

Green Polycarbonates Prepared by the Copolymerization of CO₂ with Epoxides

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ABSTRACT: Polycarbonates can be prepared by the copolymerization of epoxides with carbon dioxide as an inexpensive, abundant, nontoxic, and renewable feedstock. This review covers the synthesis, the physicochemical properties, and the growing applications of this class of green polymers. The review has been conceived to provide a useful tool for the researchers who are new to this field, as well as to offer an updated overview for those who are already actively working on this topic. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41141.

KEYWORDS: biodegradable; catalysts; characterization; copolymers; polycarbonates; properties

Received 15 May 2014; accepted 15 June 2014

DOI: 10.1002/app.41141

INTRODUCTION

The awareness of the finite availability of fossil resources generates growing interest in the production of chemicals from alternative and sustainable carbon resources, among which CO₂ is particularly attractive due to its availability, low cost, abundance, and nontoxicity. Processes involving CO₂ as a solvent and/or as substrate have been extensively studied in the last decade to provide greener routes to produce chemicals.^{1–5} However, the conversion of carbon dioxide to useful chemicals is a challenging task because CO₂ has a low free energy. A strategy to overcome the thermodynamic stability of CO₂ is based on reactions with high free energy substrates. Examples thereof are the reduction of CO₂ with H₂ to yield methanol or formic acid,^{6,7} the reaction with heterocyclic molecules such as epoxides to produce cyclic or polymeric carbonates,⁸ or aziridines to produce oxazolidinones.⁹ CO₂ fixation through reaction with the highly reactive three-membered epoxide ring to afford cyclic or polymeric carbonates [Figure 1(A)] is a teeming field of research.^{10,11} Cyclic carbonates (CC) can find applications as green solvents with useful properties (high boiling point, high flash point, high polarity, and low vapor pressure), as electrolytes in Li-ion batteries, and as intermediates for the synthesis of polymers and fine chemicals.^{12–15} Polycarbonates (PCs) represent the other interesting synthetic target of the coupling reaction between CO₂ and epoxides. This review will present and discuss the synthesis, characterization, applications, and strategies for improving the properties of these green CO₂–epoxide copolymers. Before focusing on this class of polymers, it is important to clarify the difference between conventional poly-

carbonates that are produced by using bisphenol A [Figure 1(B)], and the polycarbonates that are the subject of this review, which are obtained by the alternating copolymerization of carbon dioxide with epoxide molecules [Figure 1(A)].

Bisphenol-based polycarbonates have excellent properties as engineering plastics for a broad range of applications including data storage, electronics, optical components and as construction materials.^{16,17} On the other hand, the polycarbonates obtained from the reaction of CO₂ with epoxides typically display less suitable mechanical properties [e.g., low rigidity in

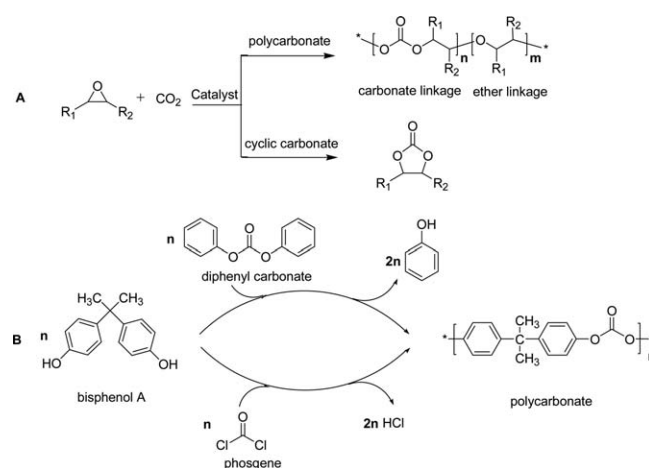


Figure 1. (A) CO₂–epoxide coupling reaction, with cyclic carbonate and polycarbonates as possible products. (B) Polycarbonate synthesized from bisphenol A.

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the case of poly(propylene carbonate) and brittleness in the case of poly(cyclohexene carbonate)] and moderate thermal stability.^{10,18,19} Although these features limit the industrial application of these polymers as engineering plastics, their biodegradability and the “greenness” of their synthesis stimulated growing research efforts to find alternative applications and to improve their properties and the efficiency of their synthesis. The first industrial applications of CO₂/epoxide copolymers are now a reality (see Applications section) and their future seems bright. This new generation of polymers derived from renewable carbon dioxide can become an environmentally friendly alternative to polymers derived from nonrenewable fossil fuels for several applications.

This review will provide a concise yet comprehensive overview of CO₂-epoxide copolymers by covering different aspects of their synthesis, their physicochemical characterization, and their current and potential applications. Throughout this article, the abbreviation polycarbonate will be used to refer to the CO₂-epoxide copolymers.

SYNTHESIS AND CHARACTERIZATION OF POLYCARBONATES PREPARED BY THE COPOLYMERIZATION OF CO₂ WITH EPOXIDES

Catalytic Reaction of CO₂ with Epoxides

The reaction of CO₂ with epoxides can generate either polycarbonates or cyclic carbonates as the possible products [Figure 1(A)]. Ideally, the copolymerization involves the alternating insertion of carbon dioxide and epoxide in the growing polymer chain. However, the consecutive insertion of two epoxides in the polymer chain can also take place, and this would lead to the presence of ether linkages in the polycarbonate [Figure 1(A)], which is typically an undesired feature (see Thermal properties section). The use of a catalyst is required in order to achieve the selective synthesis of polycarbonates with high yield and under relatively mild conditions of temperature and CO₂ pressure. Relevant research efforts have been dedicated to the development of homogeneous and heterogeneous catalysts for the CO₂-epoxide coupling reaction.^{20–23} The studies on homo-

geneous catalysts revealed different possible mechanisms for the CO₂-epoxide copolymerization. A common feature in the catalytic systems active in the CO₂-epoxide coupling reaction is a Lewis base acting as nucleophilic species, either ionic or neutral (e.g., a halide anion or an organic base).¹⁸ Oftentimes a Lewis acid site (e.g., the metal center of a complex) is involved in catalyzing this reaction in combination with the nucleophile. In bifunctional homogeneous catalysts, the nucleophile is part of a metal complex as an axial ligand or as a side arm on the ligand scaffold, whereas in binary catalytic systems the nucleophile is a separate species and is generally referred to as cocatalyst.^{24–26} A common mechanism for the catalytic reaction of CO₂ with an epoxide involves the initial coordination of the epoxide to the metal complex, which activates the epoxide toward the nucleophilic attack and ring-opening by the Lewis base (Figure 2). Then, CO₂ can insert into the metal-oxygen bond and form the carbonate species, which may undergo ring-closure to produce a cyclic carbonate, or propagate by further insertions of epoxide and CO₂ to produce the polycarbonate. Other mechanisms have also been reported, depending on the nature of the catalytic system. A detailed description of these mechanisms is outside the purpose of this review and can be found elsewhere.¹⁸

Physicochemical Properties of the polycarbonates

The yield and the selectivity of the copolymers obtained by the reaction of CO₂ with an epoxide, as well as their physicochemical properties, are determined by a combination of parameters:

- the nature of the epoxide
- the catalyst(s)
- the reaction temperature
- the CO₂ pressure
- the solvent
- the reaction time
- the presence of impurities

In view of an industrial application, it is important to optimize these parameters in order to control and tune the physicochemical properties of the polycarbonates. This implies a thorough

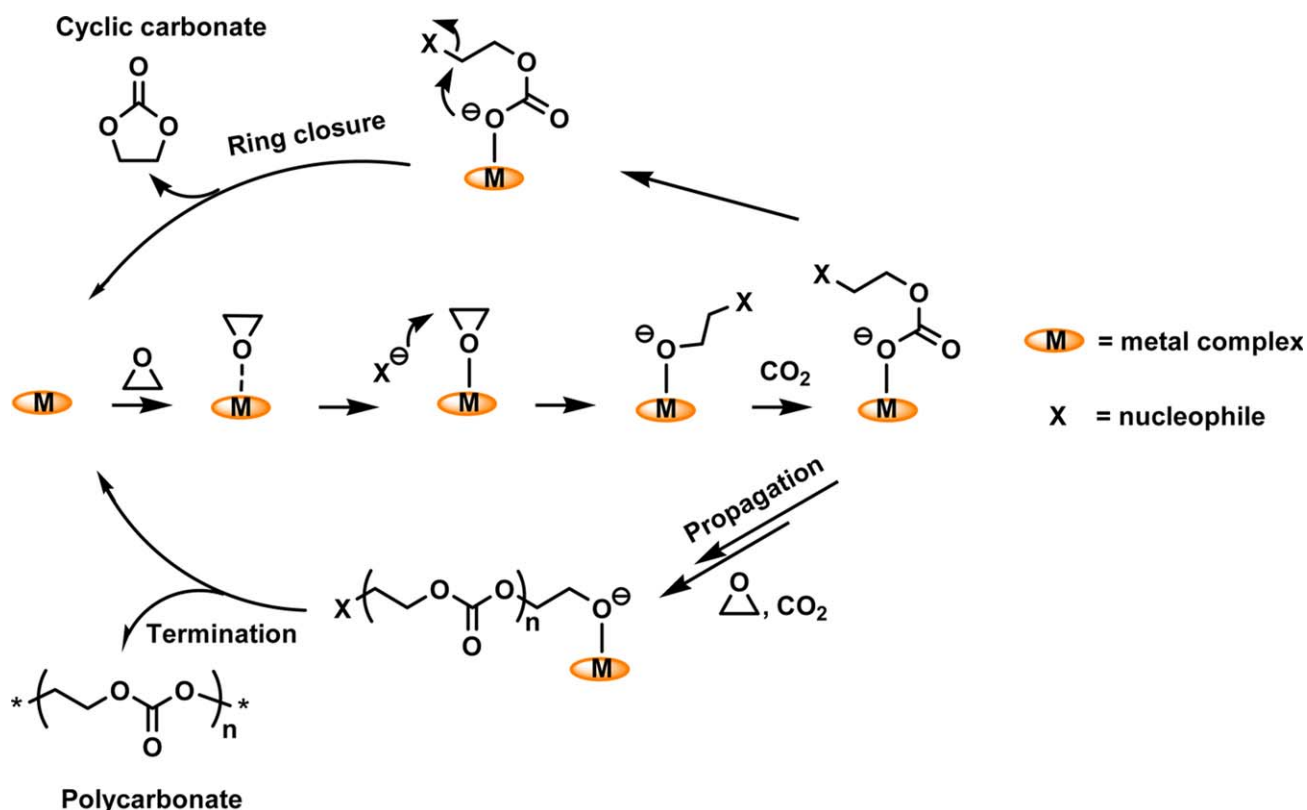


Figure 2. Mechanism for the catalytic coupling reaction of CO_2 and epoxide, involving the initial activation of the epoxide followed by nucleophilic attack and ring opening. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

