in vacuo* and collected in quantitative yield (1.5 g). ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 1.30 (s, 18H), 1.59 (m, 2H), 1.74 (s, 18H), 1.90 (m, 2H), 2.00 (m, 2H), 3.07 (m, 2H), 3.60 (m, 2H), 7.44 (d, 4J) 2.5 Hz, 2H), 7.47 (d, 4J) 3.0 Hz, 2H), 7.81 (s, 2H).

2. Representative ^{1}H NMR and ^{13}C NMR of P((BHO-*co*-PO) C) copolymers.

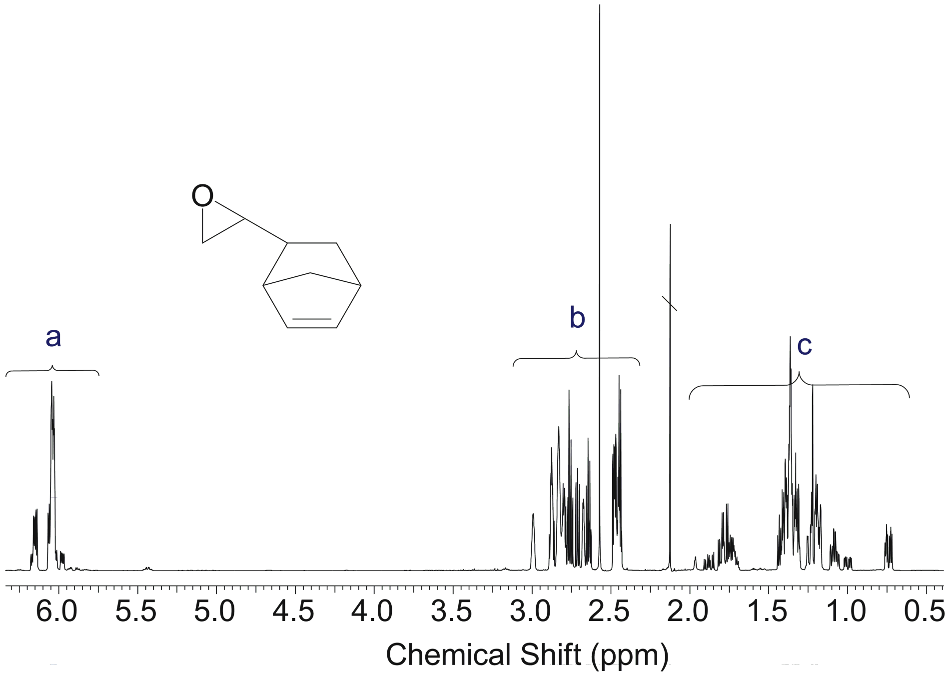

Figure S2. ^{1}H NMR spectrum of 2-Bicyclo[2.2.1]hept-5-ene-2-yl Oxirane in $CDCl_3$

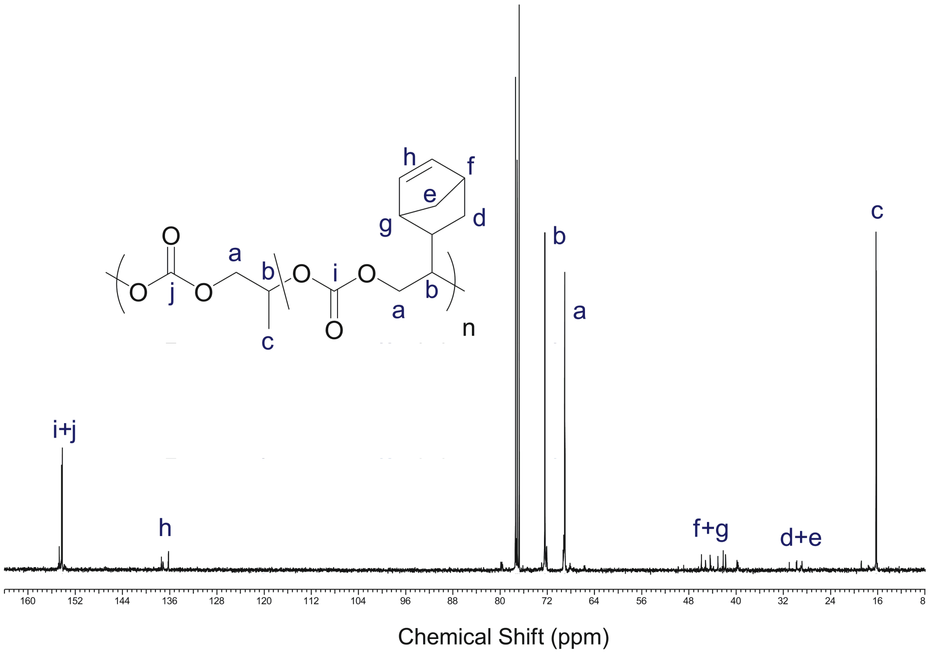

Figure S3. ^{1}H NMR spectrum of P((BHO$_7$-*co*-PO$_{53}$)-C) (sample 3, Table 1) in $CDCl_3$

3. IR spectra of the resulting polymers

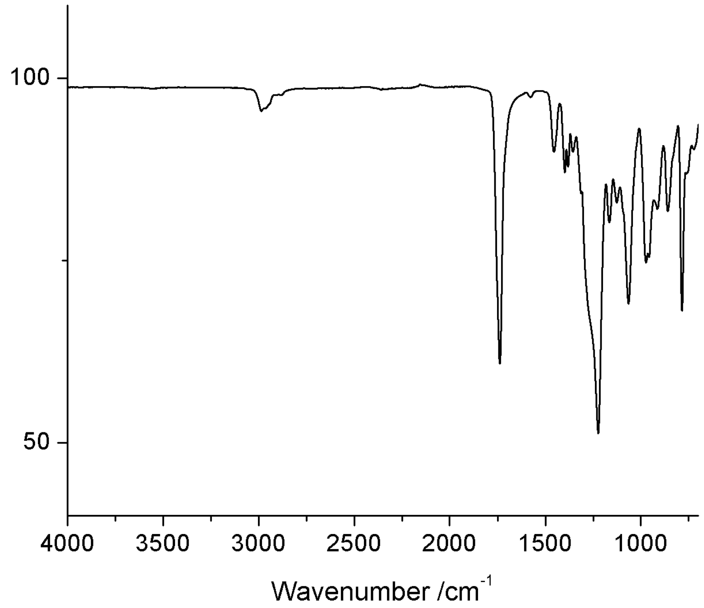

Figure S4. IR spectrum of P((BHO_7-*co*-PO_{53})-C) (sample 3, Table 1).

4. DSC Results of the resulting polymers

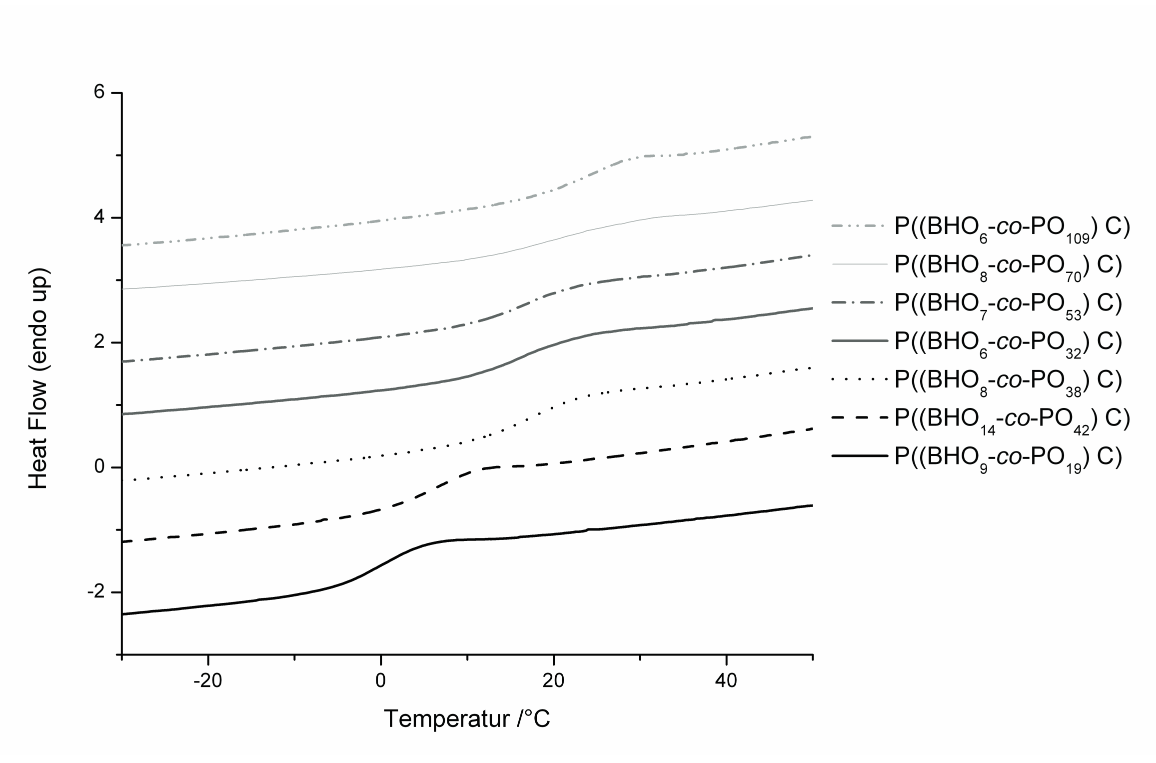

Figure S5. DSC Results of the series of functional polycarbonates

5. Crosslinking and long-chain branching

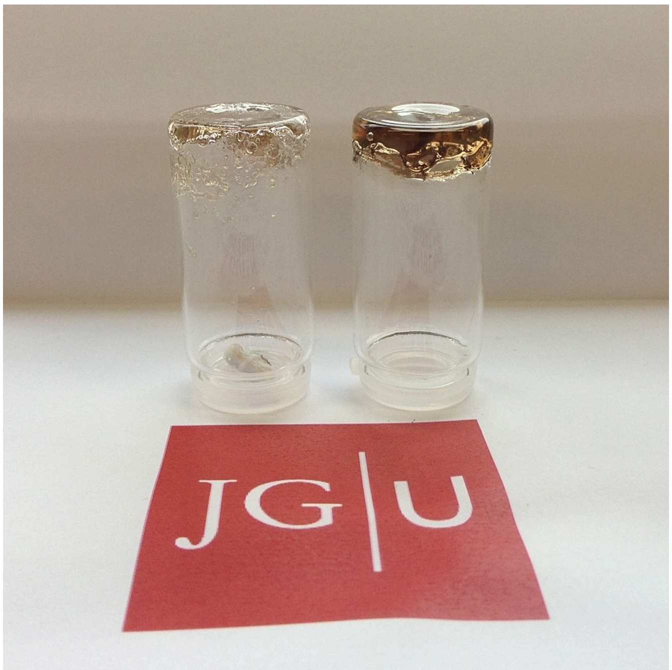

Figure S6. Completely crosslinked PPC samples, not soluble in any solvent, after reaction with Grubbs 1 catalyst in CH_2Cl_2.

