Cyclic carbonates as monomers for phosgene- and isocyanate-free polyurethanes and polycarbonates*

Sang-Hyun Pyo[1,‡], Per Persson[2], M. Amin Mollaahmad[1],
Kent Sörensen[2], Stefan Lundmark[2], and Rajni Hatti-Kaul[1]

[1]*Department of Biotechnology, Center for Chemistry and Chemical Engineering, Lund University, Box 124, SE-221 00 Lund, Sweden;* [2]*Perstorp AB, 284 80 Perstorp, Sweden*

Abstract: Polyurethanes and polycarbonates are widely used in a variety of applications including engineering, optical devices, and high-performance adhesives and coatings, etc., and are expected to find use also in the biomedical field owing to their biocompatibility and low toxicity. However, these polymers are currently produced using hazardous phosgene and isocyanates, which are derived from the reaction between an amine and phosgene. Extensive safety procedures are required to prevent exposure to phosgene and isocyanate because of its high toxicity. Therefore, the demand for the production of isocyanate-free polymers has now emerged. Among the alternative greener routes that have been proposed, a popular way is the ring-opening polymerization (ROP) of cyclic carbonate in bulk or solution, usually using metallic catalyst, metal-free initiator, or biocatalyst. This review presents the recent developments in the preparation and application of cyclic carbonates as monomers for ROP, with emphasis on phosgene- and isocyanate-free polymerization to produce aliphatic polycarbonates and polyurethanes and their copolymers.

Keywords: aliphatic polyurethanes and polycarbonates; biocatalysis; biotechnology; cyclic carbonates; green chemistry; phosgene- and isocyanate-free polymerization; polymers; ring-opening polymerization; ring-opening reactions.

INTRODUCTION

Aliphatic polyurethanes and polycarbonates

Polyurethanes and polycarbonates constitute important groups of industrial polymers besides polyesters, with applications in a variety of sectors and also known for their biodegradable and biocompatible features. The global polyurethane business is now well over 8.5 million tonnes while that of polycarbonates is estimated to be around 3 million tonnes (<http://www.icis.com/v2/chemicals/9076146/polycarbonate/uses.html>).

Polyurethanes are widely used in foams, seating, seals, and high-performance coatings and adhesives. In recent years, a variety of biomedical polyurethane elastomers exhibiting improved hydrolytic stability have been developed. Owing to their toughness, durability, biocompatibility, and improved biostability, they have been incorporated into a wide variety of implantable biomedical devices [1].

Aliphatic polycarbonates are tough, dimensionally stable thermoplastics widely used in engineering and optical applications. The most important types are the polycarbonates based on bisphenol A. Like polyurethanes, polycarbonates are expected to find use also in the biomedical field because of their biocompatibility and low toxicity [2,3–5]. Aliphatic polycarbonates may have advantages over aliphatic polyesters such as polylactide and lactide-glycolide copolymer, because of their relatively low rate of hydrolysis in aqueous media and their more amorphous nature [2]. They are also advantageous in that they do not form carboxylic acids upon degradation, which can lead to an increase in acidity of the surrounding tissue [2]. Aliphatic polycarbonates and their copolymers are biodegradable and recyclable [6,7]. Poly(tetramethylene carbonate) (PTeMC) and poly(hexamethylene carbonate) (PHMC) have been shown to be successfully biodegraded by environmental microbes [6,7].

In spite of the functionally desirable features of the polymer products, the processes for their manufacture involve highly toxic reagents, primarily phosgene but also isocyanates, which are hazardous [8–10]. Polyurethanes are produced using polyols, such as alkanediols and glycerol, and isocyanate, and are generally resistant to biodegradation [9,11]. This may be ascribed to both the complexity of the molecular structures owing to the very high reactivity of diisocyanate and lack of enzymatically cleavable linkages in the polymer chain that lead to the molecular weight reduction [9]. Aliphatic polycarbonates are produced industrially by reaction of an alkanediol with phosgene, triphosgene or dialkylcarbonates [12]. A demand has now emerged for polymers with unaltered properties, but produced without the use of toxic starting materials. Attempts have thus been made to develop routes to make polyurethanes from other sources, however, none of these have yet been commercially established [4].

This chapter provides a brief overview of the field of aliphatic polyurethanes and polycarbonates, including their raw materials, and cyclic carbonates as potential monomers for synthesis of the polymers through alternative phosgene/isocyanate-free routes.

Phosgene and isocyanate in the polymer industry

Phosgene [CAS 75-44-5] (carbonyl chloride, carbon oxychloride, chloroformyl chloride, $COCl_2$) is a colorless, low-boiling liquid, and was first prepared from a photochemical reaction of carbon monoxide with chlorine in 1812. Globally, approximately 75 % of phosgene is consumed for production of di- and polyisocyanates that are used in the preparation of polyurethanes (see Scheme 1), 20 % is used for polycarbonates, and about 5 % for the synthesis of chloroformates and carbonates, which are used as intermediates in the synthesis of pharmaceuticals and pesticides [13]. Phosgene is an insidious poison as the odor is unnoticed and the symptoms may be slow to appear [13,14]. Because of its toxicity, careful and extensive safety procedures and equipment are incorporated in plant design and operation to prevent exposure to phosgene. Practically all phosgene manufacture is captive, i.e., it is used in the manufacture of other chemicals within the plant boundaries.

Phosgene   Isocyanate   Urethane unit
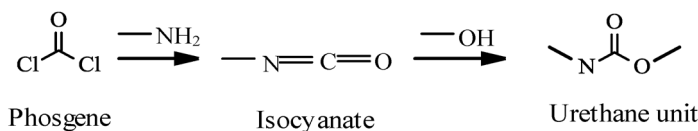
Scheme 1 Synthesis of urethane unit from phosgene and isocyanate.

Worldwide annual production of isocyanates is in excess of 4 million tons [15,16]. Aliphatic diisocyanates and polyisocyanates—in this review collectively referred to as aliphatic isocyanates—are reactive intermediate species whose terminal isocyanate functions react with hydroxyl groups of diols and polyols to form polyurethanes. The major aliphatic isocyanates produced commercially today are 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and dicyclohexylmethane-4,4'-diisocyanate (H_{12}MDI) (Fig. 1) [17].
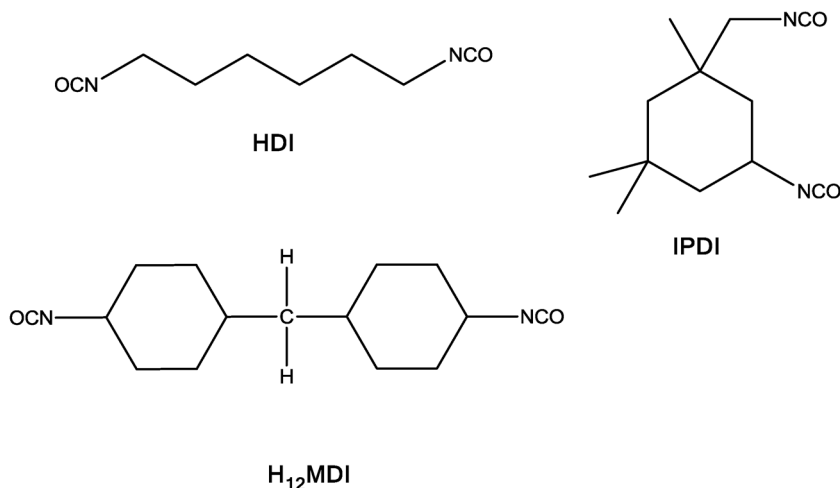

Fig. 1 The major commercial aliphatic isocyanates [17].

Nearly all of the HDI produced is directly converted to biuret or trimer adducts in order to make it safer to use. These adducts are used in coatings for cars, trucks, aircraft, wooden furniture, and in anti-corrosion applications. IPDI is also delivered in pre-reacted form and used more or less in the same applications as HDI, but also in UV-curable coatings, rocket propellants, and adhesives. H_{12}MDI is delivered in its pure form and used in formulations for plastic coatings and elastomers.

The main disadvantages with the current phosgenation process for production of isocyanates are associated with handling and storage of the highly poisonous phosgene. No alternative methods have so far managed to replace the phosgene route. The catalytic methods that have been tested are not selective enough and involve typically a catalyst based on palladium or some other precious metal that affects production costs negatively. There are methods developed to prepare isocyanates using a phosgene-free route by either reductive carbonylation of nitro compounds or by oxidative carbonylation of amines [18]. These methods are, however, mostly limited to aromatic compounds, which are out of the scope of this review.