characterization of their properties, including the regio- and stereochemistry of the polymers, the percentage of carbonate and ether linkages, the nature of the terminal groups, the molecular weight (M_w and M_n) and the polydispersity index (PDI), the glass-transition temperature (T_g), the chemical and thermal stability, and the mechanical behavior. In this section, the most widely used techniques for the characterization of polycarbonates and the strategies that can be used to improve their properties are presented and discussed. The polycarbonates produced from propylene oxide (PO), cyclohexene oxide (CHO), and styrene oxide (SO) will be discussed in detail as representatives of linear aliphatic, cyclic aliphatic (alicyclic), and aromatic epoxides, respectively. polycarbonates obtained from other epoxides and from the combination of two epoxides (terpolymers and block copolymers) will be addressed briefly in Alternative approaches for the synthesis of polycarbonates from CO_2 and epoxides section. It should be noted that the purification of the polycarbonate product is generally required in order to exclude any effect of impurities on the physicochemical properties. Purification of the polycarbonate can be carried out by precipitation from a dichloromethane solution with acidic methanol, followed by repeated washing steps with methanol to remove short polymer chains, followed by vacuum drying.²⁷

Selectivity and Yield in the Copolymerization of CO_2 with Epoxides. Both possible products of the coupling reaction between carbon dioxide and an epoxide, i.e., polycarbonates and cyclic carbonates, are interesting and potentially valuable

chemicals. However, the efficient production of each of them requires minimizing the separation and purification steps. Therefore, it is crucial to achieve high selectivity and high yield of the desired product. The selectivity of this reaction is strongly dependent on the features of the catalytic system, but is also influenced by other factors such as the nature of the substrate and the reaction conditions (temperature, CO_2 pressure).^{18,19,21,28}

- For what concerns the catalytic system, the activity and the selectivity are determined by the combination of the coordination ability of the Lewis acid site (if present), and by the balance between nucleophilicity and leaving ability of the Lewis base. A nucleophilic species with a poor leaving ability will favor the growth of the polymer chain, whereas a nucleophile with a good leaving ability will promote the ring closure reaction and the consequent formation of the cyclic carbonate product.¹⁸ Moreover, the molar ratio between the nucleophile and the Lewis acid site plays an important role on the selectivity: in the presence of an excess of nucleophile, the carbonate intermediate bound to the catalyst (Figure 2) can be displaced by a new nucleophile, thus favoring the ring closure reaction and the formation of cyclic carbonate. In a recent study with an iron amino triphenolate complex as catalyst (**1** in Figure 3) and PPNCl or Bu_4NCl as cocatalyst, it has been shown that the selectivity can be efficiently switched between cyclic and polymeric carbonate by changing the ratio between catalyst and cocatalyst.²⁷ Typically, the polycarbonate is the favored product when the molar ratio between nucleophile and Lewis acid is

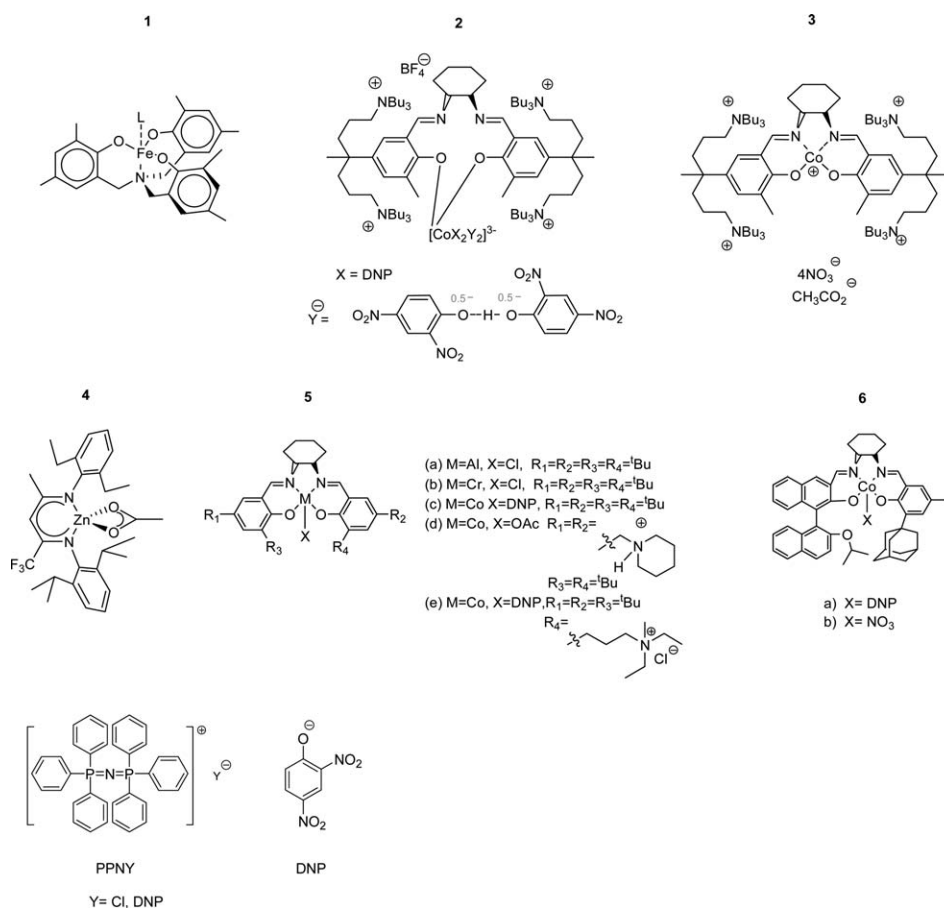


Figure 3. Selected homogeneous catalysts (1–6) and cocatalysts for the copolymerization of CO₂ and epoxides.

equal to or lower than 1. Different strategies in the design of homogeneous catalysts have been developed to achieve high activity and selectivity toward the synthesis of polycarbonates. A particularly efficient design consisted in appending quaternary ammonium salts to the ligand scaffold of metal salen complexes (2 and 3 in Figure 3). This configuration helps to keep detached charged copolymer chains in the proximity of the metal center through electrostatic attraction by the positively charged ammonium groups, and thus facilitates resuming the chain growth process.²² Another strategy involves the development of homogeneous catalysts containing two adjacent metal centers, among which dinuclear β -diimine complexes (4 in Figure 3) showed remarkable activity and selectivity in the synthesis of polycarbonates.^{18,19,23,29–32} However, many highly active complexes including the two types mentioned above are air and moisture sensitive and should be prepared and used under inert and

strictly water-free conditions, which poses a serious limitation to their possible industrial application.^{32–34} Therefore, further advances are needed in order to develop robust, active, and selective catalysts for the copolymerization of CO₂ with epoxides.

- The nature of the epoxide can favor the preferential formation of either the cyclic or the polymeric carbonate. For instance, in the reaction of CO₂ with cyclohexene oxide the ring closure is less favored than in the reaction of CO₂ with terminal aliphatic epoxides, as a consequence of the geometric strain caused by the two connected rings in cyclohexene carbonate. Therefore, the selectivity toward the polycarbonate is typically higher with cyclohexene oxide compared to propylene oxide.^{29,35} On the other hand, styrene oxide preferentially forms the cyclic carbonate product as a consequence of the electron-withdrawing inductive effect of the phenyl group, which favors the formation of an intermediate in which the ring closure with formation of the cyclic product is promoted.¹⁸

The nature of the epoxide has also a strong influence on the yield of the formed carbonate product. The steric hindrance at the carbon on which the nucleophilic attack occurs affects the rate of the epoxide ring opening and thus the rate of the reaction. In terminal epoxides such as propylene oxide, the nucleophilic attack can occur at the methanediyl group of the epoxide ring, which is sterically less hindered compared to the carbon

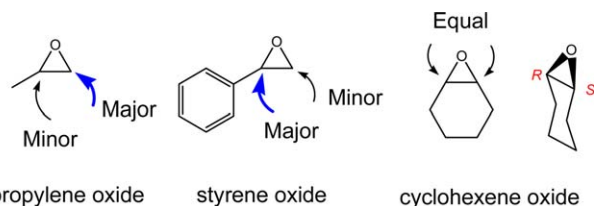


Figure 4. Most likely position for the nucleophilic attack on different epoxides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. ¹H-NMR Signals of H Atoms Belonging to Epoxide, Cyclic Carbonate, and Polycarbonate for the Reactions Involving Propylene Oxide, Cyclohexene Oxide, and Styrene Oxide as Substrates