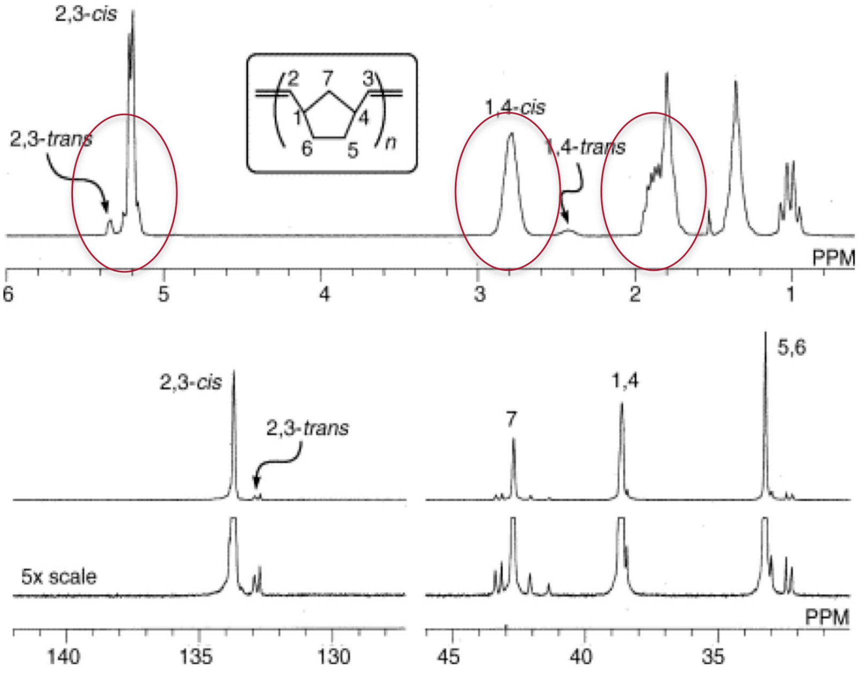

Figure S7. ^1H and ^{13}C NMR spectra of poly(norbornene) in $CDCl_3$.

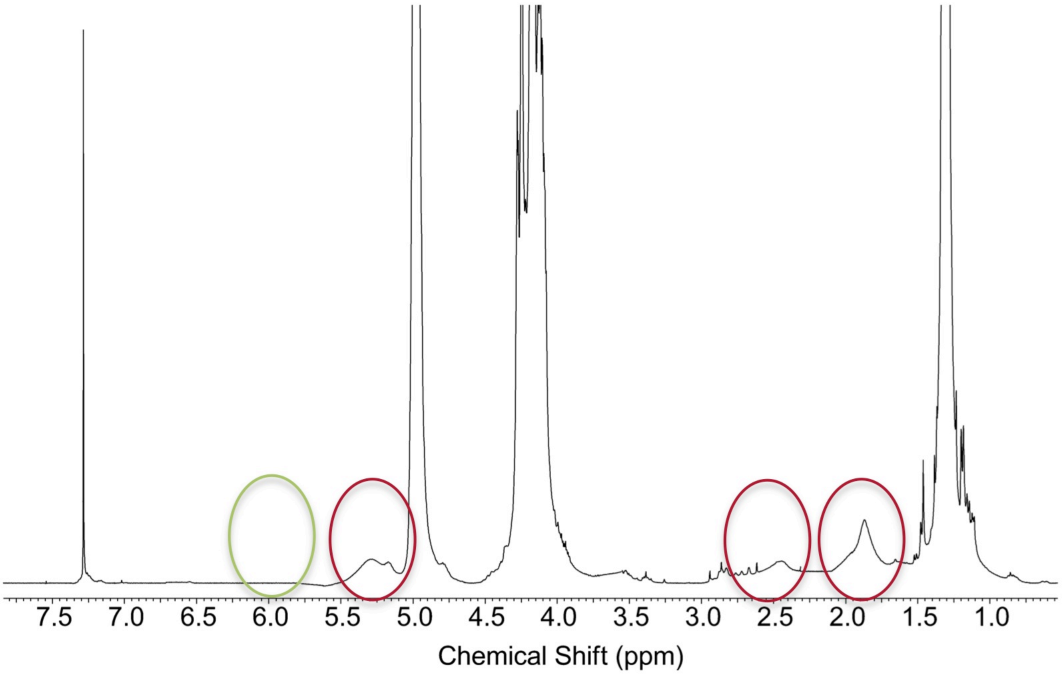

Figure S8. ^{1}H NMR spectrum of long chain branched P((BHO$_7$-*co*-PO$_{53}$)-C) (sample 3, Table 1) after reaction with Grubbs 1 catalyst.

Appendix

A.1. Stereocomplex Formation in Polylactide Multi-Arm Stars and Comb-Copolymers with Linear and Hyperbranched Multifunctional PEG

Jeannette Geschwind,[1,†] Sahas Rathi,[2] Christine Tonhauser,[1] Martina Schömer,[1] Shaw Ling Hsu,[2] E. Bryan Coughlin,[*2] and Holger Frey[*1]

[1]Institute of Organic Chemistry, Organic and Macromolecular Chemistry,
Duesbergweg 10-14,
Johannes Gutenberg-Universität Mainz, D-55099 Mainz, Germany

[2]Polymer Science and Engineering Department
University of Massachusetts Amherst, Amherst, MA 01003

[†]Graduate School Material Science in Mainz, Staudinger Weg 9, D-55128 Mainz, Germany

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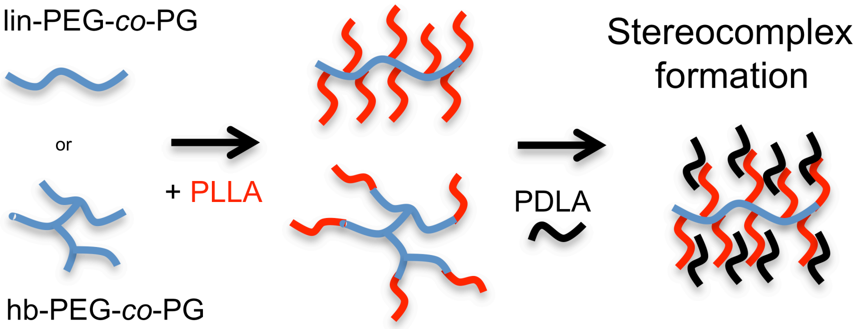


Abstract:

A systematic comparison between graft poly(L-lactide) copolymers with different topologies and their ability to form stereocomplexes with poly(D-lactide) has been performed. Comb- and hyperbranched copolymers based on functional poly(ethylene glycol) and poly(L-lactide) with molecular weights in the range of 2,000-90,000 g/mol and moderate molecular weight distributions (M_w/M_n= 1.08-1.37) were prepared via the combination of anionic and ring-opening polymerization. Two "topological isomers", a linear poly(ethylene oxide)/poly(glycerol) (PEG/PG) copolymer and a branched PEG/PG copolymer were used as backbone polymers. Furthermore, the stereocomplex formation between poly(D-lactide) and the hyperbranched and comb copolymers containing poly(L-Lactide) arms was studied. Stereocomplex formation was confirmed by DSC as well as by FT-IR and Raman spectroscopy.