The patent literature describes a two-step method based on urea-mediated conversion of aliphatic or cycloaliphatic diamines to diisocyanates without using phosgene. In the first step, a diamine is reacted with alcohol in the presence of urea [19]. The resulting diurethane is then purified and thermally cleaved to diisocyanate and alcohol [20,21]. Unwanted side reactions limiting the yield and formation of resin-like compounds disrupting the industrial processing have, however, held back industrial implementation.

Isocyanates are generally highly reactive; vapors and aerosol mists represent the main hazards, and prolonged exposure can cause sensitizing effects. Even at extremely low exposures, isocyanates are known to cause respiratory disorders, including asthma [22]. The respiratory diseases linked to occupational exposure to isocyanates have been studied and reviewed extensively [15,23–25]. Almost completely overlooked is the possibility of adverse health effects from residual isocyanates in consumer products, in particular, polyurethane-containing products. Organizations such as the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), and the American Conference of Governmental Industrial Hygienists (ACGIH) have set the exposure standards for several of these compounds at 5 ppb time-weighted average (TWA) for a full work shift and 20 ppb TWA for short-term exposure limits (STELS) or ceiling limits [26–29].

Polyurethane coatings

Urethane-based coatings belong to a currently fast-growing segment of the paint and coatings industry. Urethane coatings have properties such as excellent adhesion, high durability, good flexibility, resistance to corrosion and mechanical wear, and good optical properties, which make them suitable for high-demanding applications. Another advantage with urethanes is that they can be used in formulations with reduced organic solvent content. Reduction of organic solvents is enforced by legislations such as the U.S. Clean Air Act Amendment of 1990 and the EU Solvents Directive 2004/42/EG. These directives limit the amount of volatile organic content (VOC) allowed in lacquers and varnishes. Industrial polyurethane coatings are based on polyhydric alcohols, also known as polyols, and aliphatic isocyanates. The polyol is often a polyester or polyether, in many cases also modified with acrylic groups to enhance the cross-linking during curing. The typical linkages found in the cured film, apart from urethane, are also biuret, allophanate, urea, uretdione, and isocyanurate linkages. The formation of these different linkages is described in Fig. 2 [30].

Polyurethane coatings are either of reactive or nonreactive type. The main difference is that reactive formulations contain isocyanate groups that can react with nucleophiles such as alcohols, amines, or water. Reactive urethane coatings are either moisture-cured, one-component with blocked isocyanates or two-component types [30]. Moisture-cured formulations have the advantage that it is possible to achieve adhesion to wet substrates, which for other coating types is very difficult. The nonreactive formulations, also known as urethane alkyds, contain no unreacted isocyanates; instead, air oxidation of unsaturations in oils present in the formulation accomplishes the final curing. Polyurethane dispersions, PUD, are also of the nonreactive type, albeit with some exceptions for hybrid systems. There are also one-component coating systems where the isocyanate is blocked, commonly with 2-butanonoxime. Upon heating to 135–150 °C, the isocyanate is released and can react with the present polyols.
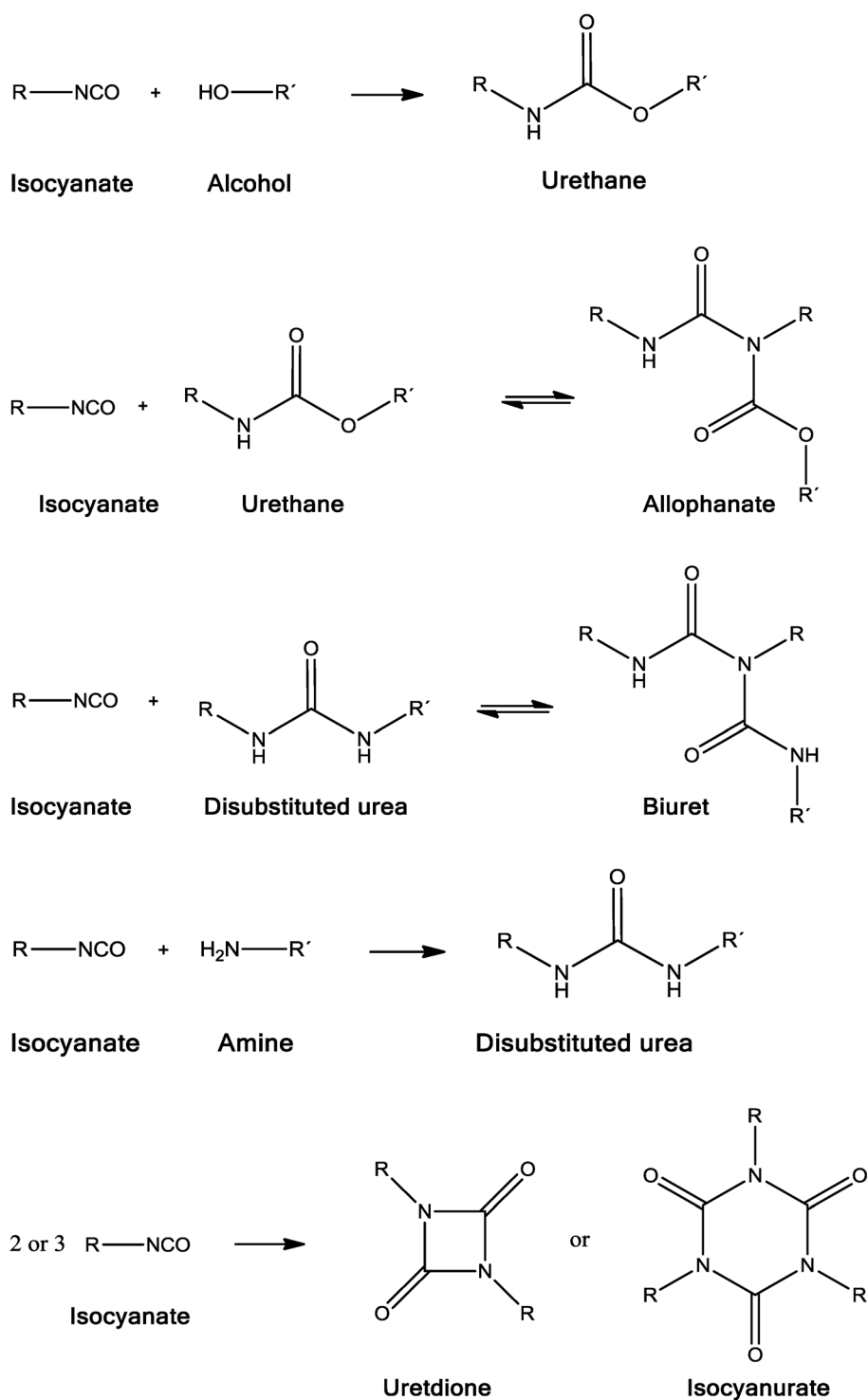
Fig. 2 Formation of the different linkages found in urethane networks.

CYCLIC CARBONATES AS MONOMERS FOR ISOCYANATE-FREE POLYMERS

Among the alternative phosgene-free routes that have been proposed for the synthesis of aliphatic polyurethanes and polycarbonates, a popular method is the ring-opening polymerization (ROP) of cyclic carbonate in bulk or solution [31]. So far, only five-membered cyclic carbonates, including ethylene carbonate (EC) and propylene carbonate, are commercially available since over 40 years, and have found numerous applications as both reactive intermediates and inert solvents [32]. Recently, glycerol carbonate (GC), a synthetic intermediate chemical in the alkylene carbonate family, has attracted attention owing to increasing interest in the utilization of glycerol, a by-product from biodiesel production [31–33]. GC is used as a precursor for lubricants, solvents, coatings, detergents, and cosmetics [34].

Chemical synthesis of cyclic carbonate

The chemistry of cyclic carbonates has been explored since the 1930s when they were first made by depolymerization of respective linear polycarbonates by Carothers et al. [35–37]. In 1930, Carothers and Van Natta reacted diethyl carbonate (DEC) with ethylene glycol and trimethylene glycol as well as with higher diols having up to 10 methylene groups. The authors concluded that five- and six-membered cyclic carbonates, i.e., EC and trimethylene carbonate (TMC), were readily formed in high yield, whereas larger diols tended to produce open polycarbonate chains [35]. The absence of functional groups, other than the obvious carbonate, limits the use in polymer technology, and there are few reports on this subject. One example in the patent literature describes cyclic alkylene carbonate adducts and their reaction with a polyol to form a polyhydroxyurethane [38].