Epoxide	Epoxide signals (ppm)	Ref	Cyclic carbonate signals (ppm)	Ref	Polycarbonate signals (ppm)	Ref	Ether linkage signals (ppm)	Ref
PO	3.3 and 3.6 (CH ₂), 3.8 (CH)	-	3.9 and 4.5 (CH ₂), 4.8 (CH)	39	4.0–4.2 (CH ₂), 4.9–5.0 (CH)	40	3.5–3.6 (CH ₂), 3.4 (CH)	39,41,42
CHO	3.1 (CH of CHO)	27	Cis-isomer at 4.6, Trans-isomer at 4.0	43	4.6 (CH)	43	Broad peak at 3.4–3.5 (CH)	43,44
SO	2.8 and 3.1 (CH ₂), 3.8 (CH)	8	4.2 and 4.7 (CH ₂), 5.6 (CH)	8	4.2–4.4 (CH ₂), 5.7–5.9 (CH)	45	3.5 (CH ₂)	45

These data refer to ¹H-NMR spectra of samples prepared using CDCl₃ as solvent to dilute the reaction solution.

atoms of the epoxide ring in internal epoxides such as cyclohexene oxide. Therefore, higher carbonate yields are observed with PO compared to CHO under the same reaction conditions.³⁶ In the case of terminal epoxides, it should be also taken into account that the nature of the substituent on the epoxide ring determines the most probable carbon atom on which the nucleophilic attack happens. In the CO₂-propylene oxide coupling reaction, the nucleophilic attack happens preferably at the less hindered carbon atom of the epoxide ring, both because of lower steric hindrance and of the electron donating nature of the methyl group (Figure 4). On the other hand, in styrene oxide the nucleophilic ring-opening takes place mainly at the more hindered carbon as a consequence of the electron-withdrawing inductive effect of the phenyl group (Figure 4). This results in a lower rate of copolymerization for styrene oxide compared to propylene oxide.^{31,37}

• Reaction conditions such as the temperature and the CO₂ pressure affect not only the yield of products, but also the selectivity between polycarbonate and cyclic carbonate. Higher temperatures lead to higher product yields but also promote the formation of cyclic carbonate, which is the thermodynamically favored product.³⁵ Therefore, the synthesis of polycarbonates is typically performed at $T < 100^{\circ}\text{C}$ and decreasing the reaction temperature to as low as 0°C has been used as a strategy to promote the formation of polycarbonates with epoxides that would otherwise tend to form cyclic carbonates (e.g., styrene oxide, indene oxide).³⁸ Performing the reaction at a CO₂ pressure and temperature at which carbon dioxide is in the liquid or supercritical state can promote the conversion of the epoxide, by providing a good contact between the components participating in the reaction and favoring the CO₂-insertion step. However, too high CO₂ can be detrimental for the epoxide conversion due to dilution of catalyst and substrate. The enhanced rate of insertion of CO₂ at higher pressure can also increase the polycarbonate selectivity by favoring the growth of the polymer chain over the back biting reaction that would lead to cyclic carbonate formation.¹⁸ Moreover, higher CO₂ pressure would promote the alternating copolymerization of epoxide and carbon dioxide over the consecutive insertion of two epoxides in the polymer chain, thus minimizing the formation of ether linkages (Figure 1).²⁷

The conversion of the epoxide substrate and the yield and selectivity of polycarbonate and cyclic carbonate in the reaction

between carbon dioxide and epoxides are typically determined by analysis of the reaction solution by ¹H-NMR spectroscopy. The characteristic position of ¹H-NMR signals of the hydrogen atoms of the epoxide, the cyclic carbonate and the polycarbonate for selected epoxide substrates (PO, CHO, and SO) are summarized in Table I. For carbonates derived from cyclohexene oxide, the selectivity toward the cyclic or the polymeric product cannot be determined by ¹H-NMR because the chemical shifts of the hydrogens on the carbonate ring in *cis*-cyclohexene carbonate [H_c and H_c' in Figure 5(a)] and on the polymer backbone in poly(cyclohexene carbonate) [H_d and H_d' in Figure 5(a)] are similar. Therefore, the selectivity between the cyclic carbonate and the polycarbonate is determined by means of IR spectroscopy.^{27,43} The selectivity can be calculated on the basis of the absorbance for the C=O vibrational mode in cyclohexene carbonate [at 1804 cm^{-1}] and in poly(cyclohexene carbonate) [at 1748 cm^{-1} , see Figure 5(b)], which are obtained from the formula: $A = \log \frac{T_0}{T_i}$, where T_0 and T_i represent the transmittance at the baseline and the transmittance of the carbonyl vibrational mode, respectively.

In the presence of ether linkages, the CO₂ content of the polycarbonate is lower than the theoretical value calculated based on a perfectly alternating copolymer of carbon dioxide and epoxide. The fraction of carbonate linkages and ether linkages in polycarbonates can be estimated from the ¹H-NMR spectrum (see Table I; in the case of poly(cyclohexene carbonate), the polymer should be first purified to remove any trace of *cis*-cyclohexene carbonate, as the two give overlapping ¹H-NMR signals at 4.6 ppm). The content of carbonate vs. ether linkages (f_{CO_2}) is expressed by the formula: $f_{\text{CO}_2} = \frac{A_c}{A_c + A_e}$, where A_c = sum of the areas of the ¹H-NMR peaks of H_d and H_d' and A_e = sum of the areas of the ¹H-NMR peak of H_e and H_e' [see Figure 5(a)].

Regio- and Stereoselectivity in the Copolymerization of CO₂ with Epoxides. The physicochemical properties of CO₂-epoxide copolymers are significantly influenced by the regio- and stereochemistry of adjacent units constituting the polymer.⁴⁶ For example, only copolymers with stereoselectivity of more than 90% are able to form crystals, which have higher T_g , melting point, decomposition temperature, toughness (i.e., the ability of the material to plastically deform without fracturing) and stiffness (i.e., the resistance of the material to deform in response to an applied force).^{18,47} Of the two carbons of the epoxide

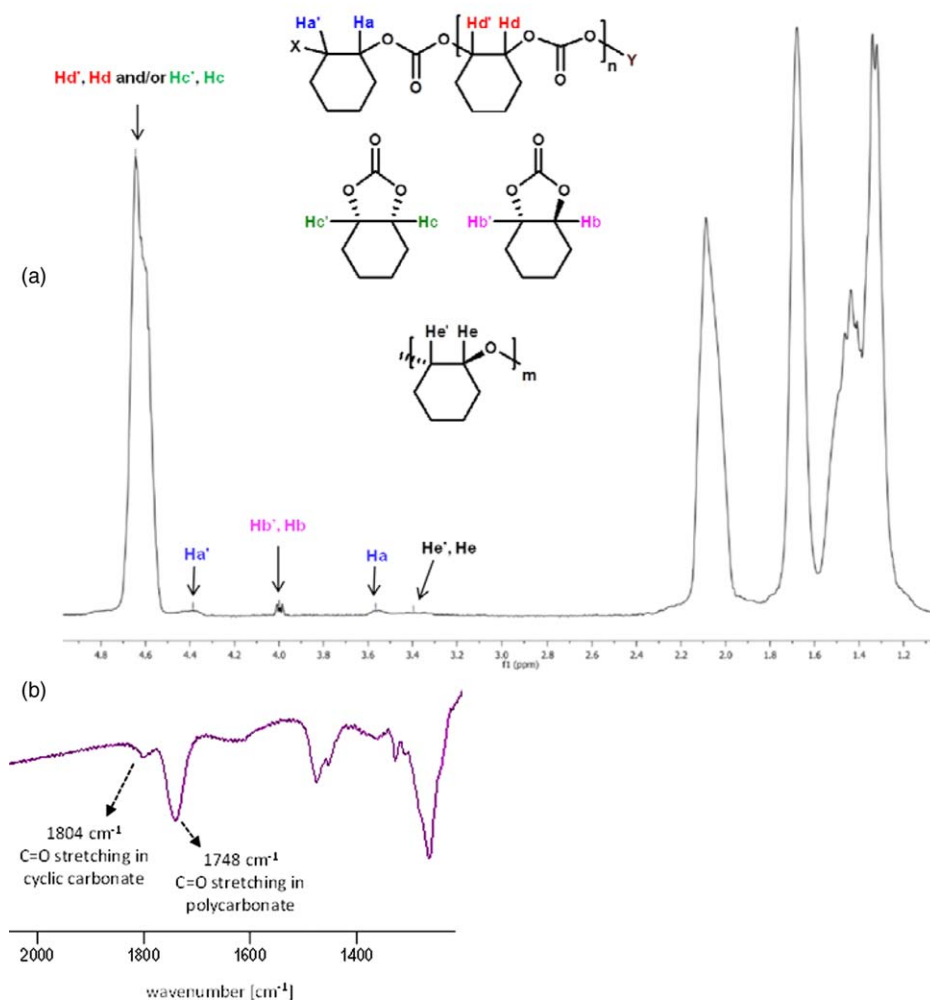


Figure 5. (a) $^1\text{H-NMR}$ spectrum of the reaction solution of a $\text{CO}_2\text{-CHO}$ copolymerization (adapted from Ref. 43); (b) FT-IR spectrum used to determine the ratio between cyclohexene carbonate and poly(cyclohexene carbonate) of a polymer-rich reaction mixture (reproduced from Ref. 27). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ring, one or both can be chiral. The chiral center is a methanetriyl group (also referred to as methine), and the nonchiral center is a methanediyl group (also referred to as methylene) (Figure 6). Terminal epoxides such as propylene oxide and styrene oxide have one methanetriyl and one methanediyl group in the epoxide ring. In internal epoxides such as cyclohexene oxide both carbon atoms are chiral methanetriyls (Figure 4). In the case of aliphatic terminal epoxides, if the nucleophilic attack occurs always at the same position (i.e., either always at the methanetriyl or always at the methanediyl group), the copolymerization is regioselective. On the other hand, if the attack occurs randomly, the copolymerization is regiorandom. The positions at which the nucleophile attacks to open the epoxide ring will also determine the stereochemistry of the final polycarbonate. If the nucleophilic attack takes place at the methanetriyl group, it causes an inversion of configuration of the chiral carbon atom ($R \rightarrow S$ or $S \rightarrow R$), whereas the chirality is retained if the nucleophilic attack occurs at the methanediyl group. Therefore, nucleophilic attack at each of two carbon groups followed by ring opening results in a different stereochemistry of the obtained polycarbonate. As a consequence, regiochemistry

and stereochemistry of polycarbonates are strongly interrelated and are generally discussed together. The regio- and stereoselectivity of the CO_2 -epoxide copolymerization is typically studied on the basis of the enantiomeric excess (ee , defined as the absolute difference between the mole fractions of each enantiomer) of the diols obtained by hydrolysis of the copolymer with aqueous NaOH , which occurs dominantly with retention of stereochemistry at the methanetriyl carbon groups.^{31,48,49}