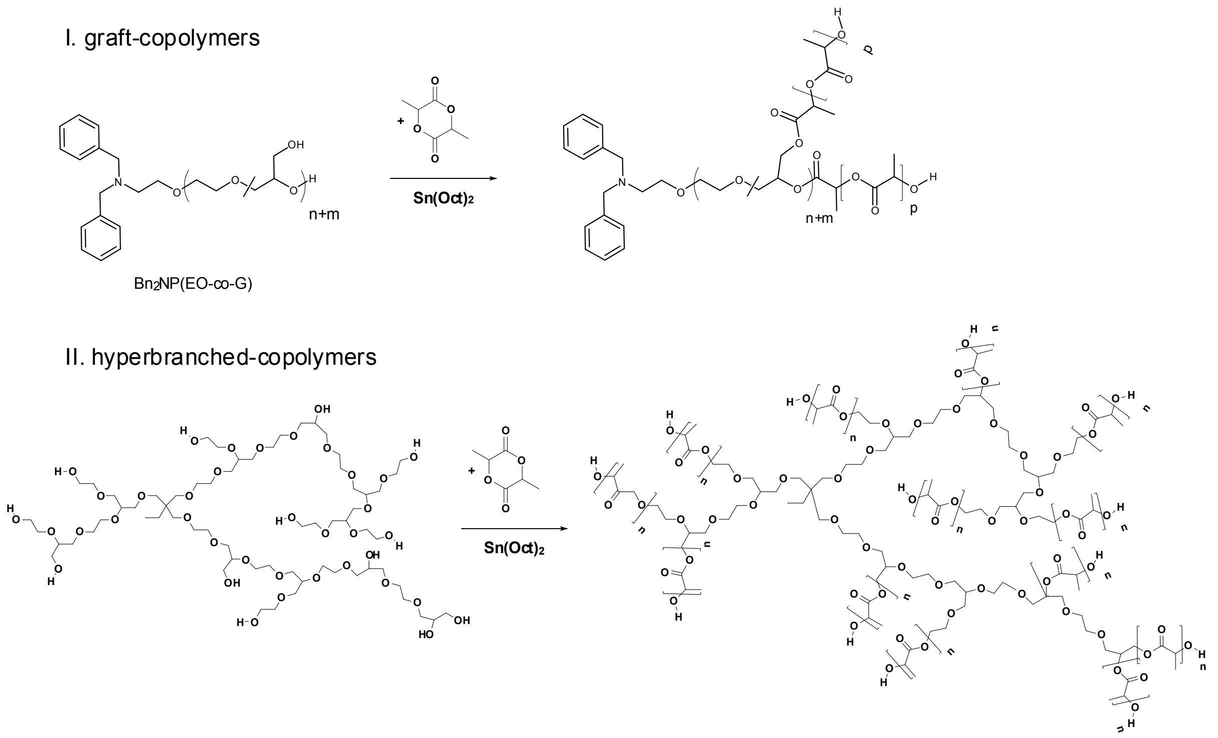
Introduction

Copolymers of poly(lactide) and poly(ethylene glycol) have attracted increasing attention, since they offer a unique combination of biodegradability, biocompatibility and hydrophilicity. They have been extensively studied since publication of seminal reports by Younes and Cohn in 1987.[1-4] A common method for the preparation of these systems is by using coordination-insertion ring-opening polymerization of lactide using $Sn(Oct)_2$ as the catalyst and poly(ethylene glycol) containing hydroxyl end-groups as a macro-initiator to obtain linear block copolymers. Furthermore star-shaped, [5-7] tree-shaped [8], and graft copolymers have been described. [9-12]

Branched polylactides have been synthesized e.g. by using pentaerythritol as an initiator yielding star-shaped PLA. [13] Hedrick *et al.* prepared well-defined star PLAs with up to 12 arms using multifunctional dendritic initiators derived from 2,2'-bis(hydroxymethyl)-propionic acid derivatives[14] and Albertson *et al.* used a spirocyclic tin catalyst to realize star-shaped PLLA.[15] Star-shaped poly(lactide) polymers with different comonomers, for example glycolide, are well described in the literature.[16-18] For example Vidovic *et al.* and Kissel *et al.* used poly(vinyl alcohol), which is hydrophilic, soluble in water and nontoxic to prepare graft-copolymers with PLA side chains that have also been tested as drug delivery systems.[19, 20] Xi and coworkers synthesized star-shaped PLA starting from hydroxyl-terminated PAMAM dendrimer cores.[21] Frey *et al.* employed well-defined hyperbranched polyglycerols (PGs) with narrow polydispersity and adjustable molecular weight.[22]

Blends of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) form stereocomplex crystallites with a distinct crystal structure, which melts at approximately 230 °C. The high melting temperature is attributed to strong van der Waals interactions that cause a specific energetic interaction-driven packing.[23,24] Hence, this stereocomplex has received attention as potential high performance biodegradable materials. Different methods for stereocomplex formation are described in literature.[25-37] The potential factors on stereocomplexation of PLLA and PDLA have been reported as well, including molecular weight of the constituents, mixing ratio, optical purities, and crystallization time and temperature.[23,38-40] For example thermal properties and crystallization behaviors of PLA and its enantiomeric blends have been analyzed by Opaprakasit et al.[41] The crystalline morphologies of PDLA/PLLA blends with equal molecular weight have been extensively studied.[39,42] Furthermore Hillmyer and coworkers studied poly(D-lactide)-poly(menthide)-poly(D-lactide) triblock copolymers as crystal nucleating agents for poly(L-lactide),[43] and Vert and coworkers studied stereocomplex induced gelation of PEG-PLLA block copolymers.[44]

There have been no studies in the literature dedicated to the influence of architecture on stereocomplex crystallization. The availability of the varied architecture PLLA-based copolymers provides an opportunity to study the impact of polymer architecture on PLA stereocomplex formation. In this work PEG-PLLA copolymers using PEG core molecules with different topologies were synthesized and characterized using NMR spectroscopy, FTIR spectroscopy, GPC, and DSC. Blends of these varied architecture PLLA co-polymers with PDLA were prepared and stereocomplex formation was studied in order to understand the impact of polymer architecture on PLA stereocomplex formation. The crystallization behavior of these blends was studied using isothermal and non-isothermal crystallization experiments.



Scheme 1: Synthesis of graft-PEG/PLLA copolymers based on functional PEG copolymers of different topology; top: linear; bottom: hyperbranched.[45-47]

Experimental Section

NMR Spectroscopy

^{1}H NMR spectra (300 MHz and 400 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded using a Bruker AC300 or a Bruker AMX400 spectrometer. All spectra were referenced internally to residual proton signals of the deuterated solvent at room temperature.

Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) of the samples was performed in DMF containing 0.25 $g \cdot L^{-1}$ of lithium bromide. An Agilent 1100 Series GPC Setup was used, including a PSS HEMA column ($10^{6}/10^{5}/10^{4}$ $g \cdot mol^{-1}$), and both UV (254 nm) and RI detectors. Calibration was performed with poly(ethylene oxide) standards provided by Polymer Standards Service (PSS). The eluent was generally used at 50 °C at a flow rate of 1 $mL \cdot min^{-1}$.

Differential Scanning Calorimetry (DSC)

DSC measurements were carried out using a Perkin-Elmer Thermal Analysis Controller TAC 7/DX in a temperature range from -100 to 200 °C, using heating rates of 4 and 10 $K \cdot min^{-1}$.

FT-IR Spectroscopy

FT-IR spectra were recorded on a Thermo Scientific iS10 FT-IR spectrometer, equipped with a diamond ATR unit and on a PerkinElmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR unit.

Raman Spectroscopy

A Jobin-Yvon Horiba LabRam HR800 dispersive Raman spectrometer was used to obtain Raman spectra of the samples. The 632.8 nm line of a helium-neon gas laser was used for excitation. Spectral resolution of less than 4 cm^{-1} was maintained near the laser line.

Optical Microscopy

Spherulite growth in the PDLA/PLLA-copolymer blends was observed using an Olympus (Tokyo, Japan) Polarized Optical Microscope (BH-2) equipped with a heating stage. The samples for optical observation were prepared by the following procedure. First, a sample of approximately 8 mg was placed between a glass slide and a Kapton film. The sample was heated to melt completely, it was then pressed to obtain a thin film and then cooled to room temperature. Subsequently, the sample was again melted and transferred to the hot stage maintained at 160 °C. All crystallization experiments were monitored using the birefringence developed for samples between two polarizers with an orthogonal polarization axis. Images of the spherulites and morphologies were taken with a digital camera.

Materials

All reagents and solvents were purchased from Acros and used as received, if not mentioned otherwise. Deuterated DMSO-d_6 and $CDCl_3$ were purchased from Deutero

GmbH. Ethoxyethyl glycidyl ether (EEGE) was prepared as described by Fitton *et al.,*[48] dried over CaH_2 and freshly distilled before use. *N,N*-Dibenzyl-2-aminoethanol was synthesized as reported previously.[49] L-lactide (98%, Aldrich Chemical Co., LLA) and stannous(II)-2-ethylhexanoate (95%, Aldrich Chemical Co., $Sn(Oct)_2$) were used as received.

Synthesis

Random copolymers of EO and glycidol as well as random copolymers of EO and EEGE were prepared as described previously.45, 46

Lactide Polymerization

The general synthetic procedure is exemplified for the graft copolymers (sample 13) and was performed in an analogous manner for all other linear, star and hyperbranched copolymers prepared. The multifunctional backbone polymer poly(ethylene glycol) (M_n 12000 g/mol) 0.5 g was dried under vacuum for at least 4 h in a Schlenk tube (reaction vessel). L-lactide (2.88 g, 20 mmol) was added, melted at 120°C and stirred under nitrogen atmosphere. Subsequently, the required amount of $Sn(Oct)_2$ catalyst (0.007 ml, 0.02 mmol, as a 10 vol.% solution in toluene) was injected into the reaction vessel. Stirring was continued, and after 8 hours the reaction mixture solidified. At the end of the reaction the mixture was allowed to cool. The solid product was dissolved in chloroform (20 mL), precipitated in hexane and dried *in vacuo*. In some cases, analysis of the copolymers by SEC showed a minor low molar mass fraction or some unreacted monomer that could be removed by dialysis in chloroform. (benzoylated dialyzing tubes (Sigma Aldrich) MWCO 1000 g/mol) The yields were greater than 90%.

Blend Preparation

Blends of the PLLA copolymers and PDLA were prepared by separately dissolving each component in dichloromethane. The two solutions were then mixed in the desired compositions and stirred vigorously. After 2 h the mixture was precipitated into a tenfold excess of cold hexane. The solid blend was filtered and dried *in vacuo* for at least 12 h.

Results and Discussion

Synthesis of the copolymers

In this investigation multi functional PEG copolymers with varying glycerol content and different topology were used to synthesize graft- or star-copolymers. Depending on the amount of hydroxyl functionalities the number of side chains can be varied. Different poly(lactide) chain lengths were obtained by varying the monomer to hydroxyl group ratio. The synthesis of the copolymers was achieved via a core-first approach, performing controlled ring-opening polymerization of L-lactide on a multifunctional polyether used as an initiator backbone polymer. For linear graft-copolymers the macroinitiator is synthesized from EO and EEGE (ethoxy ethyl glycidyl ether). Acidic removal of the ethoxy ethyl protecting group yielded linear (P(EO-*co*-G)), which compositionally is a linear poly(ethylene glycol) with a varying number of hydroxyl groups, where lactide polymerization can be initiated. On the other hand the hyperbranched macroinitiator is prepared via a direct copolymerization of glycidol and ethylene oxide.