CO_2, dialkylcarbonates, diphenylcarbonate, and phosgene derivatives have been usually used as sources of carbonate groups in the synthesis of cyclic carbonates. Lately, a number of reports have appeared on the synthesis of five- and six-membered cyclic carbonates by phosgene-free routes [39–44]. GC is currently industrially produced, albeit on a rather small scale. The various synthetic routes of GC include the reaction of glycerol with dimethyl carbonate (DMC) [45,46], and with CO_2 catalyzed by oxides of tin [47], gallium, gold, or zinc [48], and by carbonylation using carbon monoxide [49,50]. Furthermore, a method for tosylation of GC has been developed which enables linking with thiols, amines, and other nucleophiles [51]. Direct carbonation of glycerol and epoxide moieties using CO_2 or dialkylcarbonates has been demonstrated as a green route for synthesis of five-membered cyclic carbonate at high yield [41–43].

There are several examples that describe the preparation of cyclic carbonates from an oxirane and CO_2. Kim et al. [52] prepared five-membered bis(cyclic carbonate), by reacting the diglycidyl ether of bisphenol S with CO_2 using benzyltrimethyl ammonium chloride as phase-transfer catalyst. Wicks and Gutierrez [53] made cyclic carbonates from glycidyl neodecanoate and CO_2. Tamami et al. [54] transformed epoxidized soy bean oil to the corresponding cyclic carbonate. This monomer was polymerized in a following step with various aliphatic or aromatic diamines to form partly renewable polyhydroxyurethanes. Using hexamethylene diamine in 1:1 molar ratio, M_n (number average molar mass) and polydispersity index (PDI, M_w/M_n) of the polymer formed were determined as 12 900 and 1.29, respectively [52]. Five-membered cyclic formals in carbohydrates, such as 3,4-O-methylene-D-mannitol, were oxidized to the corresponding cyclic carbonate using chromium trioxide in acetic acid, as a means to selectively remove cyclic formals without affecting other functional groups present in the molecule [55]. Pattison prepared cyclic ethers from a number of triols and tetrols, including trimethylolpropane (TMP) and pentaerythritol, by reacting them with either DEC or EC [56]. A cyclic carbonate formed, as intermediate, was purified by distillation. It was concluded that cyclic carbonates containing free hydroxyl groups, such as the cyclic carbonate of TMP, are unstable and decompose rapidly at 180–200 °C to CO_2 and the corresponding cyclic ether [56].

Synthesis of six-membered TMC is traditionally achieved by reacting 1,3-propanediol with phosgene or its derivatives. Among the other reactions studied, metal-catalyzed coupling of oxetane such as trimethylene oxide with CO_2 has given high yields of TMC [11]. Endo et al. have reported a method of cyclic carbonate synthesis from propane-1,3-diol and ethyl chloroformate in the presence of a stoichiometric amount of triethylamine [57]. Transesterification of propane-1,3-diol with dialkylcarbonate catalyzed by metal or organo-catalysts has been proposed as a more environmentally benign procedure [58]. Polycyclic six-membered carbonates could be prepared by radical polymerization of acrylic monomers with pendant cyclic carbonate groups [59]. As a different approach, tris- or tetrakis (alkoxycarbonyloxy) derivatives, obtained from catalytic transesterification of the polyol, TMP with DEC, have been subjected to thermal disproportionation using Aerosil 200 at 200–220 °C followed by distillative depolymerization under reduced pressure, to give the cyclic product 5-ethyl-5-ethoxycarbonyloxymethyl-1,3-dioxane-2-one at a low yield [60].

Biocatalytic synthesis of cyclic carbonates

Biocatalytic processes provide several advantages over the conventional chemical processes due to low energy demand, less hazardous reagents, and higher selectivity. Lipases (triacylglycerol acylhydrolase, EC 3.1.1.3) constitute a class of enzymes which catalyze the hydrolysis of long-chain triglycerides in vivo to release glycerol and fatty acids, but in vitro lipases have been used to catalyze esterification, transesterification, interesterification, and other reactions with alcohols, esters, and other nucleophiles as acyl acceptors [61–64]. The diversity of reactions catalyzed makes lipases the most important group of biocatalysts for biotechnological applications. Lipase-catalyzed synthesis of biopolymers, enantiopure pharmaceuticals, agrochemicals, specialty chemicals, biodiesel, flavor compounds, etc. have been extensively reported [65–70].

Matsumura et al. reported the synthesis of poly(trimethylene carbonate) [P(TMC)] using commercially available immobilized lipase B from *Candida antarctica* (Novozyme®, N435) in a successive two-step polymerization from DEC or DMC and 1,3-propanediol via the cyclic monomer of TMC [71]. The P(TMC) could also be degradatively transformed by the same enzyme to the cyclic monomer in addition to linear and cyclic oligomers and a small amount of 1,3-propanediol (Table 1a) [72]. Later, direct enzymatic synthesis of cyclic TMC (1,3-dioxane-2-one) monomer with/without a methyl substituent was achieved using DMC or DEC and 1,3-diol with the objective of producing aliphatic polycarbonate [60]. The corresponding methyl-substituted and -unsubstituted cyclic TMCs were obtained from aliphatic 1,3-diols such as 1,3-butanediol, 2-methyl-1,3-propanediol, and 1,3-propanediol using N435 in an organic solvent (Table 1, entries b,c,d). The cyclic tetramethylene carbonate and hexamethylene carbonate dimers were prepared by reaction of 1,4-butanediol and 1,6-hexanediol, respectively, with diphenyl carbonate catalyzed by the immobilized lipase in anhydrous toluene (Table 1, entry e) [2].

Pyo et al. have recently reported the synthesis of six-membered cyclic carbonates bearing functional groups such as hydroxyl and/or alkoxycarbonyloxy groups by lipase-mediated reaction in a solvent-free medium [68]. Mono-, di-, and tri-carbonated TMP, and cyclic carbonates, were obtained by the reaction between TMP with DMC or DEC using N435 at 60 °C [68]. A large fraction of the linear carbonates in the product mixture were cyclized by disproportionation involving heating at 60–80 °C without catalyst. The final yield of cyclic carbonates was about 85 % (Table 1, entry f). The reactivity of DEC was lower than that of DMC in the enzymatic reaction [68]. The thermal cyclization was focused on equilibrium shift to cyclic carbonate, which has a minimum content of the ester ($-CO-OCH_3$), and this was achieved by continuous removal of the resulting methanol by evaporation, which prevented the reverse reaction from taking place [68].

Enzymatic synthesis of GC from glycerol and DMC was achieved with almost quantitative yield by N435 in tetrahydrofuran (THF) (Table 1, entry g) [42] and in solvent-free system (Table 1, entry h)

[73]. For the latter system, glycerol-coated silica gel instead of free glycerol was employed as the sub-strate. Biodiesel [fatty acid methyl esters (FAMEs)] and GC were simultaneously synthesized from corn oil and DMC via transesterification using N435 in solvent-free reaction in which excess DMC was used as the substrate and reaction medium (Table 1, entry i) [74].

Table 1 Example of biocatalytic synthesis of cyclic carbonates*.

Entry	Substrate	Temp./ time	Conversion (%)	Product	Ref.
a		70 °C, 24 h	70		[72]
b	R = CH₃ : DMC ; R = C₂H₅ : DEC	70 °C, 5 days	50		[60]
c		70 °C, 6 days	63		[60]
d		70 °C, 6 days	44		[60]
e		90 °C, 72 h / 70 °C, 24 h	66 / 64		[2]
f	R = CH₃ : DMC ; R = C₂H₅ : DEC	60 °C 48 h	85		[68]
g		60 °C, 30 h	94		[42]
h		70 °C, 48 h	>90		[73]
i		60 °C, 15 h	63		[74]

e. $x = 4$ cyclic TeMC dimer, $x = 6$ cyclic HMC dimer.
h. Glycerol-coated silica gel.
i. Glycerol is produced from corn oil used as raw material.
*The commercially available immobilized *C. antarctica* lipase B, N435 was used in all cases.