Regio- and Stereochemistry of Poly(propylene carbonate). In aliphatic terminal epoxides, such as propylene oxide, the nucleophilic attack occurs predominantly at the sterically less hindered carbon atom (methanediyl group) due both to its higher accessibility and to the electron-donating effect of the alkyl group on the other carbon of the epoxide ring (see Figure 4).¹⁸ However, this behavior may change by applying tailored catalyst systems (*vide infra*). Three regiosequences (head-to-tail, head-to-head, and tail-to-tail) can be obtained in the copolymerization of CO_2 with PO, depending on the position on the epoxide ring at which the nucleophilic attack takes place (see Figure 6). The head-to-tail regiosequence is obtained if two consecutive

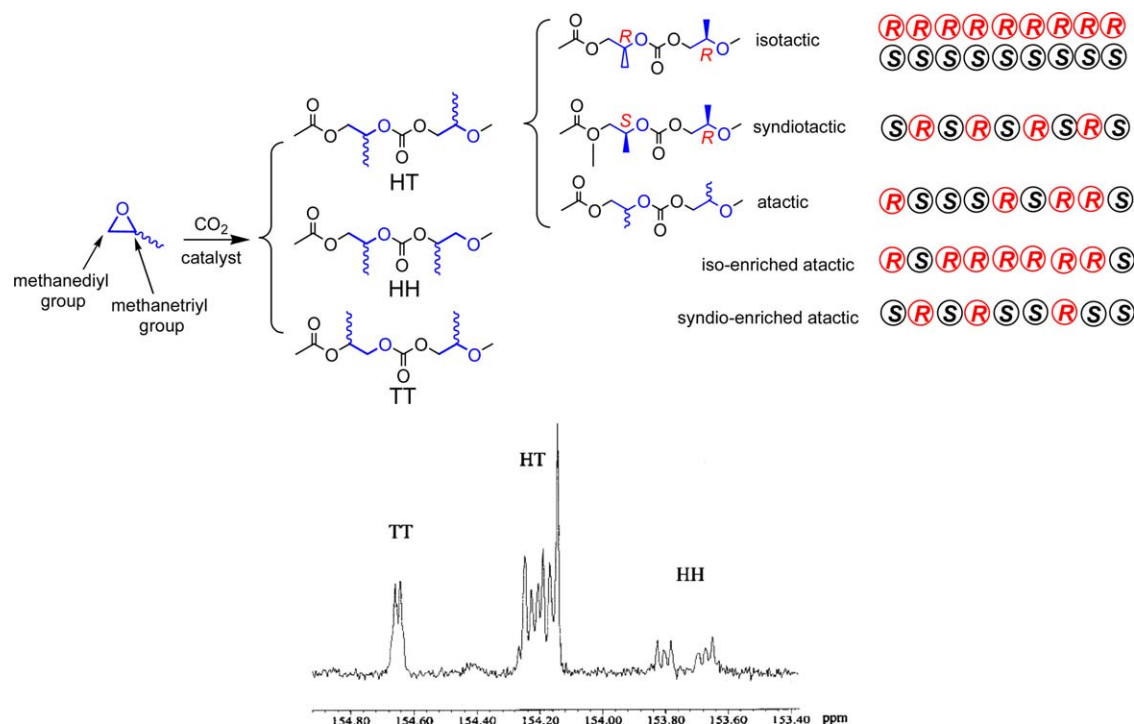


Figure 6. The three possible regiosequences for poly(propylene carbonate): head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT) and the possible stereosequences of the HT regiosequence (top); characteristic region of the ¹³C {¹H}-NMR spectrum of poly(propylene carbonate) in which the signals due to the C=O groups of the carbonate appear (adapted from Ref. 40; bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nucleophilic attacks occur at the same position (i.e., both at the methanediyl group or both at the methanetriyl group), whereas the other two regiosequences occur when two consecutive nucleophilic attacks occur at two different positions on the epoxide ring (Figure 6).^{45,46,50,51} The percentage of each regiosequence can be estimated on the basis of the signal of the carbonyl group in the ¹³C {¹H}-NMR spectrum (see Table II and Figure 6).⁴⁸ Since the nucleophilic attack takes place preferentially at the methanediyl group of PO, head-to-tail is the most common regiosequence, though typically not the only one, in poly(propylene carbonate). In this context, it should be noted that Lewis acid catalysts activate the epoxide toward nucleophilic attack, but for aliphatic terminal epoxides as PO this is coupled to a decreased preference for the nucleophilic attack at the methanediyl group, thus leading to a lower regioselectivity in the ring-opening step.⁴⁸

In the case of a HT regiosequence in poly(propylene carbonate), two stereosequences of the chiral atoms in two adjacent units are possible: isotactic junctions (i) and syndiotactic junctions (s);

Figure 6). The HT-regioregular polycarbonate that consists exclusively of i junctions is called isotactic and the one that consists only of s junctions is called syndiotactic. If both types of junctions are present randomly, the polycarbonate is atactic or stereorandom. Atactic polymers can be further classified as iso-enriched or syndio-enriched, if one of the two stereosequences occurs more frequently (Figure 6).⁴⁸ If the poly(propylene carbonate) is atactic, the ¹³C {¹H}-NMR signal of the C=O groups in the HT regiosequences consists of a complex set of peaks (see Figure 6),⁵² whereas a single peak would be observed in the case of an isotactic (or of a syndiotactic) polymer.⁴⁸ In general, depending on which carbon of the epoxide ring is preferred for the nucleophilic attack, retention or inversion of configuration of the chiral center can produce different stereosequences.⁵⁰ The formation of HT linkages in poly(propylene carbonate) typically occurs as the result of nucleophilic attack at the methanediyl group of the epoxide, and this implies that the chirality of the carbon atom in the methanetriyl groups is retained. In such case, using an enantiopure propylene oxide

Table II. Positions of the ¹³C-NMR Signals for the Carbonyl Group of Polycarbonates Obtained from the Copolymerization of Propylene Oxide, Cyclohexene Oxide, or Styrene Oxide with CO₂

Epoxide	Head-to-head (ppm)	Head-to-tail (ppm)	Tail-to-tail (ppm)	Ref
PO	153.7–153.8	154.2	154.6	40,50,52
CHO		153.2 (syndiotactic), 153.7 (isotactic)		54,56,57
SO	153.7–153.9	154.2–154.4	154.7–154.9	46,58

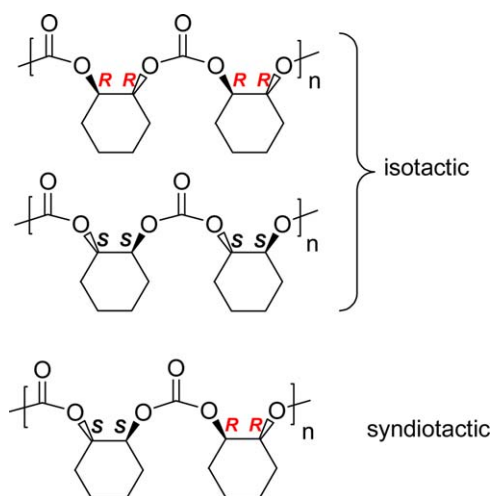


Figure 7. Isotactic and syndiotactic poly(cyclohexene carbonate). The two types of tacticity can be monitored by ^{13}C -NMR spectroscopy (see Table II). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as substrate leads to the formation of an isotactic polymer chain.⁴⁸ Regio- and stereoselective poly(propylene carbonate) can also be obtained from racemic propylene oxide, through a tailored design of the features of the complex (metal center and ligand scaffold) used as homogeneous catalyst for the copolymerization.⁵⁰ This involves a careful tuning of the symmetry of the ligand in the metal complex to create a suitable asymmetric environment around the metal center.⁵³ The asymmetric structure of the catalyst should induce a specific stereochemistry in the epoxide ring opening step, thus allowing the generation of isotactic poly(propylene carbonate) from racemic propylene