Characterization of PLLA stars based on hyperbranched PEG was already described in a recent work.[32] *hb67* P(EO-*co*-G) for example stands for a hyperbranched poly(ethylene oxide) (PEO) with 67 hydroxyl groups (samples 17-19), *hb128* P(EO-*co*-G) for a hyperbranched PEO with 128 hydroxyl groups (samples 14-16), respectively. For the hyperbranched samples, polymerizations of L-lactide with $Sn(Oct)_2$ did not reach full conversion (about 90%) due to solidification of the reaction mixture. Residual monomer was therefore removed by dialysis in chloroform.

The polymers have been characterized by NMR spectroscopy and SEC, as summarized in Table 1.

Table 1: Comparison of molecular weights obtained from NMR and SEC of the graft-copolymer samples.

#	Sample	LLA units[a)]	M_n g/mol (SEC)[b)]	PDI (SEC)
1	$Bn_2NP(EO_{335}$-*co*-$G_{11})$	-	6 200	1.17
2	$P((EO_{335}$-*co*-$G_{11})$-*g*-LLA_{97}	97	69 000	1.13
3	$Bn_2NP(EO_{234}$-*co*-$G_{26})$	-	5 400	1.16
4	$P((EO_{234}$-*co*-$G_{26})$-*g*-$LLA_{38})$	38	41 000	1.28
5	$P((EO_{234}$-*co*-$G_{26})$-*g*-$LLA_{22})$	22	24 000	1.37
6	$Bn_2NP(EO_{71}$-co-$G_{28})$	-	2 000	1.20
7	$P((EO_{71}$-co-$G_{28})$-*g*-LLA_{18}	18	10 000	1.28
8	$Bn_2NP(EO_{193}$-*co*-$G_{32})$	-	4 400	1.29
9	$P((EO_{193}$-*co*-$G_{32})$-*g*-$LLA_{48})$	48	54 000	1.14
10	$P((EO_{193}$-*co*-$G_{32})$-*g*-$LLA_{22})$	22	37 000	1.33
11	$Bn_2NP(EO_{307}$-*co*-$G_{90})$	-	6700	1.19
12	$P((EO_{307}$-*co*-$G_{90})$-*g*-$LLA_{68})$	68	82 000	1.17
13	$P((EO_{307}$-*co*-$G_{90})$-*g*-$LLA_{28})$	28	51 000	1.08
14	*hb128* P(EO-*co*-G)	-	25 000	1.79
15	*hb128*-P((EO-*co*-G)-*g*-$LLA_{42})$	42	90 000	1.13
16	*hb128*-P((EO-*co*-G)-*g*-$LLA_{24})$	24	67 000	1.21
17	*hb67* P(EO-*co*-G)	-	16 000	1.96
18	*hb67*-P((EO-*co*-G)-*g*-$LLA_{42})$	42	85 000	1.12
19	*hb67*-P((EO-*co*-G)-*g*-$LLA_{20})$	20	59 000	1.17

a) Determined by ^1H NMR and ^{13}C NMR (hyperbranched samples) b) in DMF vs. PEG-standards using the RI detector.

In Figure 1 the ^1H NMR spectrum of sample 10 ($P((EO_{234}$-*co*-$G_{26})$-*g*-$LLA_{22})$) is shown exemplarily ($CDCl_3$). In addition to the PEG backbone signal (d = 3.60 ppm), the resonances for poly(L-lactide) or poly(D,L-lactide) can be found (d = 5.17 and 1.57 ppm). The lactide side chain length and also the molecular weight were determined by comparison of the integration values from the lactide chain end-group resonances (d = 4.33 ppm) to those from poly(lactide) methine resonances (d = 5.17 ppm). Other information obtained from the spectrum is whether the reaction proceeds to complete conversion since the resonances of the methine protons in the monomer and the polymer are different. Therefore monomer signals disappear with complete conversion.

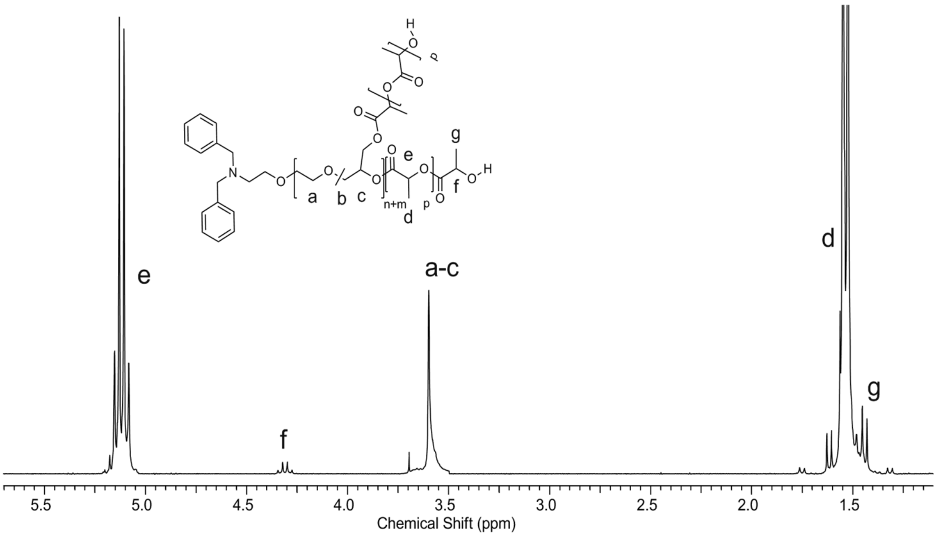


Figure 1. ^{1}H NMR of sample P((EO$_{234}$-*co*-G$_{26}$)-*g*-LA$_{22}$) in CDCl$_3$.

In this case the side chain lengths for the star-shaped samples with a hyperbranched PEG core could not be calculated from the ^{1}H NMR, because the chemical shifts the of poly(lactide) end-group signal (d = 4.33 ppm) and the signal of the hyperbranched core overlap. Instead, inverse gated ^{13}C NMR spectroscopy was used to confirm the structure of the star shaped copolymer. However, ^{13}C NMR spectroscopy provided further important information for the characterization of the hyperbranched polymers, viz. the lactide side chain degree of polymerization.

For the linear copolymer no signals assignable to $-O-CH_2-\underline{C}H_2-OH$ or $-O-\underline{C}H_2-CH_2-OH$ carbon atoms belonging to hydroxyl terminated PEG groups (d =18.2 ppm) were detected. This shows that PEG hydroxyl groups were transformed quantitatively, and no residual PEG copolymer is present in the final product.

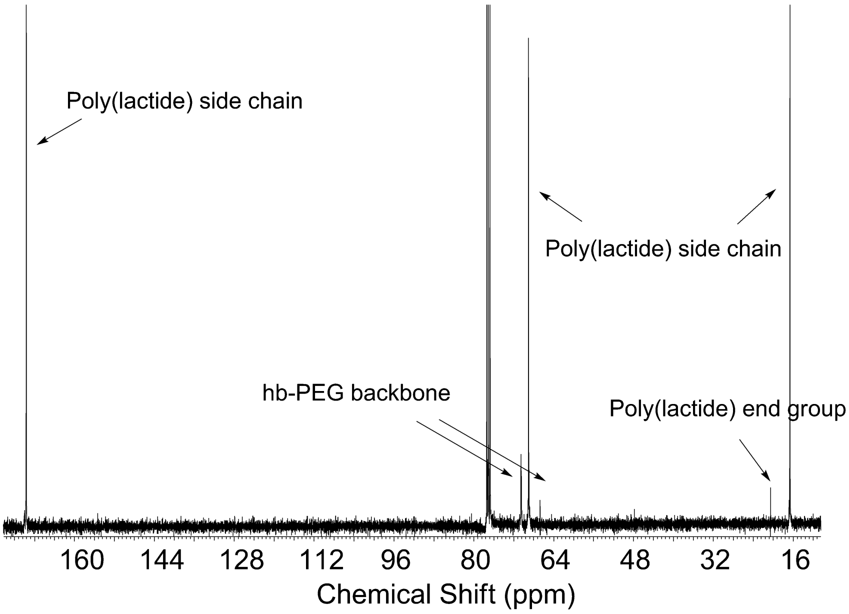


Figure 2. ^{13}C NMR of sample *hb67*-P((EO-*co*-G)-*g*-LLA$_{42}$) (sample 18) in $CDCl_3$.

The molecular weights (M_n) for all synthesized copolymers were higher than that of the starting backbone copolymer and the distributions were monomodal. This confirms that the products were not mixtures of different homopolymers, but actually copolymers. The obtained polydispersities were low to moderate (between 1.08 and 1.37), as expected for this type of ring-opening polymerization. In general, a deviation of the molecular weights determined by SEC and the calculated values based on the NMR results was found. The observed effect is due to several reasons. First of all, samples with lactide side chains differ from linear poly(ethylene oxide), which was used as a standard polymer for calibration. Furthermore, highly branched or graft architectures were synthesized. The hydrodynamic radius, which determines the elution volume of the polymer, does not increase linearly with the increase in mass. Generally star-shaped or hyperbranched copolymers show a lower hydrodynamic volume in solution compared to linear analogues of similar molar mass. This explains why the strongest underestimation of molecular weight is found for the most highly branched systems with the longest side chains. As can be seen for the hyperbranched samples the PDI decreases after the lactide grafting.