POLYMERIZATION OF CYCLIC CARBONATES FOR THE PRODUCTION OF ISOCYANATE-FREE POLYMERS

ROP of cyclic carbonates

Aliphatic polycarbonates can be obtained via ROP of their respective cyclic monomers using different kinds of initiators and catalysts according to cationic, anionic, coordination, and enzymatic mecha-nisms, or metallic compounds as catalysts [75–79], which allow full control over molecular parameters along with chain-end group fidelity.

Five-membered alkylene carbonates have been considered less for commercial use owing to thermodynamic properties in the ROP while six-membered cyclic carbonates provide more opportunities to be used in the polymerization [47,75]. The ROP of five-membered cyclic carbonates is a slow reaction that has been reported to proceed in the presence of catalysts such as metal alkoxides, metal acetylacetonates, and metal alkyls [47,80]. The polymerization involves partial decarboxylation and the loss of CO_2 such that the polymer produced contains both carbonate and ether linkages (Scheme 2). Following initiation (Scheme 2a) by an anionic species, the propagating chain predominantly adds EC via attack at the alkylene carbon (Scheme 2b), resulting in the production of an ether linkage. Thus, the polymerization of five-membered ring alkylene carbonates failed to selectively produce the thermodynamically disfavored poly(alkylene carbonate)s; the end product contained typically more than 50 % (mol/mol) ether linkages [80]. The reason is the quite low ceiling temperature (temperature at which propagation and depropagation rates are equal), which was only 25 °C for the ROP of EC, and the positive enthalpy of polymerization [81–85].
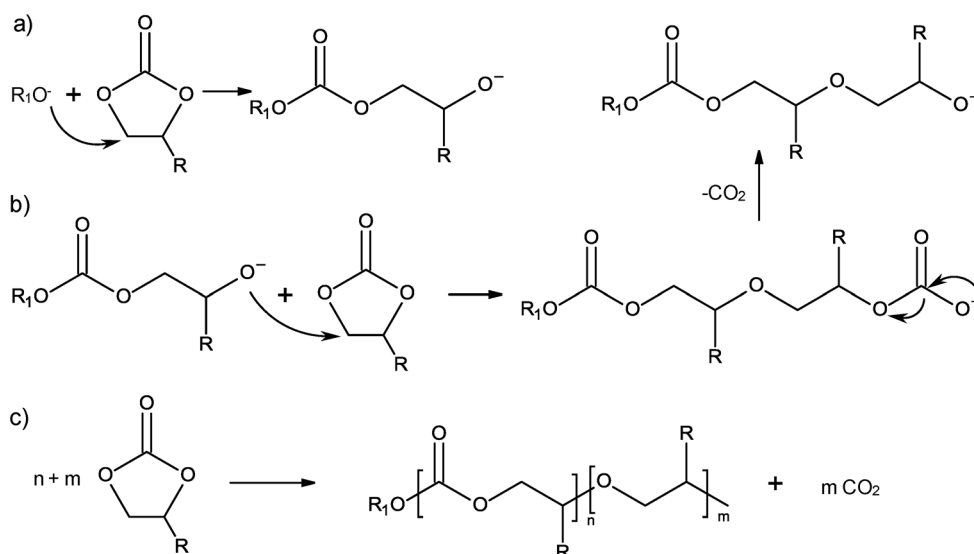
Scheme 2 ROP of five-membered ring cyclic carbonate [47,80]: (a) ring opening initiated by an anionic species; (b) propagation via nucleophilic attack on the methylene carbon yielding an ether linkage and decarboxylation; (c) overall ROP of five-membered ring alkylene carbonate to produce poly(alkylene ether carbonate).

Nevertheless, EC and other 1,3-dioxolan-2-ones have been polymerized at temperatures exceeding 100 °C [47]. Meanwhile, Vogdanis et al. reported that the entropy of ROP, ΔS_p, is positive, which means that for the process to occur spontaneously ($\Delta G_p < 0$), the enthalpy of ROP, ΔH_p, must be negative [47,82]. However, standard enthalpies of ROP of EC, resulting in pure poly(ethylene carbonate), were calculated to be 124.6, 125.6, and 112.5 kJ/mol measured at temperatures of –73, 25, and 170 °C, respectively. Since three- to seven-membered ring monomers show an entropy loss during ROP [86], the process of formation of poly(ethylene ether-carbonate) is possible only for negative enthalpy. ΔH_p for EC becomes negative at 170 °C. The reaction is additionally favored by the loss of CO_2, which partly compensates for the entropy loss [47].

Six-membered cyclic carbonate has been found to be an important class of monomers in polymer chemistry [87,88], and is smoothly transformed into the corresponding polycarbonate without volume shrinkage. This is an advantage since most polymerization processes involve volume reduction, which can cause problems such as lowering of adhesion, voids, microcracks, and residual stress in the poly-

meric material [89–91]. Moreover, six-membered cyclic carbonate is the preferred monomer for the ROP process, since in contrast to the five-membered monomer it is thermodynamically less stable than the ROP, and thus retains CO_2 during the polymerization reaction [58,92,93].

Tomita et al. [75] compared the reactivities of five- and six-membered cyclic carbonates toward amines, and evaluated the formed poly(hydroxyurethane). The reaction rates of the six-membered cyclic carbonate, 5-(2-propenyl)-1,3-dioxan-2-one, at 30–70 °C with hexylamine and benzylamine, respectively, in N,N-dimethylacetamide were 29 to 62 times higher than those of five-membered one, 4-(3-butenyl)-1,3-dioxolan-2-one [75]. The activation energy of the reaction of the six-membered cyclic carbonate with hexylamine (10.1 kJ/mol) was less than half of that of the corresponding reaction involving the five-membered cyclic carbonate (24.6 kJ/mol), probably due to the larger ring strain of six-membered cyclic carbonate [75]. Moreover, the heat of formation for reactants and products in the reactions of 1,3-dioxan-2-one and 1,3-dioxolan-2-one with methylamine was related to the ring strain energy difference (difference in the heat of formation between the initial and final states) between six- and five-membered cyclic carbonates by the semi-empirical method using the PM3 Hamiltonian (Fig. 3). The ring strain energy of the six-membered cyclic carbonate was 2.86 kcal/mol larger than that of the five-membered one.
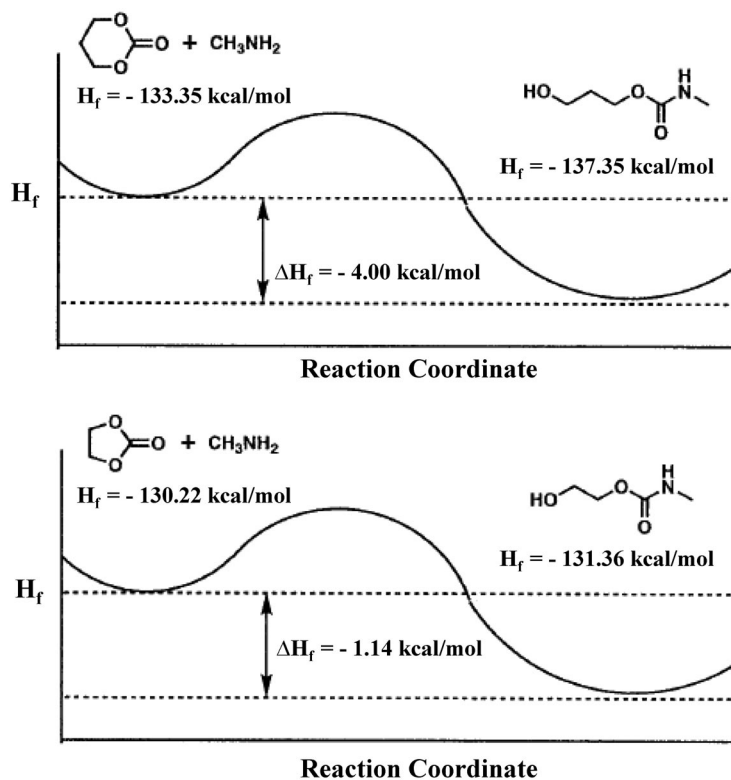
Fig. 3 Energy profiles of the reactions of 1,3-dioxan-2-one and 1,3-dioxolan-2-one with methylamine calculated by PM3 MO method [75]. Reproduced with permission from John Wiley.