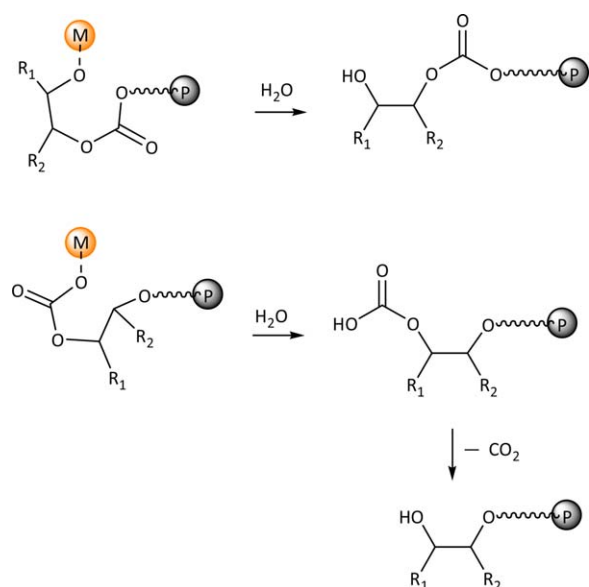


Figure 8. Chain-transfer reaction by water contaminant during the copolymerization of carbon dioxide with an epoxide, catalyzed by a metal complex (M = metal). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

oxide.^{45,54} For instance, (*R,R*)-SalenAlCl (**5a** in Figure 3) shows a preference in generating an alkoxide with *R*-configuration as a result of the ring opening of a racemic PO mixture.⁵⁰ Another example is (*R,R*)-SalenCrCl (**5b** in Figure 3), which generates an alkoxide with *S*-configuration when the attack is at the methanetriyl carbon of racemic PO.⁵⁰

The steric and electronic properties of the cocatalyst used in combination with a chiral metal complex affect not only the activity and selectivity, but also the enantioselectivity of the CO_2 -PO copolymerization.³³ This was demonstrated in a study of a Co-catalyst (**6** in Figure 3) with different cocatalysts, among which the combination of PPN-DNP (Figure 3) gave the best enantioselectivity at the ring-opening step.⁵⁵ This result was ascribed to the poor leaving ability of the anion and the bulkiness of the cation.⁵⁵

Regio- and Stereochemistry of Polycarbonates from Different Epoxides. One of the factors determining the regio- and stereochemistry of CO_2 -epoxide copolymerization is the chemical structure of the epoxide. The nature of substitutions on the epoxide ring affects the most likely position at which the epoxide ring is attacked by a nucleophile, leading to ring opening [see Selectivity and yield in the copolymerization of CO_2 with epoxides and Regio- and stereochemistry of poly(propylene carbonate) sections]. For epoxides with an electron withdrawing group as styrene oxide, the nucleophilic ring-opening occurs preferably at the methanetriyl group (Figure 3) as a consequence of the electron-withdrawing inductive effect of the phenyl group, leading to an inversion of stereochemistry at the methanetriyl carbon.^{18,59} The methanetriyl group is sterically more hindered and the balance between electronic and steric effects implies that SO undergoes the ring opening with lower regioselectivity compared to PO. This issue can be tackled by developing a chiral catalyst system with a bulky cocatalyst as (*R,R*)-SalenCoX/PPNY ($X = Y = 2,4$ -dinitrophenoxide; **5c** in Figure 3), which favors the regioselective nucleophilic attack at the methanediyl group of (*S*)-SO to obtain 99% selectivity toward poly(styrene carbonate) with HT-content of 82% and with 89% retention of stereochemistry.⁶⁰ In another work, poly(styrene carbonate) with 96% retention of the stereochemistry of the methanetriyl carbon atom of (*R*)-SO was obtained using a chiral (*S,S,S*)-SalenCoX complex and PPNY ($X = Y = 2,4$ -dinitrophenoxide) as cocatalyst (**6a** in Figure 3).⁴⁶

In the copolymerization of carbon dioxide with an alicyclic epoxide as cyclohexene oxide, there is no preferential position for the nucleophilic attack between the two chiral carbon atoms of the epoxide ring since the two positions are geometrically equivalent, though one of the two carbons has *R*- and the other *S*-configuration (Figure 4). The nucleophilic attack leads to inversion of configuration of one of the two carbon atoms, which means that the two chiral carbons will have the same configuration in the copolymer chain (Figure 7). In the absence of a chiral catalyst, the nucleophilic attack will occur at both (*R*)-C and (*S*)-C with no preference, and isotactic and syndiotactic junctions will be generated randomly. On the other hand, in the presence of a chiral catalyst as the SalenCoX complex

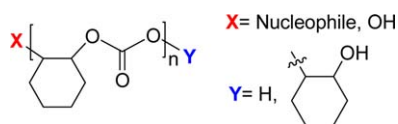


Figure 9. Structure of poly(cyclohexene carbonate) and its possible terminal groups. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(6a and 6b in Figure 3), it is possible to achieve the preferential ring opening of CHO at the (S)-C and, thus, to promote the formation of isotactic poly(cyclohexene carbonate).^{53,61}

Molecular Weight and Polydispersity. The average molecular weight of a polymer strongly affects its physical properties such as tensile strength (TS), toughness, melt viscosity, heat and chemical resistance. The average molecular weight may be tuned to achieve the desired properties for the selected application (see Applications section).^{7,62} The molecular weight of polycarbonates is typically determined by gel permeation chromatography (GPC/polycarbonate).⁶³ Polymer molecular weights are expressed in terms of weight-average molecular weight (M_w) defined as $M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$, and number-average molecular weight (M_n) defined as $M_n = \frac{\sum N_i M_i}{\sum N_i}$, where N_i represents the number of chains with mass M_i . M_n is the most commonly reported quantity. The polydispersity index is defined as $PDI = \frac{M_w}{M_n}$. Since $M_w \geq M_n$, it follows that $PDI \geq 1$. The polydispersity index provides a measure of the molecular weight distribution: the lower the PDI value, the narrower the range of molecular weights of the polymer. In the copolymerization of CO₂ with propylene oxide or cyclohexene oxide, the bimodal M_n distribution that is often observed by GPC/polycarbonate has been attributed to the presence of small amounts of adventitious water, which can act as chain-transfer agent by reacting with the growing polymer chain to yield a hydroxyl-terminated polycarbonate (Figure 8), thus preventing the chain

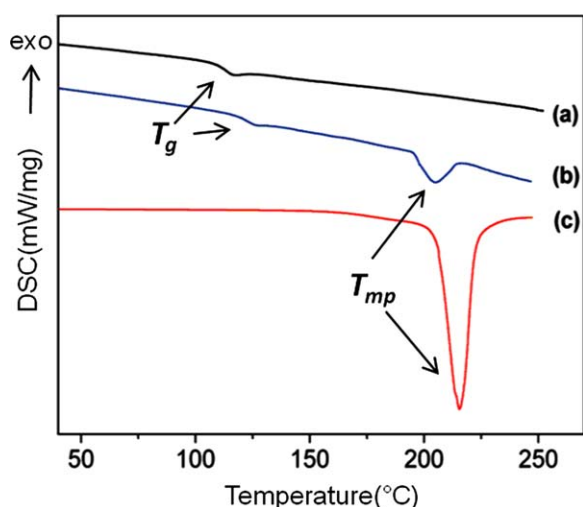


Figure 10. DSC thermograms of poly(cyclohexene carbonate): (a) atactic, (b) with 92% isotacticity, and (c) with 98% isotacticity (adapted from Ref. 53). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

growth.^{60,64,65} Similar chain-transfer reactions can take place also with other protic compounds such as alcohols, carboxylic acids or phosphoric acid.^{22,62,64,65} Increasing the amount of chain-transfer agent leads to the formation of polymers with lower M_n and low PDI .^{10,62} Another factor that can be used to control the M_n of polycarbonates is the CO₂ pressure used in the copolymerization process. High CO₂ pressure favors the contact between the catalyst and CO₂, which results in a more efficient insertion of CO₂ in the growing polymer chain, generating a longer chain with high content of carbonate linkages (see also Selectivity and yield in the copolymerization of CO₂ with epoxides section).²⁷

Terminal Groups. In the synthesis of polycarbonates, the termination of the polymer chain growth typically occurs by chain transfer caused by reaction with water or other protic compounds that might be present in the reaction mixture as impurities or because deliberately added. Chain termination due to reaction with a protic compound can lead to two possible chain ends, i.e., -OH or -OC(=O)OH, depending on the stage at which the chain transfer occurs (Figure 8). However, the latter terminal group is rather unstable and tends to convert into an alcoholic terminal group with liberation of a CO₂ molecule (Figure 8).

Upon heating, the hydroxyl groups at the chain end of polycarbonates can induce depolymerization by nucleophilic attack to the adjacent carbonyl group, leading to a back-biting reaction with formation of a cyclic carbonate.⁶⁶ Modification of the hydroxyl terminal groups by means of selected end-capping agents can have stabilizing effects and increase the decomposition temperature of polycarbonates. For this purpose, poly(propylene carbonate) has been end-capped by reaction with different compounds including maleic anhydride, benzoyl chloride, ethyl silicate, acetic anhydride, phosphorus oxychloride, and benzenesulfonyl chloride.^{66,67} This end-capping approach effectively improved the thermal stability of poly(propylene carbonate) by introducing less reactive terminal groups, thus minimizing end-initiated depolymerization.

The nature of the terminal groups of polycarbonates can be studied by means of matrix-assisted laser desorption/ionization-time of flight (MALDI-ToF) mass spectrometry (MS) and ¹³C-NMR spectroscopy. MALDI-ToF MS also provides information about the molecular weight of the polymer, though the higher molecular weight fraction is generally not observed with this technique.^{27,43} In the MALDI-ToF mass spectra of CO₂-epoxide copolymers, consecutive mass losses corresponding to the epoxide and CO₂ can be observed.⁶⁸ The observed m/z values correspond to polymers masses expressed as $nM_{\text{repeating unit}} + M_{\text{terminal groups}}$.^{27,64} The terminal groups are typically -OH groups or the nucleophile that started the reaction by ring opening of the epoxide (Figure 9).

