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Chain transfer agents utilized in epoxide and CO₂ copolymerization processes

Donald J. Darensbourg 

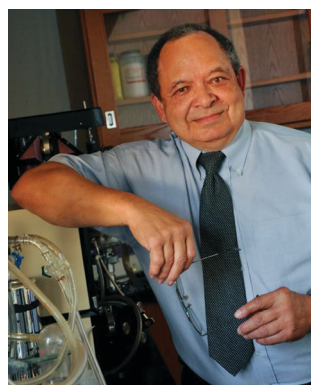
This tutorial deals initially with a comparison of the mechanistic aspects of *living* and *immortal* polymerization processes. The living polymerization pathway originated with the anionic polymerization of styrene by Szwarc, whereas immortal polymerization was first described by Inoue for the homopolymerization of epoxides using an aluminum complex. A similar behavior would be anticipated for the copolymerization of epoxides and carbon dioxide catalyzed by well-defined metal complexes. The major difference between these two pathways is rapid and reversible chain transfer reactions involving protic impurities or additives in the latter case, that is, the stoichiometry of the monomer/initiator ratio changes as a function of the nature and concentration of the chain transfer agent (CTA). For instance, in early studies of the copolymerization of epoxides and CO₂ where adventitious water was present in the copolymerization reactions, there was little control of the molecular weight of the resulting copolymer product. Presently, the presence of chain transfer with protic CTAs during the copolymerization of epoxides and CO₂ is a major positive factor in this process's commercialization. Specifically, this represents an efficient production of polyols for the synthesis of CO₂-based polyurethanes. Studies of the use of various CTAs in the synthesis of designer polymeric materials from CO₂ and epoxides are summarized herein.

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Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA.
E-mail: djdarens@chem.tamu.edu



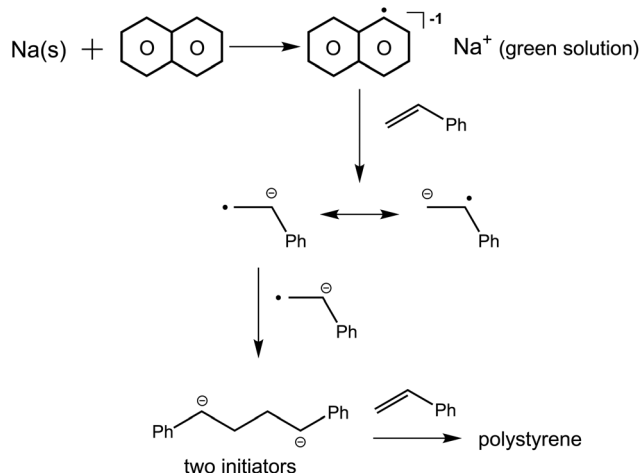
Donald J. Darensbourg

Donald J. Darensbourg was born in Baton Rouge, LA in 1941 and received his B.S. and Ph.D. degrees from California State University at Los Angeles and the University of Illinois/Urbana, respectively. Following a nine month period at the Texaco Research Center in Beacon, NY, he was on the faculties of State University of New York at Buffalo from 1969 to 1972 and Tulane University from 1973 to 1982. He has been at Texas A&M

University since 1982 where he currently is a Distinguished Professor. Among his current interests are the utilization of CO₂ as both a monomer and solvent in copolymerization reactions with oxiranes and oxetanes, and the ring-opening polymerization of renewable monomers such as lactides.

Introduction

The concept of living polymerization was first demonstrated by Professor Szwarc for the organo-alkali metal initiated polymerization of styrene.^{1–3} Specifically, the anionic polymerization process depicted in Scheme 1 was shown to provide polymers of uniform size.

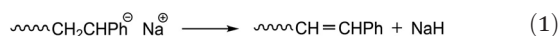


Scheme 1 Anionic polymerization of styrene.

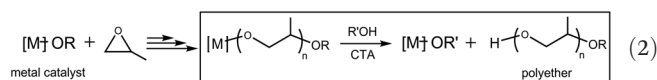
These living polymerization processes proceed by a chain growth pathway which takes place in the absence of termination steps and irreversible chain transfer. In general, these processes display the following characteristics.