Worth mentioning is the study on anionic ROP of seven-membered cyclic carbonate (1,3-dioxepan-2-one) by Endo and co-workers using *sec*-BuLi as initiator [94], which showed the relative polymerization rate to be about 35 times higher than that of the six-membered 1,3-dioxan-2-one.

In recent years, metal-free or low-toxicity catalyst/initiators systems such as alcohols/diols, acid, and enzyme for the ROP of carbonates, have increasingly attracted attention [77,95–99]. The ROP initiated by alcohols in the absence of a catalyst has been extensively investigated and allows the use of hydroxyl groups for the proper control of the molar mass, improvement in the hydrophicity/degradability, and further functionalization of the resulting biodegradable polyesters and polycarbonate [77].

Synthesis and properties of polymers prepared from cyclic carbonates

Kihara and Endo [100] studied the synthesis and properties of poly(hydroxyurethane)s made from different five-membered cyclic carbonates and primary diamines, as shown in Scheme 3. With hexamethylenediamine or dodecamethyldiamine, polymers with M_n of 20 000–30 000 were made. When short-chain diamines were used, lower polymer molecular weights were obtained. The high chemoselectivity of an amine toward a cyclic carbonate was shown by adding water, methanol, or ethyl acetate to the solvent—this had negligible effect on the M_n of the resulting polymer.
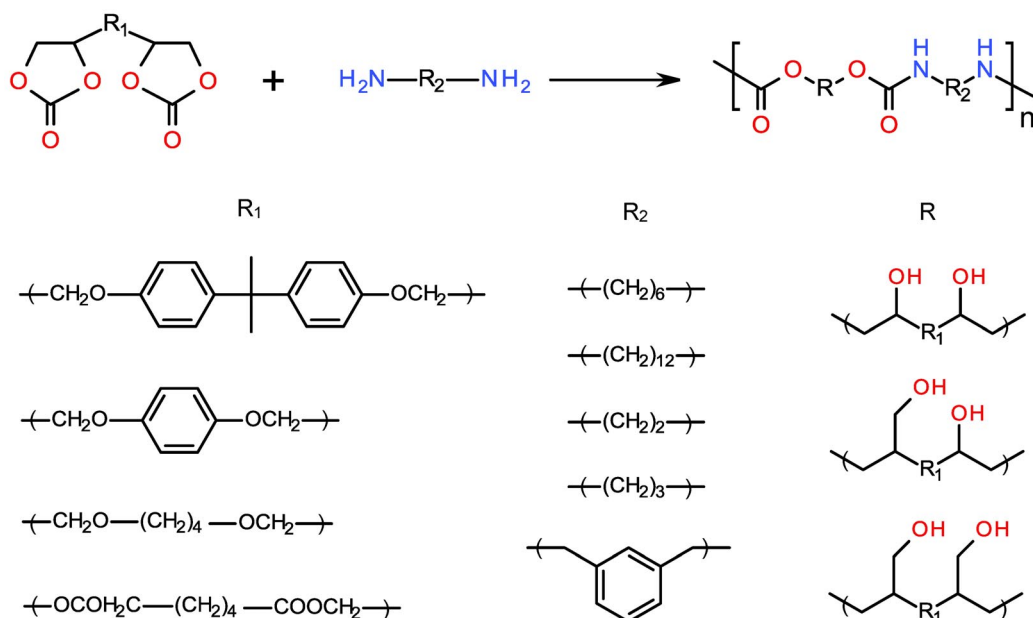
Scheme 3 Preparation of poly(hydroxyurethane)s from various five-membered cyclic carbonates and primary diamines [100]. Reproduced with permission from John Wiley.

Webster and Crain [101] studied functional polymers prepared in the free-radical copolymerization reaction of vinyl EC with vinyl ester monomers. The five-membered cyclic carbonates were mixed together with various amines, solvents, and additives in coating formulations. Primary amines and cyclic secondary amines were the most reactive. Aromatic amines, primary amines on a tertiary carbon, and acyclic secondary amines did not react. The effect of amine-carbonate stoichiometry was also studied. Higher levels of amine generally resulted in higher solvent resistance of the cured coating film.

Wicks and Gutierrez [102] made cyclic carbonates from glycidyl neodecanoate and CO_2. The cyclic carbonate was reacted with either ethylene diamine, 1,6-hexanediamine, or isophorone diamine to form bis-urethanes. Comparison was made with propylene carbonate, which in the reaction with isophorone diamine gave a liquid with a viscosity of 85 Pa·s. The cyclic carbonate of glycidyl neo-

decanoate gave liquid product with all three diamines, with viscosities between 30 and 47 Pa·s. The low viscosity helps reduce the need for solvent in coating formulations.

Hoecker and co-workers synthesized phenoxycarbonyloxymethyl ethylene carbonate from GC and phenyl chloroformate, which in a subsequent step was reacted with aliphatic diamines to form poly(hydroxyurethane)s [103]. The polymers were amorphous, and the glass-transition temperature (T_g) decreased with increasing number of methylene groups between the urethane linkages.

Tamami et al. [54] studied polyurethane networks prepared from soybean oil cyclic carbonate and 1,6-hexanediamine and other amines. It was shown that T_g and mechanical properties varied depending on the type of amine used. Li et al. also studied this reaction and concluded that a high purity of the carbonated soybean oil was not required to achieve polyurethanes of good performance [104].

Polyurethane preparations using acrylic and siloxane-modified cyclic carbonate and primary amines for use in UV- and thermostable coatings were studied by Figovsky et al. [105]. Hosgor et al. [106] reacted cyclic carbonate-modified silica particles with the cyclic carbonate of bis(4-glycidyloxy phenyl)phenyl phosphine oxide and 1,6-hexanediamine to form a polyurethane/silica nanocomposite, suitable as thermally stable coating composition.

One-pot synthesis of polyurethane from bisphenol A diglycidyl ether, CO_2, and diamine was accomplished by Ochiai et al. [107]. The resulting mixture was in situ modified by acetylation, benzoylation, or silylation in order to reduce the hydrophilicity of the polymers and hence expand the range of possible applications. Bisphenol A diglycidyl ether, CO_2, and an azo compound were also used to produce poly(azo)urethane (Fig. 4), and evaluated as Langmuir films. The properties indicated a possible use as temperature sensor [108].
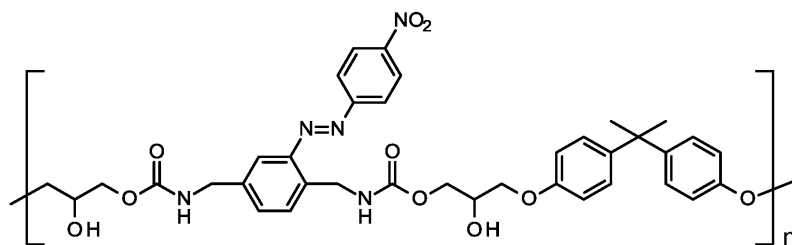
Fig. 4 Non-isocyanate poly(azo)urethane.

TMC was copolymerized with ε-caprolactone and an initiator to form a star-shaped polymer. With pentaerythritol used as initiator, a rubber-like material was formed that swelled in chloroform. This low-molecular-weight compound was used as a macro-initiator in a subsequent lactide/glycolide polymerization to produce a tough material with good mechanical properties [109].

Liu et al. [110] described the synthesis of aliphatic polycarbonates from cyclic six-membered carbonates with pendant ester groups, 5-methyl-5-methoxycarbonyl-1,3-dioxan-2-one (MMTC) and 5-methyl-5-ethoxycarbonyl-1,3-dioxan-2-one (Scheme 4). The carbonate monomers were prepared by reacting the corresponding diol with ethylchloroformate. The polymerization was carried out without solvent at 80 °C catalyzed by tin octoate [Sn(Oct)$_2$].