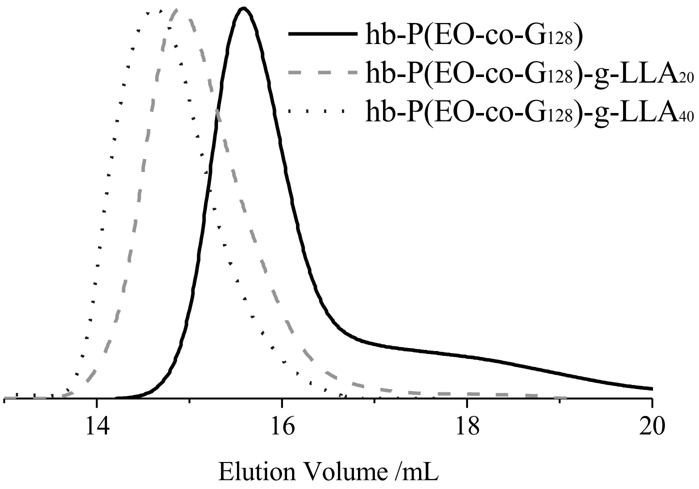


Figure 3: Typical SEC traces of some of the hyperbranched copolymers. (samples 14-16)

Thermal characterization with DSC

Table 2. DSC results of the graft copolymer samples.

#	Sample	T_g °C	T_m °C	Δ H_m (J/g)	χ^c a
1	$Bn_2NP(EO_{335}$-*co*-$G_{11})$	-48			
2	$P((EO_{335}$-*co*-$G_{11})$-*g*-LLA_{97}	38	159	51.49	0.51
3	$Bn_2NP(EO_{234}$-*co*-$G_{26})$	-59			
4	$P((EO_{234}$-*co*-$G_{26})$-*g*-$LLA_{38})$	36	137	50.30	0.50
5	$P((EO_{234}$-*co*-$G_{26})$-*g*-$LLA_{22})$	29	125	40.27	0.37
6	$Bn_2NP(EO_{71}$-co-$G_{28})$	-56			
7	$P((EO_{71}$-co-G28)-*g*-LLA_{18}	33	134	28.54	0.31
8	$Bn_2NP(EO_{193}$-*co*-$G_{32})$	-53			
9	$P((EO_{193}$-*co*-$G_{32})$-*g*-$LLA_{48})$	45	158	52.52	0.54
10	$P((EO_{193}$-*co*-$G_{32})$-*g*-$LLA_{22})$	33	146	26.95	0.26
11	$Bn_2NP(EO_{307}$-*co*-$G_{90})$	-49			
12	$P((EO_{307}$-*co*-$G_{90})$-*g*-$LLA_{68})$	42	154	49.23	0.51
13	$P((EO_{307}$-*co*-$G_{90})$-*g*-$LLA_{28})$	39	137	12.97	0.13

The thermal behavior of the prepared copolymers has been quantified by differential scanning calorimetry (DSC). The results of the second heating scan, glass transition temperature (T_g), melting point and degree of crystallization of all L-lactide graft-copolymers are shown in Table 2.

In all cases no glass transition temperature or melting point for the PEG or PLLA homopolymer constituents were detected. These results indicate that PEG/PLLA copolymers with no homopolymer contaminants were obtained, as determined by the SEC data.

In general, glass transition temperatures and melting points of both star and brush structures increase with increasing amount of polylactide side chains and the side chain degree of polymerization. The melting temperature shifts to a higher temperature with an increasing L-LA/PEG ratio. Compared to pure PLLA (T_m= 170-180 °C) the melting temperatures are lowered for the copolymers. This can be explained by two factors, i) by the backbone polymer affecting the crystallization, and ii) by the molecular architecture of the copolymers. In all samples the poly(lactide) side chain degree of polymerization varies between 14 and 50 lactic acid units. Therefore oligomers linked to a PEG backbone are present in the samples, and oligomer melting points are in general lower than polymer melting points.[50] Similar results were found for the star-shaped samples containing a hyperbranched core, as reported recently.[47]

Star copolymers based on PLLA and PEG showed a decrease in degree of crystallization by increasing the number of branches. As for the graft-copolymers melting points and glass transition temperatures decrease for shorter side chain degree of polymerization. A difference can also be found between the different kinds of branched architectures. The graft-copolymers 2, 4, 5, and 7 showed a higher degree of crystallization than star-shaped copolymers with a hyperbranched core. So not only the composition, but also the architecture of the copolymers affects their thermal behavior. The degree of crystallization was calculated from the following equation:

$$\chi c = \Delta Hm / \Delta H^{\infty} m * f^{LLA} w$$

With Δ H_m as the area under the melting endotherm, f^{LLA} as the weight fraction of the PLLA and Δ H^{∞}_m as the theoretical heat of fusion of the PLLA homopolymer at 100% crystallinity. The Δ H_m value (93 J/g) was obtained from the literature.[50]

The reduced degree of crystallization with branching is due to an increase in free chain-ends, disrupting the fold pattern of the crystal. ΔH_m decreases as the number of arms increases, but increases with longer side chains. This can also be observed by looking at the crystallization peak. Figure 4 shows the DSC curves for two graft-copolymers and two hyperbranched samples containing poly(L-lactide) side chains. For the graft-copolymers the crystallization peak is very sharp and occurs at lower temperatures, whereas for the hyperbranched samples the crystallization peak is broad. This can be explained by the hyperbranched topology. In the hyperbranched samples not all side chains are located at the exterior of the polymer because hyperbranched PEG contains some hydroxyl groups in the interior. Consequently, the growing polylactide side chain cannot easily adopt conformations that permit interaction with other chains.

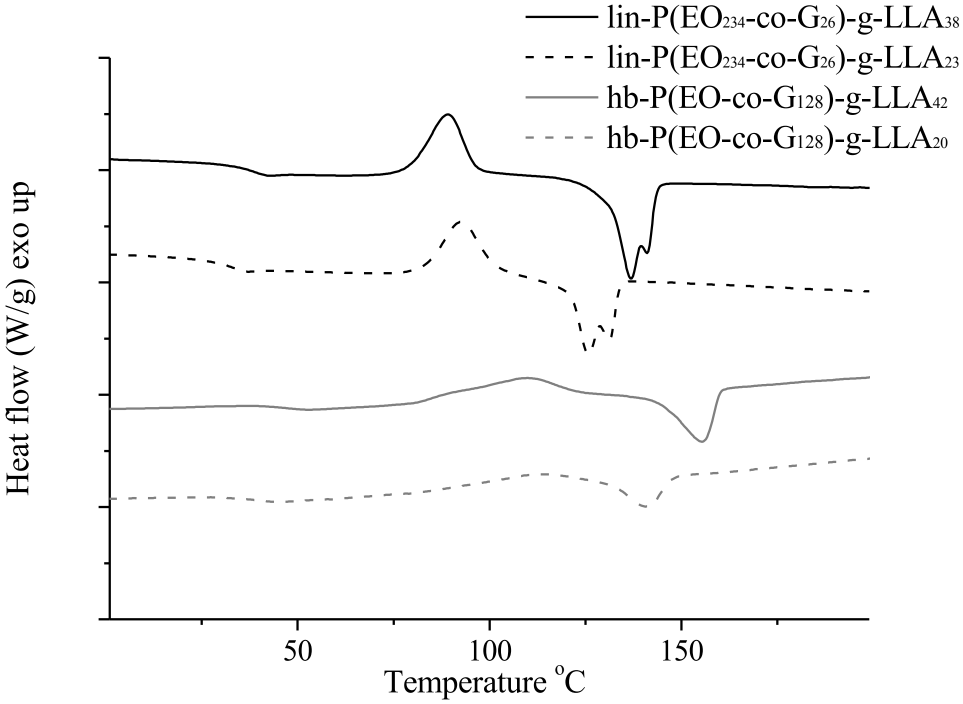


Figure 4. DSC results for some typical graft- and hyperbranched samples.

The interaction between the poly(lactide) side chains are reduced because of a more open star structure for highly branched architectures. It was noted that the melting peak was broadened, as the degree of branching increased. This was more pronounced for the hyperbranched copolymers compared to the graft-copolymers (Figure 4). Two melting endotherms are observed in most of the graft-copolymers. This phenomenon has been interpreted by the presence of two different crystal structures, α and the less stable α'structure.[50]

The crystallization and glass transition temperature of the PEG within the copolymers are not detected in the DSC traces because of its low mass fraction. Both PEG and PLLA are able to crystallize and the crystallization behavior of crystalline-crystalline block copolymers is sophisticated. Several studies report that poly(ethylene glycol) and poly(L-lactide) are partially miscible, so no phase separation occurs.[51, 52] Because of this only one melting point and one glass transition, lying between that of the two homopolymers, can be detected, as can be seen in Table 3.

Blending and Stereocomplexation

To study the influence of the prepared copolymers for lactide homopolymer materials a blend was prepared. For blend preparation solution mixing was used. Three different copolymers with a constant degree of polymerization for the polylactide side chains of about 40 lactic acid units and similar molecular weights of the PEG macroinitiator (M_n approx. 12,000 g/mol) and PDLA homopolymer (30 000 g/mol) were used for blending.

The following abbreviations were used to simplify the blend names. $P((EO_{234}\text{-}co\text{-}G_{26})\text{-}g\text{-}LLA_{38})$ is $graft_{10}$, $P((EO_{193}\text{-}co\text{-}G_{32})\text{-}g\text{-}LLA_{48})$ is $graft_{15}$ and $hb_{67}\text{-}P((EO\text{-}co\text{-}G)\text{-}g\text{-}LLA_{40})$ is hb_{20}. The subscript numbers indicate the amount of glycerol monomers in wt% (glycerol either linear or branched) present in the backbone of the copolymer. Furthermore, a triblock copolymer with PEG mid-block and polylactide end-blocks was used for blending to compare the different architectures. The compositions of the blends prepared are shown in Table 3. As it can be seen from Table 3, the $graft_{10}$, $graft_{15}$ and hyperbranched blends containing similar amounts of PEG and PLLA and allowed for the investigation of the impact of polymer architecture on stereocomplex formation. The triblock blends contain much higher amounts of PEG and lower amounts of PLLA. Thus, the PLLA/ PDLA ratio is similar in the first three blends, while it is much lower in the triblock copolymer/ PDLA blends.