- Polymerization proceeds until all monomer is consumed, with addition of a new monomer leading to block copolymers.
- The number average molecular weight, M_n , is a linear function of conversion, and results in a narrow molecular weight (Poisson) distribution.
- The number of active centers is constant and is not dependent on conversion, or put another way, the number of polymer chains are the same as the number of initiators.
- The average molecular weight controlled by the monomer/initiator stoichiometry.

Such polymers produced possess controlled molecular weights and end-active chains which can provide block polymers. These living polymerization processes can be terminated by quenching the reaction, *e.g.*, by the addition of a protic compound. It is nonetheless noteworthy, that these living processes do not live forever, eventually dying. In the above instance, the polymerization reaction very slowly terminates *via* formation of sodium hydride as illustrated in eqn (1).⁴



Professor Inoue and coworkers in 1985 described polymerization processes which have several of the characteristics of a living polymerization reaction.⁵ These processes are referred to as *immortal polymerization* reactions.^{6–8} An example of such a process is represented in eqn (2). As depicted in eqn (2), following the formation of a metal alkoxide in the ring-opening polymerization of an epoxide catalyzed by a metal complex, the addition of a protic source leads to a chain transfer reaction.



The boxed portion of eqn (2) represents a chain transfer process in the routine sense with the resulting polymer being *dead*, with concomitant formation of $[\text{M}]^+\text{OR}'$ providing a new reactive site for polymer growth. However, the polyether product itself can serve as a protic source and react as a chain transfer agent with metal attached polymer chain. That is, the process is reversible, thereby leading to renewal growth of the polymer chain. If chain transfer is rapid and reversible, the molecular weight of the polymer is expected to remain narrow. Relevant to this polymerization process, we and others have been investigating the copolymerization of epoxides and CO_2 in the presence of various chain transfer agents. Herein, current studies involving CTAs in the preparation of polycarbonates are reviewed.

Similar to the process shown in eqn (2), copolymerization reactions of epoxides and carbon dioxide catalyzed by metal complexes share many of the features of a living polymerization process. However, in general, the observed molecular weights of the copolymers are much lower than their theore-

tical value based on the monomer/initiator stoichiometry. In addition, the thus afforded copolymers exhibit bimodal gel permeation chromatography (GPC) traces, with each molecular weight profile displaying a narrow molecular weight distribution. For summaries of these copolymerization reactions, see the numerous published reviews on this subject.^{9–22}

The bimodal molecular weight distributions, along with MALDI-TOF studies, have been interpreted as being due to a rapid and reversible chain transfer reaction with adventitious water.^{23,24} Further support for this behavior is seen when water is carefully excluded from the copolymerization process, where the reactions provide copolymers with the expected molecular weights.²⁵ Similarly, upon addition of a large excess of the CTA methanol during the copolymerization of propylene oxide and CO_2 , the copolymer containing a methoxy end group was obtained as the main product with the expected molecular weight with a narrow D .²⁶ In studies involving the copolymerization of CO_2 and cyclohexene oxide or propylene oxide monomers, it has been shown that the chain transfer agent is also due to catalytic hydrolysis of the epoxide, leading to the corresponding diol, which serves as CTA.^{27,28} If a known quantity of water is added to the copolymerization reaction, the molecular weight of the resulting copolymer decreases with the increasing quantity of added CTA (Fig. 1). Scheme 2 describes the reaction pathways for polycarbonate production from epoxides and CO_2 in the presence of added or adventitious chain transfer agent. In addition, it is possible to provide nearly 100% polyols if X is the hydrolysable trifluoroacetate initiator.^{29–31}

The most economically viable products thus far provided by the copolymerization of epoxides and carbon dioxide are polyols for the synthesis of thermoplastic polyurethanes. These important polymers are produced at a level in excess of 20 million tons annually by the step growth polymerization of diisocyanates with macro-diols, generally hydroxyl-terminated polyethers or polyesters, eqn (3). The physical properties of the polyurethane are dependent on the nature of R and R'. A sizable quantity of polyurethane currently produced employs macro-polyols formed from ethylene oxide and propylene oxide using various chain-transfer agents, *e.g.*, 1,2-propanediol, adipic acid, *etc.*^{32–34} Hence, the addition of CO_2 to these