The copolymerization of MMTC with lactide catalyzed by Sn(Oct)$_2$ was studied by Zhou et al. [111]. At 10 % molar fraction of MMTC, the highest M_n, 51 700 was reached at a yield of 82 % and PDI of 1.85. The reactivity ratios of MMTC and D,L-lactide were determined and could explain that the molar content of MMTC was lower in the resulting polymer than in the feed. Nederberg et al. [112] used thiourea-amine catalysts to polymerize TMC. The resulting polycarbonates had molecular weights of up to 50 000 g mol^{-1} and polydispersities below 1.08.
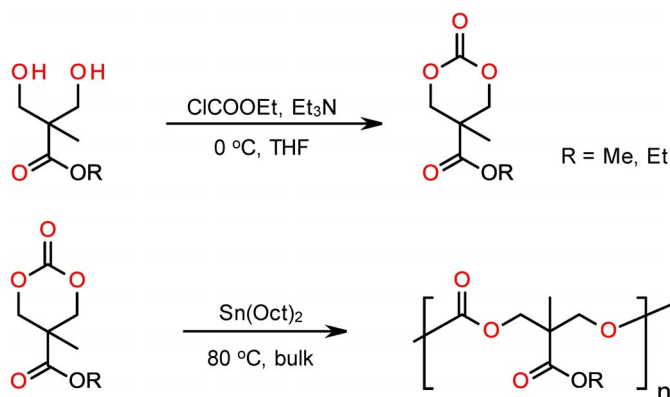
Scheme 4 Preparation of cyclic carbonates based on esters of methyl-2,2-bis(hydroxymethyl)propionate, and subsequent polymerization.

Five- and six-membered cyclic carbonates can be opened by diamines to produce urethane units without using any catalyst as shown in Scheme 5. A diurethanediol [DUD, 1,6-bis(hydroxyethyloxy-carbonylamino)hexane]) was obtained at high yield (>94 %) in the reaction of EC with 1,6-hexane-diamine carried out at room temperature without any catalyst. The polycondensation of α,ω-bis(hydroxyethyloxycarbonylamine)alkane with α,ω-diols containing six or more carbon atoms in a molecule ($m \geq 6$) led to [n,m]polyurethane in the presence of tin catalysts at 150 °C [113].
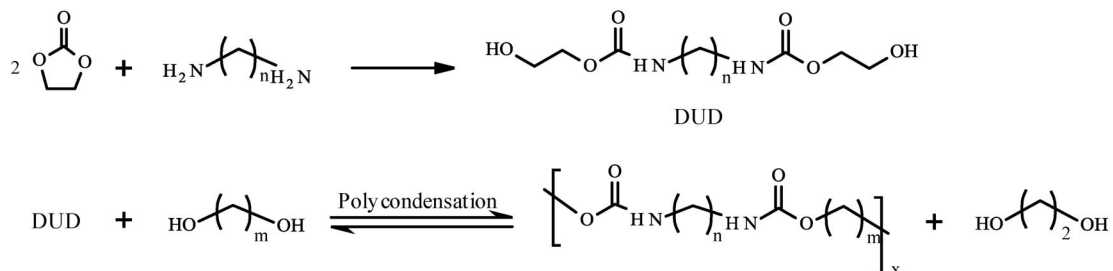
Scheme 5 Ring opening of EC with 1,6-hexanediamine and its polycondensation to polyurethane [113]. Reproduced with permission from Elsevier.

ROP of cyclic carbonates using biocatalysis

Enzyme-catalyzed ROP attracts increasing attention as a new way of synthesis of biodegradable poly-mers [114]. Lipase was found to catalyze the polymerization reactions to give polyesters and polycar-bonates in vitro [115,116]. In ROP, a number of cyclic monomers have been polymerized using bio-catalysis; typical examples include cyclic carbonate, cyclic ester (lactone), and lactide (Fig. 5) [116]. Lipase-catalyzed ROP of various lactones were published earlier than those of cyclic carbonates [95,117–119].
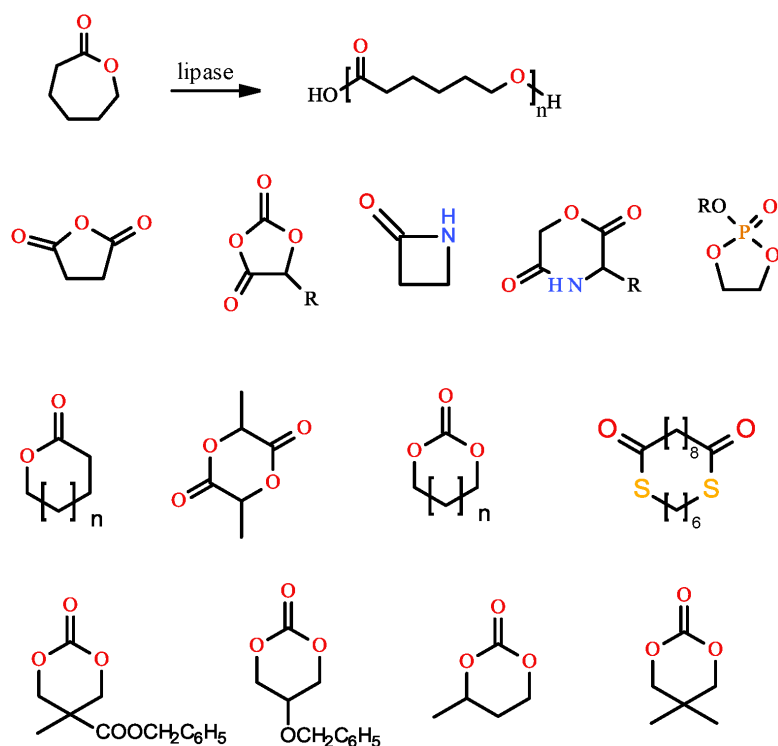
Fig. 5 Typical examples of cyclic monomers for enzyme-catalyzed ROPs [116].

In 1997, ROP of six-membered 1,3-dioxan-2-one to P(TMC) using lipases from *Candida antarctica*, *Candida cylindracea*, and porcine pancreas was reported (Table 2, entries a–c), and has received much attention as one way of improving the mechanical properties of biodegradable polyesters such as polycaprolactone, polylactide, and poly(hydroxyalkanoate) by introducing carbonate linkages [95,96,99,121]. The carbonate linkage in the polymer chain may be expected to be enzymatically hydrolyzable but more hydrolytically stable than an ester linkage [80,95]. Furthermore, the copolymerization of cyclic lactones and carbonates needs pure monomers and anhydrous conditions as well as organometallic catalysts, which must be completely removed before use in medical applications, while enzyme-catalyzed polymerization of six-membered cyclic esters and carbonates seems to be a method avoiding these difficulties [80].

Using renewable resources, the concept of sustainable chemical recycling system was demonstrated to make polycarbonate via cyclic carbonate catalyzed by enzyme at different stages, i.e., in the synthesis of cyclic carbonate as well as in the polymerization and in the depolymerization steps [60] (Scheme 6). DMC and 1,3-propanediol were used as raw materials for synthesis of TMC, which was subsequently polymerized. DMC is an environmentally benign chemical having interesting solvating properties, low toxicity, and high biodegradability [122–125], while 1,3-propanediol is one of the oldest known products of microbial fermentation produced from renewable resources, and is a valuable bifunctional molecule [126]. The enzymatic transformation of P(TMC) (M_n of 3000–48 000) using *C. antarctica* lipase in acetonitrile resulted in the corresponding cyclic monomer with up to 80 % yield. The TMC readily polymerized again using the lipase as summarized in Scheme 6 [60,72].