Table 3. Composition of the blends prepared.

#	**Name**	**architecture**	**glycidol units**	**blend PEG content (wt%)**	**blend PLLA content (wt%)**
A	PDLA/tribl(25%)	Triblock	0	17.50	7.50
B	PDLA/graft$_{10}$(25%)	Graft	10	1.75	23.25
C	PDLA/graft$_{15}$(25%)	Graft	15	1.25	23.75
D	PDLA/hb$_{20}$(25%)	Hyperbranched	20	2.00	23.00
E	PDLA/tribl(40%)	Triblock	0	28.00	12.00
F	PDLA/graft$_{10}$(40%)	Graft	10	2.80	37.20
G	PDLA/graft$_{15}$(40%)	Graft	15	2.00	38.00
H	PDLA/hb$_{20}$(40%)	Hyperbranched	20	3.20	36.80

Analysis of the as-precipitated blends

In order to analyze the structure of the blends formed upon solution precipitation, DSC was performed on the as-precipitated blends (figure 5). Stereocomplex formation between PDLA and PLLA can be studied by differential scanning calorimetry, since the stereocomplex melting point is about 50 °C higher compared to that of pure poly(lactide) homopolymer. Quantitative information on the thermal behavior can be obtained by comparing the melting enthalpies of the stereocomplex crystals and the homopolymer crystals. As it can be seen from the melting enthalpy of the homopolymer crystals and stereocomplex crystals in figure 5, a mixture of stereocomplex crystals and homopolymer crystals are formed in case of the 25% blends. Because of the low content of PLLA in the triblock copolymer blend the amount of stereocomplex crystals is lower than the amount of triblock crystals. For the graft$_{10}$, graft$_{15}$ and hyperbranched blends the amount of stereocomplex crystals decreases and homopolymer crystals increases with increase in graft density indicating that stereocomplex formation is hindered with increasing graft density. In case of the 40% blends, only the stereocomplex crystals are formed in the graft$_{10}$ and graft$_{15}$ blends while both stereocomplex and homopolymer crystals are formed in case of the hyperbranched blends. From the DSC data on the as-precipitated blends we can conclude that stereocomplex formation during solution precipitation is hindered with increasing graft density and branching.

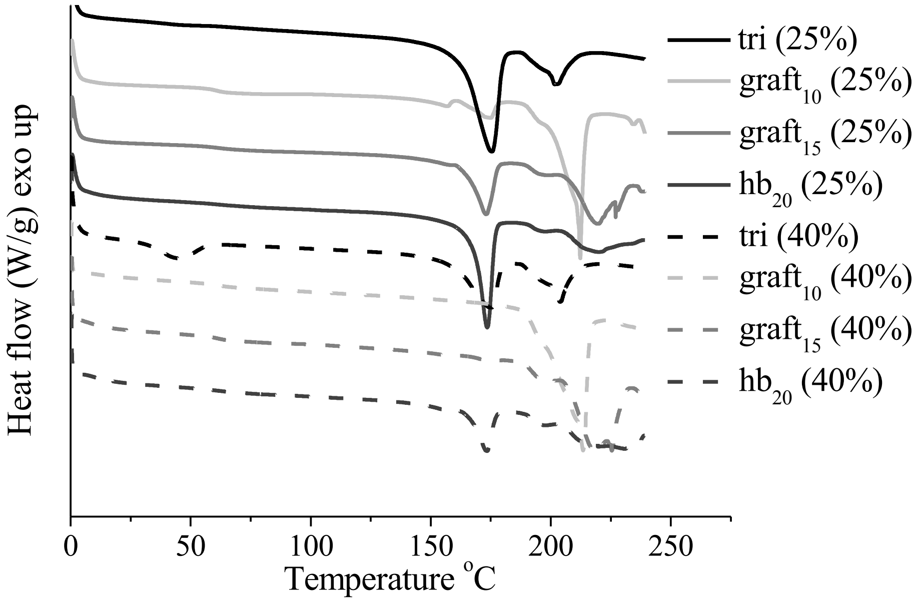


Figure 5. DSC traces of as precipitated blends (1st heating).

Non-isothermal crystallization

Table 4. DSC results for all prepared blends. (2nd heating run; heating rate of 20 °C/min was used. The measured temperature range was 0 °C to 250 °C (for some samples only 240 °C, due to degradation of the sample at higher temperatures)).

#	Sample	T_g °C	T_{m1} °C	T_{m2} °C	ΔH_{m1} J/g	ΔH_{m2} J/g
A	PDLA/tribl(25%)	X	169	200	23	9
B	PDLA/tribl(40%)	X	168	200	24	9
C	PDLA/graft$_{10}$(25%)	49	162	201	3	29
D	PDLA/graft$_{10}$(40%)	45	X	194	X	41
E	PDLA/graft$_{15}$(25%)	46	165	221	13	26
F	PDLA/graft$_{15}$(40%)	44	X	220	X	54
G	PDLA/hb$_{20}$(25%)	54	X	212	X	4
H	PDLA/hb$_{20}$(40%)	51	X	209	X	22

In order to further study the influence of polymer architecture on stereocomplex formation, isothermal and non-isothermal crystallization experiments were performed. The non-isothermal crystallization experiment was performed in the DSC. The as-precipitated blends were heated above the melting point of the stereocomplex to erase the thermal history, cooled at 20 °C/min to 0°C and then reheated to evaluate the extent of the crystal formation during the cooling cycle. The results of the second heating scan are shown in Table 4 and Figure 6.

All prepared blends, regardless of the topology of the functional PEG, showed stereocomplex formation and an elevated melting point between 194 and 220 °C. Depending on PLLA/PDLA ratio different amounts of stereocomplex crystals are formed. In theory, for equimolar blends with $\chi_D = 0.5$ the melting enthalpy of stereocomplex crystallites reaches its maximum and decreases with a deviation of χ_D from 0.5 and the melting enthalpy of homocrystallites increases. The mixing ratio χ_D is defined as follows:

χ_D = Weight of PLLA/Weights of PLLA plus PDLA

The data suggests that the melting enthalpy for stereocomplex crystallites is always higher for the 40% blends than for the 25%, since more PLLA is present in the latter samples, so the mixing ratio is closer to 0.5. In the graft-copolymer blends with 40% copolymer as well as in the hyperbranched copolymer blends with 40% copolymer the mixing ratio is almost 0.4, as the blends contain less than 2% PEG backbone polymer. Because of the high PLLA/PDLA ratio only the stereocomplex crystals are formed in the graft-copolymer blend samples. In case of the hyperbranched copolymer blends, despite a similar PLLA/ PDLA ratio to the graft copolymer blends, stereocomplex melting enthalpy is much lower compared to the graft copolymer blends. Moreover, the stereocomplex crystallization occurs during the heating cycle in the hyperbranched copolymer blends, indicating that stereocomplex crystallization is hindered in these blends as the stereocomplex crystallization could not occur during the cooling cycle like in the other blends.

The triblock copolymer blends showed a different behavior as the amount of PEG is very high compared to the graft- and hyperbranched copolymer blends. For the triblock copolymer blends two melting peaks are observed, as for the graft and hyperbranched blends. However, the melting enthalpy of the homopolymer is considerably higher than the melting enthalpy for stereocomplex melting. This suggests that less stereocomplex is formed. In these blends the PLLA/PDLA ratio is low, leading to less stereocomplex formation and more homopolymer crystallization. A third melting point at around 50 °C was observed in the 40% triblock copolymer blend. This melting point can be assigned to the poly(ethylene glycol) melting, since the amount of PEG in the blend is about 28%.

The hindrance for stereocomplex crystallization observed experimentally in case of the hyperbranched copolymer blends can be explained by the following hypotheses which are mainly based on steric effects introduced by the densely branched structure. First, some polylactide chains are located in the center of the hyperbranched core and are not accessible for stereocomplex formation with the surrounding PDLA. Furthermore there are many side chains connected to a rather small core, so steric hindrance may cause limited accessibility for stereocomplexation formation.

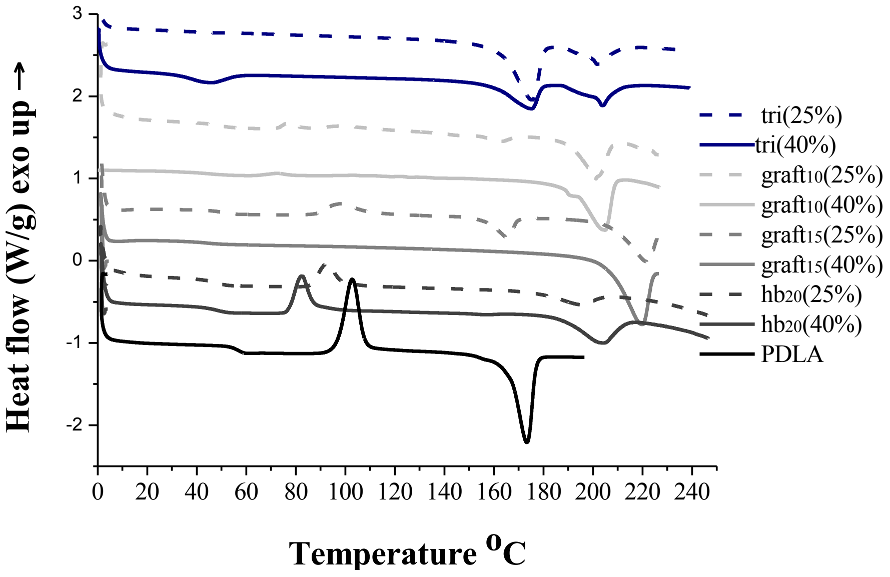


Figure 6. DSC results for all prepared blends (2nd heating scan).