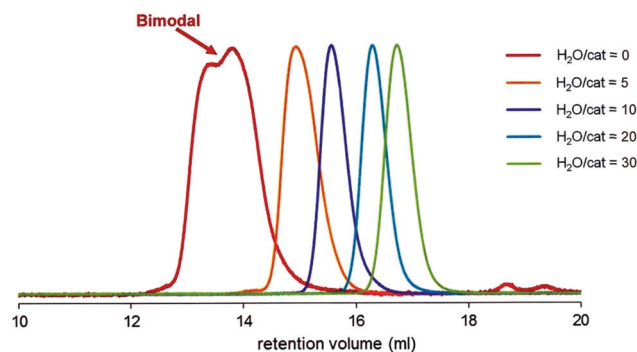
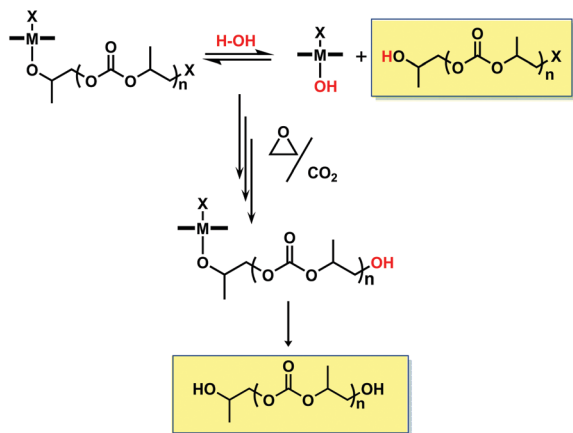
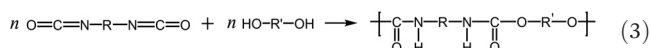


Fig. 1 GPC traces of polycarbonate production in the presence of adventitious H_2O followed by known quantities of water.



Scheme 2 Immortal copolymerization of propylene oxide and CO₂ in the presence of water.

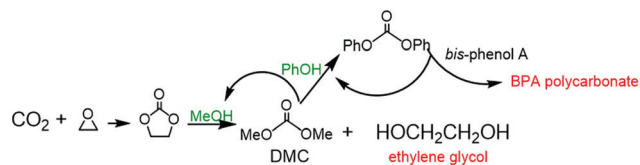
polyols has the potential to decrease the petrochemical based content by about 50%.



Currently, *Covestro* is marketing a poly(ether carbonate) polyol for the synthesis of flexible foam polyurethanes.³⁵ The *Covestro* process incorporates about 20% CO₂ into the polyol which when coupled with isocyanates affords a product on par with conventional materials made exclusively with fossil resources. For example, this polymeric material is used in providing the first mattresses made in part from CO₂.³⁶ On the other hand, catalyst systems for the coupling of CO₂ and epoxides in the presence of CTAs are well-studied for the production of completely alternating copolymers. These catalysts generally consist of cobalt, chromium, and aluminum coordination complexes with salen(salicylaldimine) ligands in the presence of onium salts. This latter technology is employed by Novomer (now part of Saudi Aramco) in the United States, and SK Energy in Korea.^{37,38} Eonice in the UK utilizes zinc catalysts which generally leads to polyols containing various quantities of ether linkages.³⁹

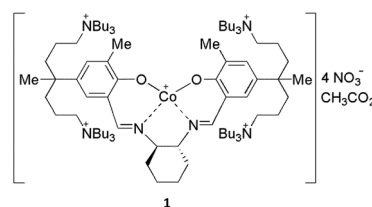
It is worthy of note that Asahi Kasei Corp. in Japan has developed and commercialized a process for effectively producing BPA polycarbonate *via* a method incorporating CO₂ which avoids the use of phosgene.⁴⁰ This process simultaneously produces high purity monoethylene glycol(MEG) in high yield (see Scheme 3). Since both diphenylcarbonate and bisphenol-A are solid, the reaction can be carried out in the absence of organic solvents. About 1000 kt per year of this material is produced at several locations worldwide.

One of the early, more informative studies of immortal copolymerization of propylene oxide and CO₂ was carried out by Lee and coworkers in 2010.⁴¹ These researchers examined the copolymerization of propylene oxide and CO₂ in the presence of various ratios of the CTA (adipic acid) to their multifunctional cobalt catalyst which contained tethered quaternary ammonium salts, complex **1**. Surprisingly, unlike a closely related cobalt catalyst with different anions which exhibited



Scheme 3 Asahi Kasei's non-phosgene polycarbonate process.

induction periods of hours in the presence of protic additives, catalyst **1** maintained excellent catalytic activity in the presence of large quantities of adipic acid. That is, similar TOFs to that in the absence of adipic acid were observed at [adipic acid]/[**1**] up to 200. Furthermore, ¹H NMR measurements demonstrated that all of the adipic acid took part in copolymer chain-growth, and the polycarbonate samples displayed as expected a decrease in *M_n* values accompanying an increase in [adipic acid]/[**1**] ratio.