A number of other examples of lipase-catalyzed ROP of cyclic carbonates are listed in Table 2. Soeda et al. reported that a biodegradable low-molecular-weight DUD was reacted with DEC using lipase to produce enzymatically recyclable poly(carbonate-urethane) (PCU) [127]. The PCU was enzy-
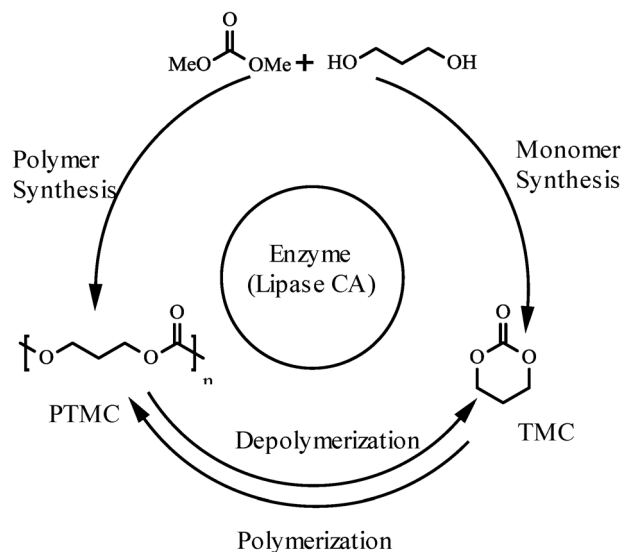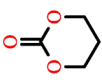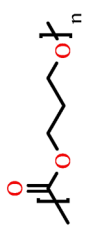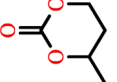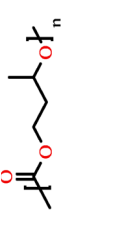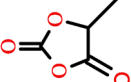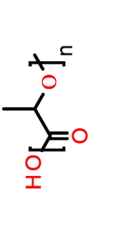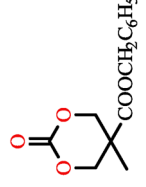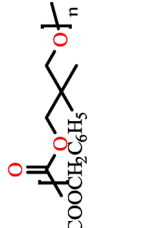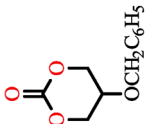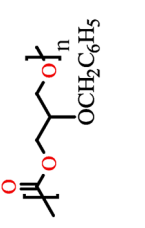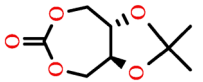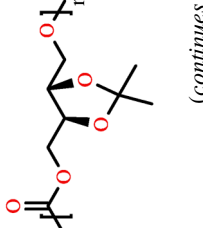
Scheme 6 Sustainable polymer production and recycling system [60]. Reproduced with permission from John Wiley.

matically degraded in anisole into the cyclic carbonate-urethane oligomer with M_w of around 400. The cyclic oligomer was readily polymerized to produce PCU with a maximum M_w of 42 000 in 93 % yield.

The methyl-substituted trimethylene carbonate (Me-TMC) was polymerized at 100 °C in bulk in the presence of porcine pancreatic lipase (PPL) to yield the corresponding polycarbonate with M_w of 10 400 (Table 2, entry d) [60]. Both lipase PS (*Pseudomonas sp.* lipase immobilized on ceramic) and N435 were shown to promote the ROP of the *O*-carboxylic anhydride derived from lactic acid (Table 2, entry e) [128]. Water-soluble polycarbonate having pendant carboxyl groups on the main-chain carbons was synthesized by enzyme-catalyzed ROP of a carbonate monomer, 5-methyl-5-benzyloxycarbonyl-1,3-dioxan-2-one (MBC) (Table 2, entry f) [129]. Poly(5-benzyloxy-trimethylene carbonate) (PBTMC), a functional polycarbonate, was synthesized by enzymatic ROP in bulk at 150 °C using PPL or *Candida rugosa* lipase as catalyst (Table 2, entry g) [130]. Enantiomerically pure functional polycarbonate was synthesized from a seven-membered cyclic carbonate monomer derived from naturally occurring L-tartaric acid by N435 at 80 °C in bulk (Table 2, entry h) [131]. ROP of 2,2-dimethyltrimethylene carbonate (DTC) catalyzed by PPL immobilized on aminopropyl silica nanoparticles (IMPPL) was explored (Table 2, entry j) [132]. ^{1}H NMR spectra suggested no evidence of decarboxylation during propagation. Generally, the polymers obtained by enzymatic ROP in bulk show relatively broad M_w distribution due to the diffusion constraints of polymerization system including enzyme, monomers, and polymers. However, in this work, all the obtained poly(dimethyl trimethylene carbonate) poly(DTC) exhibited a relatively narrow M_w distribution. This may be ascribed to the good miscibility and dispersibility of the nanoscaled particles of IMPPL in the polymerization medium [132].
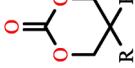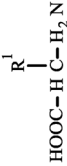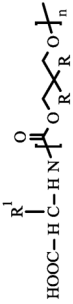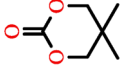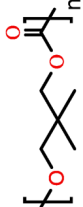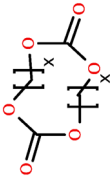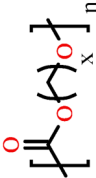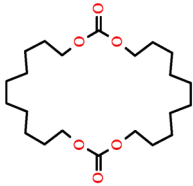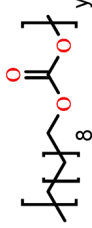
In contrast to the PTeMC, produced by the conventional polycondensation of 1,4-butanediol and triphosgene in chloroform, with low molecular weight (M_n = 2000) and yield (43 %) [2,133], high-molecular-weight PTeMC (M_w = 119 000) and PHMC (M_w = 399 000) were prepared by the lipase-catalyzed polymerization of 1,4-butanediol or 1,6-hexanediol and diphenyl carbonate via the formation of a cyclic dimer in dilute toluene solution (Table 2, entry k) [2]. As known, the high ring strain is to a great extent responsible for the spontaneous thermal polymerization of six- or seven-membered cyclic carbonates [114]. It is anticipated that the depressed ring strain with the enlarged ring size may endow the cyclic carbonate monomers with much higher stability so as to lessen the feasibility of thermal polymerization at high temperature. Twenty-six-membered cyclic carbonate, cyclobis-(decamethylene car-

Table 2 Lipase-catalyzed ROP of various cyclic carbonates.

Entry	Monomers	Lipase	Temp./time	Conversion (%)	Molecular weight	Product	Ref.
a		*C. antarctica*	75 °C, 72 h	100	M_n 2500, M_w/M_n 4.1		[96]
b		PPL[1]	100 °C, 24 h	99	M_n 76500, M_w/M_n 4.1		[95]
c		N435	70 °C, 120 h	97	M_n 15000, M_w/M_n 2.2		[99]
d		PPL[1]	100 °C, 5 days	67	M_n 10400, M_w/M_n 3.7		[60]
		Lipozyme RM IM		45	M_n 2300, M_w/M_n 1.2		
e		N435	80 °C, 25 h	98	M_n 20600, M_w/M_n 1.22		[128]
		Amano PS-CII[2]	80 °C, 4 h	97	M_n 22400, M_w/M_n 1.28		
f	COOCH₂C₆H₅	AK Lipase[3]	80 °C, 72 h	97	M_n 6100, M_w/M_n 1.65		[129]
		PPL[1]		98	M_n 1300, M_w/M_n 1.38		
		N435		86	M_n 4400, M_w/M_n 2.12		
g	OCH₂C₆H₅	PPL[1]	150 °C, 8 h	98	M_n 18955, M_w/M_n 2.28		[130]
		C. rugosa		93	M_n 9833, M_w/M_n 2.21		
h		N435	80 °C, 24 h	88	M_n 15500, M_w/M_n 1.7		[131]

(continues on next page)

Table 2 (*Continued*).

Entry	Monomers	Lipase	Temp./time	Conversion (%)	Molecular weight	Product	Ref.
i			80–100 °C, 24 h	>90	M_n 9900–15 000 M_w/M_n 1.52–1.67		[134]
j		PPL[1]	130 °C, 5 days	81	M_n 10 900, M_w/M_n 1.3		[132]
k	x = 4: TeMC dimer x = 6: HMC dimer	N435	120 °C, 6 days 110 °C, 24 h	78 66	M_w 199 000, M_w/M_n 2.2 M_w 399 000, M_w/M_n 2.8		[2]
l		N 435	75 °C, 48 h	99	M_n 54 100, M_w/M_n 1.69		[114]

[1]PPL: porcine pancreatic lipase.
[2]Amano PS-CII: lipase Amano PS-CII from *Pseudomonas* sp. (immobilized on ceramic).
[3]AK lipase: *Pseudomonas fluorescens* (AK) lipase.

bonate) [$(DMC)_2$], contains two carbonate bonds in a single cyclic compound, and was polymerized using N435 as catalyst in toluene to produce a polymer with molecular weight (M_n) of 54 100 in 99 % yield (Table 2, entry l) [114].

For the synthesis of poly(DTC) and poly(TMP), in the presence of amino acid, at a (DTC or TMC)/[amino acid] molar ratio of 100, the monomer conversions were above 92 % (Table 2, entry i) [134]. ROP of DTC or TMC proceeded well in the presence of five different natural amino acids (L-alanine, L-valine, L-leucine, L-proline, and L-phenylalanine). These results are in line with those of Persson et al. [135] concerning ROP of ε-caprolactone in the presence of L-lactic acid.