Isothermal crystallization

The crystalline morphology and the spherulitic growth process of all blends were investigated by Polarized Optical Microscopy (POM). Thin film samples were prepared by isothermal crystallization at 160 °C. For the homopolymer large spherulites with an average radius of about 2 mm and typical Maltese Cross pattern were formed. In general, if nucleation is slow and crystal growth is fast, only few large spherulites are formed. For the prepared samples two different kinds of morphologies were formed, viz. spherulitic and dendritic morphologies, as it can be seen from Figure 7. Figure 7 B is what may be called a classic spherulite, with bright contrast deriving from birefringence indicating a crystalline entity. Spherulites have the same crystallographic axis along every radius, whereas dendrites, which are also highly branched, possess a common single crystal orientation (Figure 7 A). The crystallization behavior and the morphology of PLLA depends on both the nucleation activation and the mobility of chain segments.

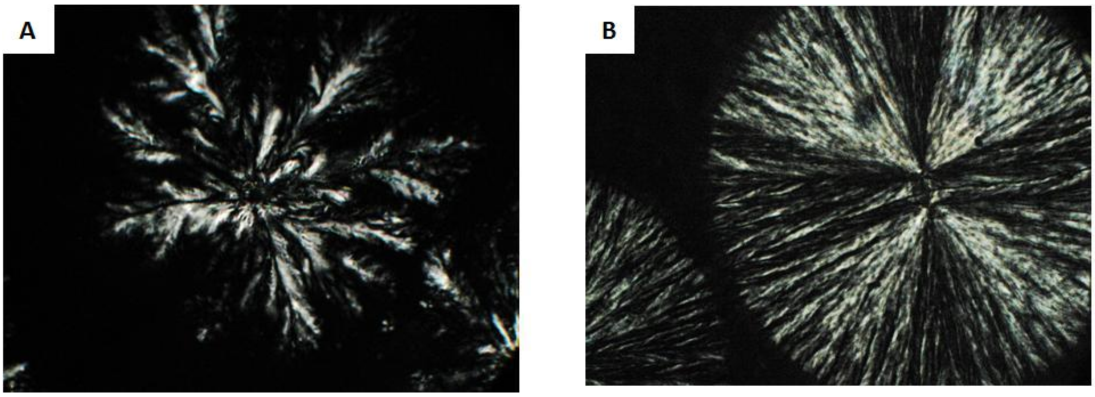


Figure 7. A: Dendritic morphology grown from a triblock copolymer blend (Table 2 entry B) ; B: Spherulites grown from a 40% blend hyperbranched sample (Table 2 entry H).

Figure 8 shows the morphologies formed by isothermal crystallization of the prepared blends. As expected, for all samples smaller spherulites/dendrites compared to the homopolymer were formed.

It can be seen that most of the 40% blend samples and some of the 25% blend samples show a typical spherulitic morphology. For all the triblock copolymer blends and the hyperbranched and graft$_{10}$ 25% blends no clear Maltese cross patterns were observed. The morphology of the 25% hyperbranched blend samples differs from the other samples.

Raman mapping on the crystallites prove the crystals are entirely composed of racemic crystallites except in case of the 25% hyperbranched copolymer blend (Figure 9). The isothermal crystallization experiment coupled with Raman mapping proves that in all the blends apart from the 25% hyperbranched copolymer blend, stereocomplex crystallization occurs preferentially to homopolymer crystallization. In case of the 25% hyperbranched copolymer blend because of the increased steric hindrance, stereocomplex formation is impeded and both homopolymer crystallization and stereocomplex crystallization occur (Figure 9).

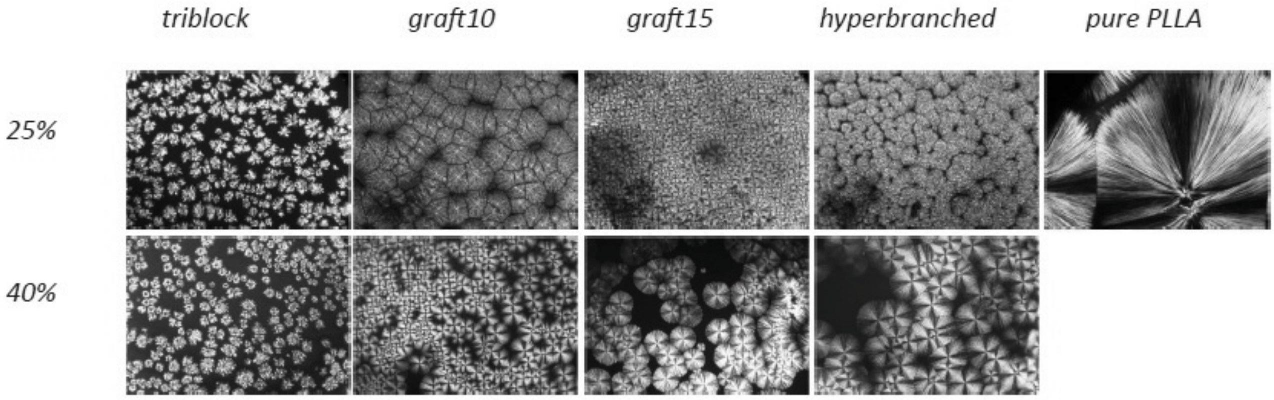


Figure 8. Spherulites of the blends containing 25% and 40 % copolymer (Isothermal crystallization at 160 °C) compared to pure PDLA.

The triblock copolymer blends do not show spherulitic morphologies. Instead they form typical dendritic morphologies because of the presence of large amounts of PEG in this blend which because of its covalent bonds with the PLLA is trapped in the interlamellar and interfibrillar regions of stereocomplex crystals. Numerous interspherulitic amorphous regions are also found in the triblock copolymer blend. This translates to stereocomplex crystals dispersed in a continuous amorphous phase. Raman mapping on the continuous amorphous phase indicates that the amorphous region contains amorphous PDLA and the non-crystallized triblock copolymer. The lower content of PLLA in these blends compared to the hyperbranched and graft copolymer blends results in fewer nucleation sites for stereocomplex crystallization, leading to a different morphology in comparison to the other blends. A recent paper has reported that such morphological features can enhance the mechanical properties of semicrystalline PLA.[34]

Due to the small amount of PEG core molecules in the graft- and hyperbranched samples, poly(ethylene glycol) could not be detected by Raman spectroscopy. However, since only stereocomplex crystallization takes place and the PEG chains are connected to the PLLA side chains, the core molecules must be present in the intraspherulitic amorphous regions. Comparing the different blends more isotropic (black) regions are obtained for samples with higher PEG content. By using Polarized Optical Microscopy it could be confirmed that spherulites formed under non equimolar conditions are more defective in crystalline structure or more irregular in orientation of the lamellae than those formed under equimolar conditions.

Raman Mapping

Raman spectroscopy was used to map the composition of the different regions obtained by isothermal crystallization of thin films of the blends at 160 ^{o}C. Kister and coworkers observed spectral changes in peak shapes upon poly(lactide) stereocomplexation.[53,54] The C=O stretching mode is especially sensitive to the packing and the conformation of the poly(lactide) chain.

For pure crystalline PDLA (α-crystal) this peak splits into components corresponding to A, B, E_1 and E_2 modes. A, B, E_1 and E_2 modes are Raman active, whereas only A and E_1 modes are IR active. These modes are observed at 1749, 1763, 1769 and 1773 cm^{-1}. In case of amorphous PDLA broad bands are obtained. The spectrum of the pure stereocomplex shows a sharp peak at 1745 cm^{-1} and a broad band at 1760-1780 cm^{-1}. This peak was assigned to the A-type mode corresponding to the fully symmetric vibration.[53]

Raman mapping was performed on the spherulites as well as on isotropic interspherulitic amorphous regions found in the triblock copolymer blends. Figure 9 shows the Raman spectra obtained at the different points for the 25% blends. Spectra obtained from the spherulites are labeled with a suffix “s” and those from the amorphous regions are labeled with a suffix “b”. The crystalline regions show the characteristic peaks of the PLA stereocomplex in all blends. The 25% hyperbranched blend crystals, however, exhibit additional bands. Three peaks were obtained, as known from pure crystalline PDLA, but the overall shape was different. The third peak at 1745 cm^{-1} was higher than expected for the α-crystal structure. Thus, this peak seems to be an overlap of the stereocomplex and an α-crystal band. It can be inferred that in case of the 25% hyperbranched blend stereocomplex as well as homopolymer crystallites (α-crystals) are formed. In case of the 40% blends, the crystals in all the blends show peaks characteristic of the stereocomplex crystals. As the

PLLA/ PDLA ratio is closer to unity in these blends, on isothermal crystallization stereocomplex crystals were found to be exclusively formed.