Other di-, tri- and tetracarboxylic acids have served as effective CTAs for the preparation of diols, triols, and tetraols in the copolymerization of CO₂ and propylene oxide using zinc-cobalt double metal cyanide catalysts (Fig. 2).^{42–44} Reaction times were generally long for complete conversion of propylene oxide, which was thought to be due to free carboxylic acid groups. The long reaction times of these processes were greatly reduced by a preactivation process, where acid-bound oligo-

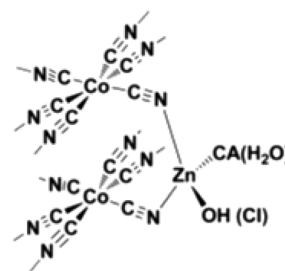
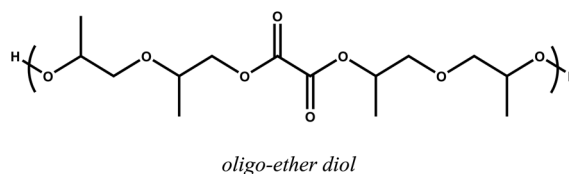


Fig. 2 Oligo-ether diol and proposed structure of zinc-cobalt double metal cyanide catalyst.

ether diols, triols, or tetraols are formed in advance of the copolymerization process. For example, the oligo-ether diol from oxalic acid and propylene oxide is represented below. For these zinc-cobalt double metal cyanide catalysts in the presence of a proton-containing initiator, there is a significant influence of the acidity on the copolymerization system. That is, for a weak organic acid (pK_{a1} : 4.43–4.72) the acid acts as a CTA. On the other hand, for a strong organic acid ($1.87 < pK_{a1} < 4.2$) it acts to first initiate propylene oxide homopolymerization subsequent to the *in situ* formed polyols acting as a new chain transfer agent in the early stage of the copolymerization process. The structures of the oligo-ether triol and the oligo (carbonate-ether) triol obtained from 1,3,5-benzenetricarboxylic (trimesic) acid are shown in Fig. 3.

A green flame-retarding poly(propylene carbonate) has been synthesized by carrying out the immortal polymerization of propylene oxide and carbon dioxide in the presence of a variety of organo-phosphorous compounds. These materials were achieved employing diphenylphosphinic acid ($\text{Ph}_2\text{P}(\text{O})(\text{OH})$), phenylphosphonic acid ($\text{PhP}(\text{O})(\text{OH})_2$), or phosphoric acid ($\text{P}(\text{O})(\text{OH})_3$) as chain transfer agents using the very active catalyst **1**.⁴⁵ The copolymerization process was found to proceed with a high catalytic activity ($10\,000\text{--}20\,000\text{ h}^{-1}$ @ $70\text{--}75\text{ }^\circ\text{C}$) even with large concentrations of CTAs, *i.e.*, $\frac{[\text{CTA}]}{[\text{1}]} = 200\text{--}1600$.

A thermoplastic polyurethane was prepared from the stoichiometric addition of toluene-2,4-diisocyanate to the poly(propylene carbonate)-diol obtained using $\text{PhP}(\text{O})(\text{OH})_2$ as CTA.

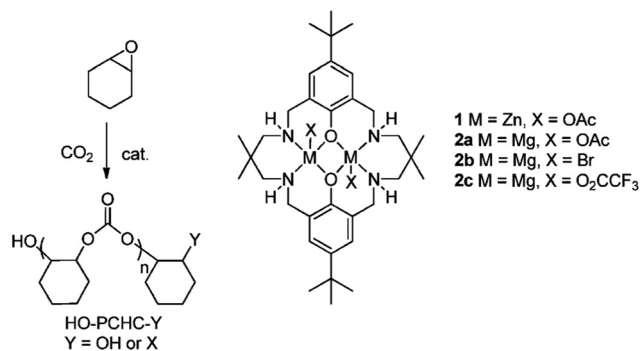
Similarly, the preparation of various polyurethanes, including flame-retarding polyurethanes, have been prepared from the reactions of low-molecular weight poly(propylene carbonate)-diols and diisocyanates.⁴⁶ The PPC-diols were synthesized by the copolymerization of propylene oxide and CO_2 accompanied by the chain-transfer agents (1,2-propanediol, terephthalic acid, 2,6-naphthalenedicarboxylic acid, and phenylphosphonic acid) catalyzed by complex **1**. The thus-produced macro-diols were reacted *in situ* with 4,4'-methylene bis (phenyl isocyanate) to afford a polymer with an enhanced T_g of $60\text{ }^\circ\text{C}$. As noted previously, a non-flammable polyurethane