Table 3 provides the examples of copolymers produced by ROP of cyclic carbonates using different lipases. These include copolymerization of 5-benzyloxy-trimethylene carbonate (BTMC) with 5,5-dimethyl-trimethylene carbonate (DTC), BTMC with 1,4-dioxan-2-one (DON), and MBC with TMC [130,136,137]. Higher reactivities of BTMC and MBC led to higher content of these monomers in poly(BTMC-co-DON) and poly(MBC-co-TMC) copolymers.

OTHER PRECURSORS FOR ISOCYANATE-FREE POLYURETHANES AND POLYCARBONATES

The isocyanate-free route for the synthesis of aliphatic polycarbonates has been mainly focused on transesterification of dialkylcarbonate and on the ROP of various cyclic monomers such as cyclic esters and cyclic carbonates. Synthesis of linear aliphatic polycarbonate polyols from a linear alkane diol has also been reported, e.g., zinc-catalyzed sequential copolymerization of CO_2 and epoxides to polycarbonates in 1969 was a potential large-scale CO_2-based polycarbonate production process [138]. The copolymerization of CO_2 with cyclohexene oxide using zinc complex, which was synthesized by using 13-diiminate and a pyridine alcohol ligand, gave a polymer (M_n 21 000) with very high carbonate linkage (>90 %) and narrow polydispersity (<1.3) (Table 4, entry a) [139]. DEC and diols, such as 1,3-propanediol and 1,4-butanediol, were enzymatically polymerized at 40–80 °C to yield the corresponding aliphatic polycarbonates in a successive two-step polymerization (Table 4, entry b) [9]. 1,6-Hexanediol and DMC were reacted using calcium catalyst to give polycarbonate polyols with M_n ranging between 700 and 1700 (Table 4, entry c) [140]. The alternating copolymerization of CO_2 and epoxide to give polycarbonate has attracted the attention of many chemists, enabling the utilization of CO_2 as a safe, clean, and abundant raw material in synthetic chemistry [141,142].

Despite many attempts to develop non-phosgene and non-diisocyanate routes for the synthesis of polyurethanes, none has been commercially established except for two small-scale plants for aliphatic isocyanates erected in the early 1990s [9,143]. Polyurethane can be prepared by ROP of cyclic carbamate, cyclic urea, and aziridine. For thermodynamic reasons only the unsubstituted six- and seven-membered cyclic carbamates were polymerized by ROP [144]. The cationic ROP of trimethylene urethane (TU; systematic name, tetrahydro-2H-1,3-oxazin-2-one,) with methyl trifluoromethanesulfonate (TfOMe) and trifluoromethanesulfonic acid (TfOH), as initiators, and of tetramethylene urethane (TeU, hexahydro-1,3-oxazepin-2-one) with TfOMe as the initiator to yield polymers with regular microstructures, poly(trimethylene urethane) [poly-(TU), (2)] and poly(tetramethylene urethane) [poly(TeU)], respectively, have been reported (Table 4 entries d,e) [145,146]. Tetramethylene urea was copolymerized with γ-butyrolactone, leading to an alternating poly(amide urethane) with alternating carbonyl-amino-tetramethylene-amino and carbonyl-trimethylene-oxy repeating units (Table 4, entry f) [147]. The reaction of 2-methylaziridine and CO_2 under supercritical conditions to give polymer products with a high content (0.62) of urethane units, and an increase in CO_2 pressure resulted in marked improvement in yield (Table 4 entry g) [148]. However, these methods were associated with some problems such as high reaction temperatures, non-atmospheric pressures, low yield, and/or long reaction time.

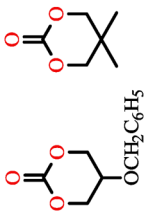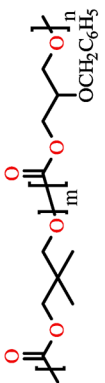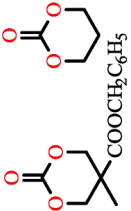**Table 3** Lipase-catalyzed copolymerization of cyclic carbonates.
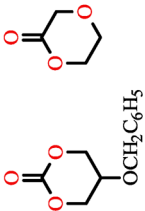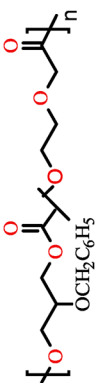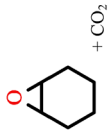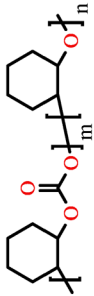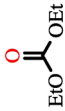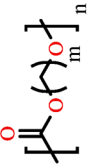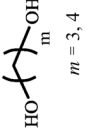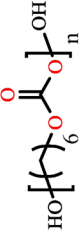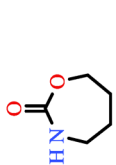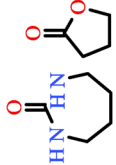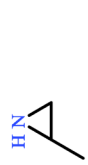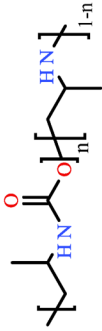
Entry	Monomers	Catalyst	Temp./time	Conversion (%)	Molecular weight	Product	Ref.
a	(cyclic carbonate monomers; OCH$_2$C$_6$H$_5$)	Immobilized porcine pancreas lipase	150 °C, 24 h	83	M_n 26400 M_w/M_n 1.74	(copolymer; OCH$_2$C$_6$H$_5$)	[130]
b	(cyclic carbonate monomers; COOCH$_2$C$_6$H$_5$)	*Pseudomonas fluorescens* (AK) lipase	80 °C, 72 h	85	M_n 7500 M_w/M_n 4.4	(copolymer; COOCH$_2$C$_6$H$_5$)	[136]
c	(cyclic carbonate monomers; OCH$_2$C$_6$H$_5$)	Immobilized porcine pancreas lipase	150 °C, 24 h	80	M_n 20200 M_w/M_n 1.82	(copolymer; OCH$_2$C$_6$H$_5$)	[137]

Table 4 Other precursors for isocyanate-free polycarbonates and polyurethanes.

Entry	Monomers	Catalyst.	Temp./time	Conversion (%)	Molecular weight	Product	Ref.
a	$+ CO_2$	Zn complexes	50 °C, 2 h		M_w 21 000 M_w/M_n 1.21		[139]
b	EtO—OEt, HO—OH $m = 3, 4$	N435	70 °C, 24 + 7 h	34	M_w 10 600 M_w/M_n 1.6		[9]
			70 °C, 24 + 7 h	60	M_w 24 200 M_w/M_n 2.2	$m = 3$, P(TMC), $m = 4$, P(TeMC)	
c	MeO—OMe, HO—OH	Calcium	100–150 °C, 24 + 7 h		M_w 1641 M_w/M_n 1.47		[140]
d		TfOMe	100 °C, 24 h	77	M_n 32 600 M_w/M_n 2.45		[145]
e		TfOMe	67 °C, 24 h	90	M_n 3500 M_w/M_n 1.93		[146]
f		Dibutyl magnesium	100 °C, 24 h	84	M_n 21 600 M_w/M_n 1.67		[147]
g		Supercritical CO_2, 22 MPa	100 °C, 24 h	27	M_w 27 000		[148]

FUTURE PERSPECTIVES

The chemical industry is facing increasing demand for more environmentally benign and safe processes and products. Production of isocyanate-free polymers attracts increasing attention and has great potential to avoid the use of toxic and environmentally hazard materials. More research and development remain before a transition to more sustainable production of these polymers can take off. Recent developments in the preparation of various cyclic carbonates and their ROPs to produce isocyanate-free polymers hold promise. Five-membered cyclic carbonates have the potential to be produced using renewable resources such as glycerol and CO_2, and the range of possible applications for these monomers in ROP is likely to be expanded as a result of the increasing interest of both industry and academia. Six-membered cyclic carbonates will provide great opportunities in the production of isocyanate-free polycarbonates and polyurethanes. A variety of cyclic carbonate bearing various functional groups can be prepared and polymerized with tailor-made properties to find use in large-volume industrial applications as well as in general and high-end materials such as implantable biomedical devices. The mild conditions provided by the enzymatic processes as compared to the other forms of catalysis for preparation of these cyclic carbonates and their polymerization are attractive, and the potential for improvement in enzyme technology such as enzyme stability, activity, and selectivity is substantial.

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