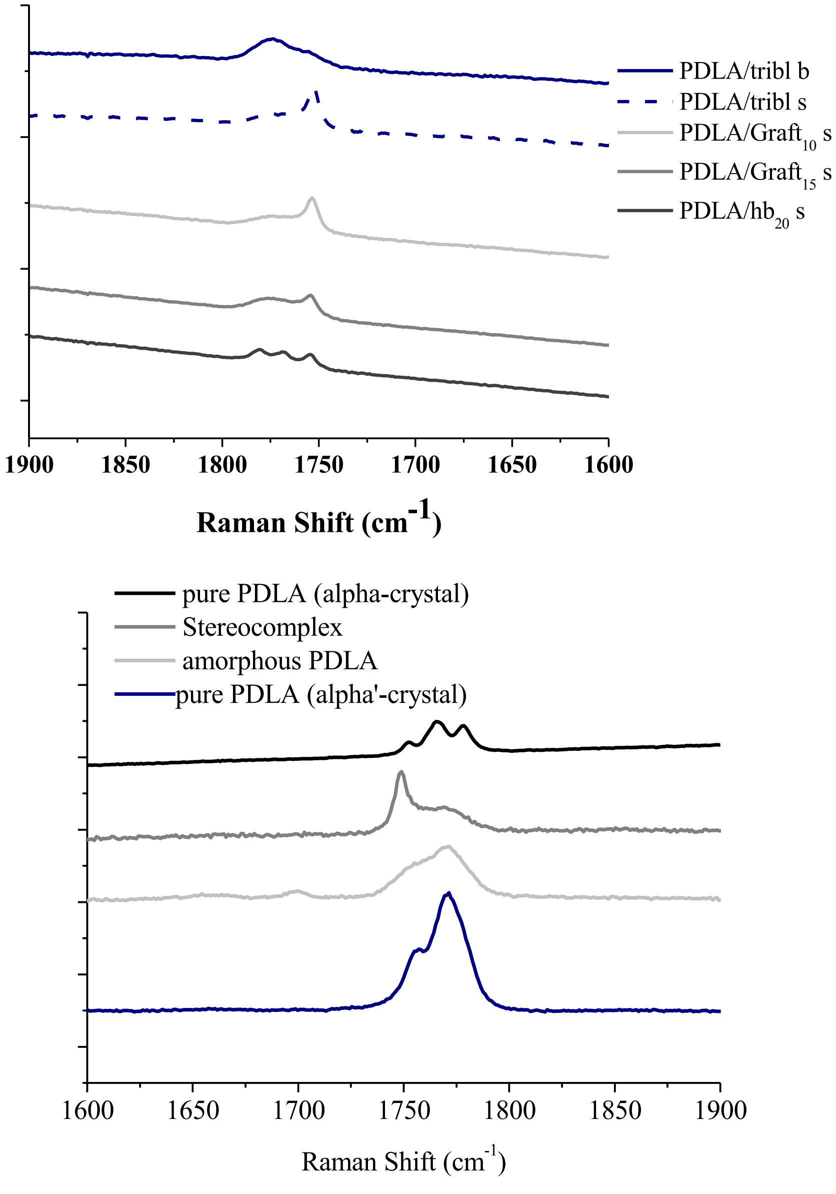


Figure 9. Raman mapping on the 25% blends (top); reference spectra (bottom).

Conclusion

It was shown that both graft and star-shaped multi-arm copolymers based on polylactide and PEG/PG copolymers can be synthesized employing the core-first strategy. The average degree of polymerization of poly(lactide) arms is adjustable by the monomer/initiator ratio.

The occurrence of homopolymerization was observed for some samples, which could be due to traces of moisture in the reaction. For the full structure elucidation of the resulting polymers extensive investigations, including SEC, NMR spectroscopy, DSC and FT-IR spectroscopy have been performed.

A systematically varied series of polymers with molecular weights between 10 000 and 90 000 g/mol was obtained. The molecular weight distribution was narrow for all reactions and the polydispersity index was low for all polymers (between 1.08 and 1.37). It was shown that depending on the side chain degree of polymerization the melting point and glass transition temperature was decreased compared to pure poly(lactide). The shorter the side chain, the lower the corresponding temperatures. Furthermore, the polymer architecture influences the degree of crystallization of polylactide in the samples, resulting in lower crystallinity for the hyperbranched star-shaped copolymers.

Stereocomplexation of the prepared multiarm graft- and star block copolymers has been studied and compared. Different methods were used to evaluate the PLA stereocomplexation. DSC measurements showed a second and higher melting peak for the stereocomplex at 200-220 °C. Isothermal crystallization experiments were performed to study the blend crystallization. Raman mapping was used to probe the resultant morphology formed. It was found that in all blends except the 25% hyperbranched copolymer blend, stereocomplex crystals formed preferentially over the homopolymer crystals. In case of the triblock copolymer blends, because of the large amount of PEG and small amount of PLLA, a very different morphology was obtained compared to the graft and hyperbranched copolymer blends. Finally, the isothermal and non-isothermal crystallization experiments proved that stereocomplex formation was hindered in case of the hyperbranched copolymer blends. The results of this study are of general importance with respect to polylactide stereocomplexation in complex PLA architectures.

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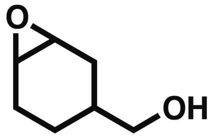
A.2. Future Work

Based on the results obtained in this thesis, considerable application potential for the new polycarbonate architectures presented is obvious. For instance, specifically labeled polymers with a certain function in bio-, materials-, medical- and life science can be envisaged. Some planned projects, which have been tested for feasibility in an exploratory manner in the context of this thesis, are listed below.

Branched Polycarbonates

First results for the synthesis of branched and potentially hyperbranched polycarbonates have been reported in this thesis (chapter 4.2).



3,4-Epoxycyclohexylmethanol

3,4-Epoxycyclohexylmethanol is an oxirane with an additional hydroxyl group, and its nucleophilic ring-opening reaction affords the corresponding product with two hydroxyl groups. Therefore, 3,4-epoxycyclohexylmethanol can be regarded as an AB_2-type trifunctional monomer for polycarbonate synthesis, and its ring-opening polymerization is expected to lead to a hyperbranched polycarbonate with numerous hydroxyl end groups that can be used as a multifunctional prepolymer for adhesive, sealant, and coating materials. To adjust the degree of branching and thus the number of end groups, cyclohexene oxide can be used as a comonomer, diluting the branching density in a deliberate manner.

Polycarbonate block copolymers as surfactants

The synthesis of di- and triblock copolymers consisting of a hydrophobic poly(propylene carbonate) part linked to a hydrophilic poly(ethylene glycol) chain, as described in chapter 2.1 should enable the emulsion polymerization of e.g., styrene with the block copolymers acting as the emulsifier. After the styrene polymerization is finished, the hydrophobic PPC block of the emulsifier can be easily degraded, and the surfactant can be removed from the latex particles.

Copolymerization with ethylene oxide

Poly(ethylene carbonate) (PEC) has attracted little attention in the past, although it is one of only few polymers reported to undergo rapid enzyme-mediated bioabsorption in vivo. Due to this property, PEC is highly interesting for the controlled release of drugs, since drug release would be controlled exclusively by polymer degradation. To date no functional groups have been incorporated at the PEC backbone, and no variation of the polymer architecture has been described. As described in the previous work, copolymerization with different epoxides as well as structure variation is also possible with ethylene oxide as a comonomer and may lead to new, highly interesting biodegradable materials.

Copolymerization with aziridines [1]

Copolymeric products from 2-methylaziridine and carbon dioxide showed sharp and rapid phase transition in response to both temperature and pH. The properties may be controlled by varying the reaction conditions. The reaction of aziridines with CO_2 proceeds competitively with homopolymerization of the aziridines, leading to copolymers containing aliphatic urethane and amine units.

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A.3. Curriculum Vitae Jeannette Hilf née Geschwind

A.4. List of Publications

From CO_2 to Multifunctional Poly(carbonate)s with Controlled Number of Functional Groups to Graft Polymers
J. Geschwind; F. Wurm; H. Frey,
Macromol. Chem.Phys. **2013**, *214,* 892-901

Stable, Hydroxyl-Functional Polycarbonates with Glycerol Side Chains Based on CO_2 and Isopropylidene(glyceryl glycidyl ether)
J. Geschwind; H. Frey,
Macromol Rapid Commun, **2013,** *34*, 150-155

Poly(1,2-glycerol carbonate):
A Simple Polymer Structure obtained From CO_2 and Glycidyl ethers
J. Geschwind and H.Frey,
Macromolecules, **2013,** *46 (9),* 3280-3287

Stereocomplex Formation in Polylactide Multi-Arm Stars and Comb-Copolymers with Linear and Hyperbranched Multifunctional PEG
J. Geschwind, S. Rathi, C. Mangold, M. Schömer, Bryan E. Coughlin and Holger Frey,
Macromol. Chem. Phys., **2013,** *214 (13),* 1434-1444

Propargyl-functional Aliphatic Poly(carbonate) directly prepared from Carbon Dioxide and Glycidyl Propargyl Ether
J. Hilf and H. Frey
Macromol. Rapid Commun., **2013**, *34*, 1395-1400

Multifunctional CO_2 containing Poly(carbonate) Copolymers with Variable Number of Hydroxyl Groups
J. Hilf, A. Phillips and H. Frey
Polymer Chemistry, **2014**, *5*, 814-818.

CO_2-Based Non-ionic Surfactants:
Poly(ethylene glycol)-*b*-Poly(propylene carbonate) Block Copolymers
J. Hilf, P. Schulze and H. Frey,
Macromol. Chem. Phys., **2013**, *214 (24),* 2848-2855

Controlled Synthesis of Multi-Arm Star Polyether-Polycarbonate Polyols Based on Propylene Oxide and CO_2
J. Hilf, P. Schulze, J. Seiwert and H. Frey,
Macromol. Rapid Commun., **2014,** DOI: 10.1002/marc.20130066

A.5. Conference Contributions

PLLA Stars and Brushes Based on Functional PEG: Crystallization Agents for Poly(lactide)
243th ACS National Meeting, San Diego, CA, United States
J. Geschwind, S.Rathi, C. Mangold, M. Schömer, S. L. Hsu, E. B. Coughlin and H. Frey

Multifunctional CO_2 containing poly(carbonate) copolymers with tailored number of hydroxyl groups
245th ACS National Meeting, New Orleans, LA, United States
J. Geschwind and H. Frey

From CO_2 to multifunctional poly(carbonate)s with controlled number of functional groups for grafting via click chemistry
245th ACS National Meeting, New Orleans, LA, United States
J. Geschwind, F. Wurm and H. Frey

Functional Polycarbonates from Carbon Dioxide and Tailored Epoxide Building Blocks
2nd Conference on CO_2 as Feedstock for Chemistry and Polymers, 2013, Essen, Germany
J. Hilf and H. Frey