Thermal Properties. The behavior of polycarbonates upon heating depends on their chemical structure, on the presence of ether linkages in their backbone, on their tacticity (and the related degree of crystallinity), on their molecular weight, on their end groups, on intermolecular dipolar interactions and on the presence of residual impurities (e.g., solvents, metal residues, acids applied for the separation of the copolymer, cyclic carbonate byproduct).⁶⁹⁻⁷² Only polymers with a high stereoregularity can form crystalline structures or at least contain

Table III. Selected Thermal and Mechanical Properties of Regiorandom Polycarbonates Obtained from CO₂-Epoxide Copolymerization

Polycarbonate	M_n (kg mol ⁻¹), [PDI]	T_g (°C) ^a	IDT (°C) ^b	$T_{d50\%}$ (°C) ^c	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (J/cm)	Ref.
Poly(ethylene carbonate)	-	10	217	-	3-8	-	>600	-	69
Poly(propylene carbonate)	7.5 [3.8]	28	235	-	212	9	8	-	69
"	-	38	-	-	1353	14.7	203.1	7.27	78
"	69.5 [1.09]	42	-	252	-	-	-	-	25
Poly(butene carbonate)	180 [1.15]	9	-	241	-	-	-	-	79
Poly(pentene carbonate)	7.5 [5.1]	-4	246	-	-	-	-	-	69
Poly(hexene carbonate)	9.5 [4.8]	-10	250	-	-	-	-	-	69
"	-	-15	-	253	-	-	-	-	79
Poly(cyclohexene carbonate)	8 [4.2]	105	282	-	2460	11.8	0.5	-	69
"	63 [1.06]	118	-	310	-	-	-	-	25
"	-	125	-	-	2707	29.4	1.3	1.31	78
Bisphenol A polycarbonate	-	149	-	458	2000-2800	43-51	15-75	9	10,80

^a Measured by means of DSC.^b Measured by means of DSC (in air).^c Measured by means of TGA.

regions displaying crystallinity (in which case they should be denoted as semicrystalline). For such polycarbonates, it is possible to observe a defined melting point (T_{mp}) in the form of a sharp endothermic peak in the thermograms measured by differential scanning calorimetry (DSC). Isotactic poly(cyclohexene carbonate) displays a melting point as high as 215–230°C, whereas syndiotactic poly(cyclohexene carbonate)s are mostly amorphous, with no observable melting point.^{54,61} DSC analysis of amorphous polycarbonates allows identifying the glass-transition temperature (T_g), i.e., the temperature at which the polymer undergoes a reversible transformation from glass state to a rubber-like state, as the temperature corresponding to a change in slope in the DSC thermogram (identified by an inflection point).⁶⁹ DSC thermograms of semicrystalline polycarbonates may display both T_g and T_{mp} (see Figure 10).⁵³ The glass-transition temperature of polycarbonates increases with their molecular weight up to a certain value of M_n , above which the T_g becomes approximately constant.⁷³ An example of the relationship between M_n and T_g is provided by the comparison between two poly(propylene carbonate) samples with the same regioregularity (90% HT content) and different M_n (4 and 115 kg/mol), which showed that the polymer with lower M_n value displays lower T_g (37.3°C against 44.5°C).⁷⁴ T_g is also affected by the regio- and stereoregularity of the polycarbonate: isotactic poly(propylene carbonate) exhibits a T_g of 47°C, which is about 10°C higher than that of the corresponding atactic polycarbonate.⁷⁵ A similar trend is followed by poly(cyclohexene carbonate) (see Figure 10). There is a direct relation between the T_g of a CO₂-epoxide copolymer and its composition. The presence of ether linkages in the polymer backbone (see Catalytic reaction of CO₂ with epoxides and Selectivity and yield in the copolymerization of CO₂ with epoxides sections) leads to polymers with lower T_g . The effect of the polyether linkages on

the glass-transition temperature can be expressed by the formula: $\frac{1}{T_g} = \frac{W_{PC}}{T_{g,PC}} + \frac{W_{PE}}{T_{g,PE}}$, where $W_{polycarbonate}$ and W_{PE} are the weight fraction of the carbonate and ether linkages, respectively, and $T_{g,PC}$ and $T_{g,PE}$ are the glass-transition temperatures of the pure polycarbonate and of the pure polyether, respectively. Polyether of propylene oxide has lower T_g than poly(propylene carbonate). Therefore, the more ether linkages are present in the polymer structure, the lower T_g is expected. For example, poly(propylene carbonate) with 40–60% ether linkages showed T_g of 8°C, while poly(propylene carbonate) with 17% ether linkages showed T_g of 38–42°C.⁷⁶ The glass-transition temperature of polycarbonates also depends on the nature of the epoxide used as substrate in the copolymerization. The T_g increases with increasing chain stiffness: for example, poly(hexene carbonate) is less rigid and has significantly lower T_g compared to poly(cyclohexene carbonate) (Table III). The T_g of poly(cyclohexene carbonate) is similar to that of polystyrene, but lower than that of conventional bisphenol-based polycarbonates.^{7,43} The T_g of polycarbonates based on aliphatic terminal epoxides decreases with increasing length of the alkyl side chain [e.g., in order of decreasing T_g value: poly(pentene carbonate) > poly(hexene carbonate) > poly(octene carbonate)].⁶⁹ This trend is ascribed to the larger free volume present in polycarbonates prepared with epoxides having longer alkyl chains, which causes a decrease in the dipolar interactions between the polymer chains.

If heated at sufficiently high temperature, polycarbonates start to chemically decompose. The thermal decomposition can be studied by DSC and thermal gravimetric analysis (TGA) and the obtained information can be used to estimate the optimum operating conditions for the processing and application of polycarbonates.⁶⁹ When the analysis is performed by DSC, the reported quantity is typically the initial decomposition temperature (IDT) of the polycarbonate. When the measurement is

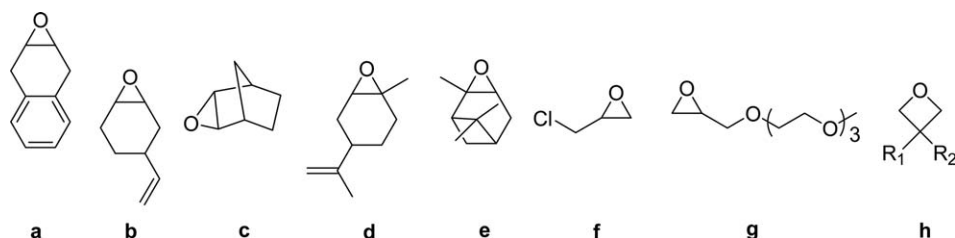


Figure 11. Less-explored substrates for the copolymerization with carbon dioxide.

carried out by TGA, the thermal decomposition temperature is generally expressed by specifying the percentage of mass loss at that temperature (e.g., $T_{d50\%}$, see Table III). It has been proposed that the decomposition of CO_2 -epoxide copolymers starts through depolymerization via a back-biting mechanism with formation of the corresponding cyclic carbonate (see also Terminal groups section). In such case, it has been suggested that the T_d values measured by TGA might be due to desorption of the formed cyclic carbonate, which occurs at higher temperature compared to the onset of the depolymerization.³⁹ The analysis of a series of CO_2 -epoxide copolymers showed that the higher the hydrocarbon content in the polymer, the higher the IDT (Table III). In addition, polycarbonates with a rigid backbone such as poly(cyclohexene carbonate) show higher IDT compared to CO_2 -epoxide copolymers with a more flexible backbone, such as poly(propylene carbonate) (Table III).⁶⁹ Poly(cyclohexene carbonate) is melt-processable because of its high decomposition temperature ($T_{d50\%}$ above 300°C).⁶⁹ Regio- and stereoregular copolymers have higher IDT than the corresponding atactic polycarbonates. Poly(propylene carbonate) consisting of two isotactic polymer chains at each end (one *R* and one *S*) was prepared by stepwise copolymerization with the two enantiopure epoxides using SalenCoOAc as catalyst (**5d** in Figure 3).⁷⁷ This stereoblock-isotactic polycarbonate showed higher decomposition temperature ($T_{d50\%} = 253^\circ\text{C}$) compared to atactic poly(propylene carbonate) ($T_{d50\%} = 224^\circ\text{C}$) and also to isotactic *R*-poly(propylene carbonate) ($T_{d50\%} = 227^\circ\text{C}$). The higher decomposition temperature was ascribed to the stereocomplex formation between adjacent (*S*)- and (*R*)-poly(propylene carbonate) blocks.

Mechanical Properties. The mechanical properties of polycarbonates (Table III) can differ significantly as a function of the nature of the epoxide used in the copolymerization with CO_2 . For example, poly(cyclohexene carbonate) is a brittle material at room temperature,⁴³ whereas poly(ethylene carbonate) displays rubber-like properties.⁶⁹ Understanding the mechanical behavior of polymers when they are subjected to an external force is essential for their applications. In tensile testing, the polymer specimen is subjected to high-strain deformation until it ultimately ruptures. The tensile modulus (E , also known as elastic modulus or Young's modulus) and the tensile strength (TS) can be experimentally determined from the graph of stress-strain over the entire strain range: the slope of the curve provides the tensile modulus and the highest point of the curve marks the TS. The higher the E the more stress the polymer can tolerate before deformation and rupture.⁶⁹ There is a direct correlation between the tensile modulus of polycarbonates and their T_g

(Table III).⁶⁹ Other important mechanical properties of polymers include the elongation at break and the impact strength. The elongation at break is calculated as the percentage of elongation at the moment of rupture in the tensile test. The impact strength is the resistance of a polymer against a suddenly applied load. Polymers that show high impact strength and large elongation at break have rubbery properties. Poly(propylene carbonate) shows higher elongation at break and impact strength compared to poly(cyclohexene carbonate) (Table III). For these features, poly(propylene carbonate) is suitable for application as additive to increase the elasticity of other polymers (see Applications section).³⁹ On the other hand, polycarbonates with low T_g such as poly(propylene carbonate) are not applicable as engineering plastics, for which purpose they should show high stability over a wide temperature range, under mechanical stress and harsh chemical and physical conditions. Poly(cyclohexene carbonate) displays better mechanical properties in terms of tensile modulus and strength compared to polycarbonates with low T_g (Table III), but its brittleness (lower impact strength and elongation at break compared to bisphenol-based polycarbonates) limits its applicability.⁴⁴

Other Physicochemical Properties. Biodegradability. Biodegradation is the process in which a material breaks down into simpler compounds by itself or as a result of the action of enzymes or microorganisms. Recently, a big concern has been raised over plastic wastes because of environmental hazards of plastic debris.⁸¹ One of the strategies to tackle this issue involves the substitution of conventional plastics with biodegradable plastics. Differently from bisphenol-based polycarbonate, CO_2 -epoxide copolymers are generally biodegradable.²⁶ The structure, morphology, molecular weight, and surface properties of polycarbonates influence their biodegradation.⁸² Poly(propylene carbonate) is biodegradable in air, in water, and in soil, and does not emit any toxic substance via degradation or random chain-breaking processes.⁸³ Hydrolysis plays a major role in the degradation process. The rate of biodegradation of poly(propylene carbonate) has been found to be strongly dependent on the conditions to which the polymer is subjected.³⁹ On the other hand, if the purpose is to avoid degradation of CO_2 -epoxide copolymers, the removal or deactivation of the Lewis-acid catalyst and storage at low temperature and in the dark are recommended.⁸³

Solubility. Solvents and antisolvents are used in many different processes within the polymer manufacturing industry, e.g., in

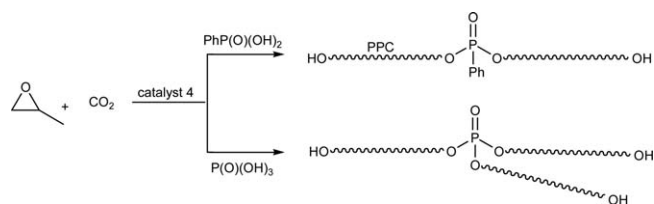


Figure 12. Proposed structure of flame-retarding poly(propylene carbonate) polyols prepared by using phosphorous compounds as chain-transfer agents [the wavy lines represent the poly(propylene carbonate) chains].

polymer casting and coating processes to make thin polymer films, in the fabrication of devices and in making foams.⁸⁴ Therefore, information about the solubility of polycarbonates is of practical importance. polycarbonates dissolve in moderately polar solvents such as tetrahydrofuran, CH_2Cl_2 , and CHCl_3 . Poly(propylene carbonate) does not dissolve in long chain alkanes and alkanols, water, and ethylene glycol and poorly dissolves in methanol and substituted aromatic compounds.³⁹ Polymers containing both ether linkages and carbonate linkages have been reported to be a rare example of nonfluorinated polymers that exhibit high solubility in supercritical CO_2 .⁸⁵ Notably, the solubility of these polymers in CO_2 is higher than both pure polycarbonates and pure polyethers.

Hydrophilicity. Hydrophilicity is an important property of polycarbonates for potential biomedical applications as membranes, carriers for drug delivery, and polymeric scaffolds for tissue regeneration.⁸⁶ The hydrophilicity/hydrophobicity of polycarbonates can be tuned by introducing functional groups such as alkyl, $-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$, and $-\text{COOR}$ on the polymer chain.^{87,88}

Alternative Approaches for the Synthesis of polycarbonates from CO_2 and Epoxides

Copolymerization of CO_2 with Less-Explored Epoxides and with Oxetanes. The alternating copolymerization of carbon dioxide with epoxides has been mainly studied with a limited set of epoxides, among which propylene oxide and cyclohexene

oxide received larger attention (see Physicochemical properties of the polycarbonates section). The copolymerization reaction has been investigated also with other epoxides having different electron-withdrawing or electron-donating groups, such as 1,4-dihydronaphthalene oxide (**a** in Figure 11),⁸⁹ 4-vinyl-1,2-epoxyhexane (**b**),⁹⁰ exo-norbornene oxide (**c**), limonene oxide (**d**),⁹¹ α -pinene oxide (**e**), and epichlorohydrin (**f**).⁴⁷ There is particular interest in reacting these last three epoxides with CO_2 because, differently from other epoxides, these compounds can be produced from biorenewable resources.²⁹ The use of these epoxides as substrates to produce polycarbonates would represent a new, fully green route based on nonpetrochemical feedstocks. Limonene oxide can be considered a green alternative to cyclohexene oxide. Moreover, the double bond functionality of limonene oxide would offer opportunities for modification and crosslinking of the polycarbonates polymer chain. Oxetanes, i.e., four-membered cyclic ethers (**h** in Figure 11), are the closest homologues to epoxides. Recently, these compounds were studied as monomers in the coupling reaction with CO_2 to produce copolymers.⁹² Oxetanes are less reactive than epoxides due to the lower ring strain, but they are thermodynamically more prone to produce polycarbonates rather than cyclic carbonates in the CO_2 -oxetane coupling reaction. The formation of the polycarbonate can occur via direct CO_2 -oxetane copolymerization and/or via ring-opening polymerization (ROP) of the generated six-membered ring cyclic carbonate.^{92,93}

Copolymerization of CO_2 with Epoxides in the Presence of Chain-Transfer Agents. The influence of chain-transfer agents on the molecular weight of CO_2 -epoxide copolymers was discussed in Molecular weight and polydispersity section. A chain transfer agent may also introduce new features into the polycarbonate, and if it contains more than one protic group it can act as connection point between two or more polymer chains. For instance, the addition of phenylphosphonic acid [$\text{PhP}(\text{O})(\text{OH})_2$] or phosphoric acid [H_3PO_4] as chain transfer agent in CO_2 -PO copolymerization catalyzed by a cobalt salen

Table IV. Selected Terpolymerizations of Two Epoxides with CO_2

Entry	Monomers	Catalyst	Ratio between the two epoxides In the feed ^a	Ratio between the two epoxides In the terpolymer ^b	M_n (kg/mol)	T_g ($^\circ\text{C}$)	$T_{d50\%}$ ($^\circ\text{C}$)	Ref.
1	SO/PO	5e	50 : 50	29 : 71	21	55	271	31
2	SO/CHO	5e	50 : 50	48 : 52	20	100	295	31
3	PO/BO	2	50 : 50	62 : 38	164	29	235	79
4	"	2	20 : 80	29 : 71	145	19	225	79
5	PO/HO	2	50 : 50	68 : 32	120	19	237	79
6	"	2	20 : 80	35 : 65	51	-2	241	79
7	PO/CHO	2	50 : 50	67 : 33	134	65	258	79
8	"	2	20 : 80	36 : 64	110	96	260	79
9	CHO/EO	5e	50 : 50	37 : 63	48	32	289	25
10	CHO/PO	5e	50 : 50	52 : 48	51	79	292	25
11	CHO/BO	5e	50 : 50	56 : 44	42	68	298	25
12	CHO/HO	5e	50 : 50	65 : 35	40	72	302	25

^aPercentage of each monomer in the reaction mixture.

^bPercentage of each polycarbonate in the final terpolymer chain.

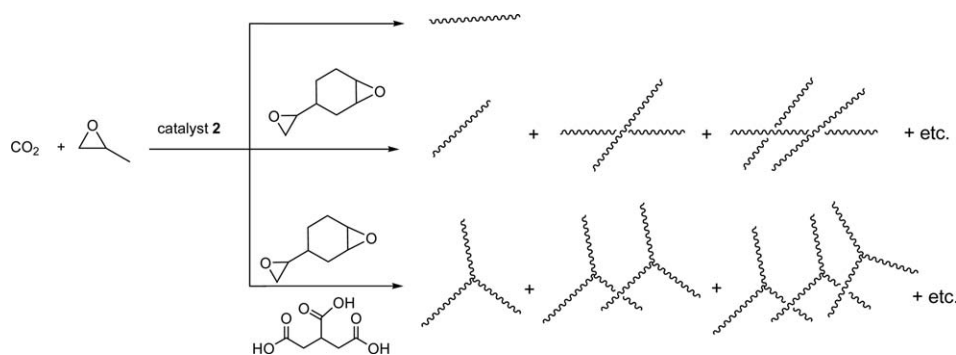


Figure 13. Possible types of interconnected poly(propylene carbonate) chains obtained by adding a small amount of vinylcyclohexene dioxide to the synthesis mixture of the CO₂-PO copolymerization.

complex (3 in Figure 3) generated flame-retarding poly(propylene carbonate)s, which have been proposed to display a phosphorus-containing group at the mid-point and -OH groups at chain ends (Figure 12).⁶²

Terpolymerization. A recently developed strategy to tune and improve the physical properties of polycarbonates consists in coupling CO₂ with two different epoxide molecules (terpolymerization). However, these reactions are hard to achieve because of the different reactivity and rate of copolymerization of different epoxides with CO₂.^{10,31,69} Terpolymerization of CO₂-SO-CHO and CO₂-SO-PO with different monomer ratios have been reported using a chiral SalenCo/PPN-DNP binary catalyst system (5e in Figure 3).³¹ These studies showed that two connected propylene carbonate units have a higher chance to form compared to propylene carbonate-styrene carbonate units, due to the lower reactivity of SO compared to PO (Table IV, Entry 1). This led to a lower ratio of SO in the formed terpolymer. On the other hand, the terpolymerization of CO₂-SO-CHO yielded a polycarbonate with very similar content of the two epoxides (Table IV, Entry 2). This result can be ascribed to the much smaller difference in reactivity between SO and CHO. Terpolymers of propylene oxide with a series of other epoxides, i.e., CO₂-PO-CHO, CO₂-PO-HO, and CO₂-PO-BO (HO = 1-hexene oxide; BO = butene oxide), were prepared using a functionalized SalenCo complex (2 in Figure 3) as catalyst.⁷⁹ These terpolymers display higher decomposition temperature compared to pure poly(propylene carbonate) (Table IV, Entries 3–8). Moreover, the choice of the epoxide combined with propylene oxide in the terpolymer allowed tuning the *T_g* value of the polycarbonate between -2 and 96°C (Table IV, Entries 3–8). In another study, the *T_g* of terpolymers of cyclohexene oxide with

a series of other epoxides could be tuned between 32°C and 79°C (Table IV, Entries 9–12).²⁵ A terpolymer of CO₂, PO, and 2-((2-(2-(2-methoxyethoxy)ethoxy)methyl)oxirane (ME₃MO, compound **g** in Figure 11) showed promising features for biomedical applications such as enhanced hydrophilicity, higher degradation rate and better cell adhesion compared to poly(propylene carbonate).⁹⁴

Addition of a small amount of vinylcyclohexene dioxide (0.01–0.06 mol %) in the CO₂-PO copolymerization catalyzed by a SalenCo complex (2 in Figure 3) led to the generation of connected polymer chains and resulted in increased molecular weight and *PDI* of the final copolymer.⁹⁵ The topology and the properties of the obtained polymer could be further changed by including in the reaction mixture a chain-transfer agent containing carboxyl groups [tricarballic acid (C₃H₅(CO₂H)₃), 1,2,3,4-butanetetracarboxylic acid (C₄H₆(CO₂H)₄), or adipic acid (C₄H₈(CO₂H)₂; Figure 13]. These chain-transfer agents can act as a connection point between different polymer chains, similarly to what described in Copolymerization of CO₂ with epoxides in the presence of chain-transfer agents section.

Block Copolymerization. Block copolymerization consists in creating different CO₂-epoxide copolymer blocks in the polycarbonate chain by introducing *in situ* a second epoxide right after the copolymerization of carbon dioxide with the first epoxide, using the same catalyst system. This is a new strategy for tuning the properties of polycarbonates such as the *T_g*, the hydrophilicity and the biodegradability. Block copolymerization represents a straightforward alternative to terpolymerization to obtain polycarbonates consisting of different epoxides in a controlled way. The obtained multiblock polycarbonates contain two or more discrete blocks (Figure 14).^{90,96} An example of the synthesis of multiblock polycarbonates utilized various cyclohexene oxide derivatives with different alcoholic, lipophilic, hydrophilic, and fluorophilic functional groups. The sequential copolymerization was achieved by injecting a new epoxide into the solution containing the catalyst every 15 minutes.⁹⁰

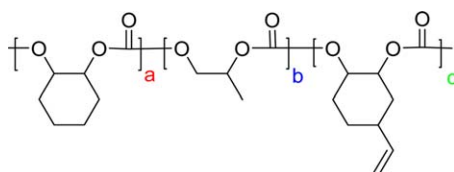


Figure 14. Block copolymer of CO₂ with cyclohexene oxide, propylene oxide and 4-vinyl-1,2-cyclohexene oxide. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

APPLICATIONS

polycarbonates obtained from bisphenol A (see Introduction section) have a large variety of applications as engineering plastics because of their excellent physical properties.^{16,18} They are

produced from bisphenol A and phosgene, which is a highly toxic compound, or via a greener route involving the reaction of bisphenol A with diphenyl carbonate, which can be obtained from a cyclic carbonate prepared from an epoxide and CO₂ (Figure 1).¹⁶ On the other hand, polycarbonates prepared by the alternating CO₂-epoxide copolymerization are not applicable as engineering plastics because they display inferior mechanical properties and chemical and thermal stability compared to those of the bisphenol-based polycarbonate (see Table III and Thermal properties, Mechanical properties and Other physicochemical properties sections). Different strategies have been investigated to improve the mechanical and thermal properties of CO₂-epoxide copolymers, including terpolymerization and block copolymerization (see Terpolymerization and Block copolymerization sections), postpolymerization modifications (e.g., crosslinking⁹⁷), blending with other polymeric materials or mixing with inorganic solids.^{39,67,97,98} Some of these approaches have already been considered for industrial production. BASF and Siemens studied polymers based on poly(hydroxybutyrate) and poly(propylene carbonate) as alternatives to acrylonitrile butadiene styrene (ABS) plastic.⁹⁹ Bayer is producing a highly elastic, scratch-resistant polymer by blending polycarbonates and ABS.¹⁰⁰ The strategies involving the formation of composites of polycarbonates with inorganic materials can require an enhancement of the ability of the CO₂-epoxide copolymers to wet or adhere to the selected inorganic solid (e.g., glass plates or fibers). This can be achieved by incorporation of functional groups (e.g., silicon-, boron-, or phosphorous-containing functional groups, sulfonic, or carboxylic acid groups) in the side chains or as terminal groups of the polymer.¹⁰¹ The obtained composite materials have been proposed to be suitable for medical, electrical, and automotive applications.¹⁰¹

Besides the above-mentioned attempts to overcome the current limitations in the application of CO₂-epoxide copolymers as engineering plastics, many other attractive alternative applications of these polycarbonates have been investigated in recent years. Some of these applications have already been industrialized or are on the verge of being commercialized. Bayer is using low-molecular-weight poly(propylene carbonate) as a polyol component in the synthesis of polyurethanes,^{7,83} particularly for their widespread application as flexible and rigid foams.^{7,102} Novomer investigated many parameters in the synthesis and postsynthetic modification of CO₂-epoxide copolymers,^{101,103,104} and is developing thermoplastics based on poly(propylene carbonate) and poly(ethylene carbonate) as an alternative to petroleum-based plastics such as polypropylene and polystyrene.¹⁰⁵ DSM in conjunction with Novomer has been considering the commercialization of a range of polymer resins based on poly(propylene carbonate) and poly(cyclohexene carbonate) for application as adhesives, coatings and inks.¹⁰⁶ Poly(propylene carbonate)s that contain polyether linkages find application as pore-forming agents in the ceramic industry.⁷

A variety of other applications has been proposed and is currently under investigation for CO₂-epoxide copolymers. Among these polycarbonates, the potential applications of poly(propylene carbonate) have been studied more extensively. Typically,

each of these applications tries to take advantage from one or more features conferred by the physicochemical properties of this polymer. Poly(propylene carbonate) displays features such as adhesion, processability, and thermal degradability that make it potentially useful for application as organic filler in packaging material and containers.¹⁰⁷ Poly(propylene carbonate) has also possible applications as adhesive in oxygen- and water-resistant materials and as water and gas barrier adhesive in laminate formation.^{39,62,108} Poly(propylene carbonate) is biodegradable and biocompatible as it generates nontoxic products by enzymatic degradation in the body.¹⁰⁹ Therefore, it has potential application in medical implants. Poly(propylene carbonate) can also be used in combination with other polymers (such as starch) to make biodegradable plastics.^{39,98,110} Upon ignition, poly(propylene carbonate) burns in air with a heat of combustion that is about 1/3 of that of natural gas, and produces no toxic gas nor any ash as it decomposes in air in a controlled way generating CO₂ and water.³³ Since the products of the combustion and degradation of this polymer are not-toxic, flame-retarding poly(propylene carbonate)s having a phosphorus-containing group at the mid-point (see Copolymerization of CO₂ with epoxides in the presence of chain-transfer agents section) have been developed as a green alternative to halogenated flame-retarding polymers such as polyvinyl chloride, which have been banned by the European Union.⁶² Further potential applications of poly(propylene carbonate)s with high molecular weight are in passive electronic components and as binder and lubricant in ceramics,¹¹¹ while those with low molecular weight might be used as coating resins and as surfactants.^{62,83,112}

OUTLOOK

polycarbonates prepared by the alternating copolymerization of carbon dioxide with epoxides are a class of polymers attracting growing attention both in the academic and the industrial world. The interest toward these materials arises from their biodegradability and their greenness connected to the use of a waste product as the greenhouse gas CO₂ as feedstock. There is ample space for creative development in this field of research. Future efforts can be directed to the development of robust and versatile catalytic systems that are able to work under industrially acceptable conditions while achieving excellent yield and selectivity toward polycarbonates. Ideally, these catalysts should also allow controlling the polymers properties in terms of molecular weight and regio- and stereochemistry. These studies on the synthesis of polycarbonates could also involve the investigation of bio-based epoxides as renewable substrates and the introduction of functional groups in the polymer chain to allow further modification of the material. Important developments can be expected also at the level of polymer engineering through postsynthetic treatments, which can range from crosslinking to the preparation of (nano)composites with inorganic materials and blending with other polymers. The prospect of these research activities is to gain further ability in tuning the physicochemical properties of the polycarbonates and to broaden the range and relevance of their applications, thus providing an attractive and more sustainable alternative to petroleum-based polymers.

ACKNOWLEDGMENTS

The authors acknowledge Dr. Ceren Özdilek for useful scientific discussion. The authors acknowledge sponsoring in the frame of a START1 research program.

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