was obtained when employing an organophosphorous compound as chain-transfer agent.

The use of low-molecular weight polycarbonate polyols for the synthesis of polyurethanes and other copolymers continues to maintain much interest.⁴⁷ Prominent among these studies are the immortal copolymerization reactions of cyclohexene oxide and CO_2 using the renewable CTA, water.^{48,49} Using their well-developed dinuclear catalysts systems, Kember and Williams demonstrated the magnesium catalysts to be much more active than their zinc analogs (Scheme 4).

For example, the magnesium catalysts depicted in Scheme 4 were active at very low loading to selectively provide copolymers with 99% carbonate repeating units. These catalysts were also shown to be highly active at atmospheric CO_2 pressure and produced polyols in the presence of up to 30 equiv. (3 mol%) water. Importantly, when using the catalyst where $\text{X} = \text{O}_2\text{CCF}_3$ in excessive quantities of water, the trifluoroacetate end group in the copolymer was greatly reduced. In further studies, the α,ω -hydroxy-telechelic poly(cyclohexene carbonate) prepared using the dizinc catalysts, where $\text{X} = \text{OAc}$ or O_2CCF_3 , afforded ABA triblock copolymers with lactides employing an yttrium amide catalyst.⁵⁰

In closely related studies, we have examined a similar immortal copolymerization reaction of styrene oxide and CO_2



Scheme 4 Copolymerization of cyclohexene oxide and CO_2 using dinuclear catalyst.

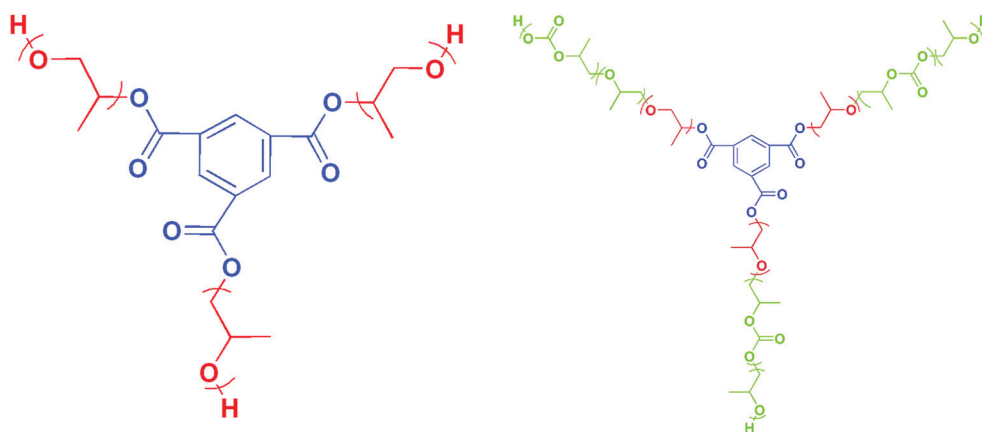
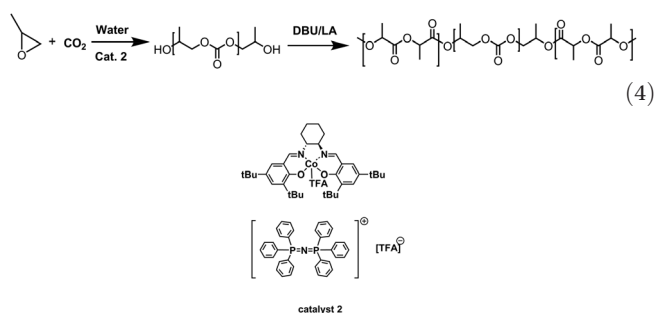


Fig. 3 Structures of triol obtained from 1,3,5-benzenetricarboxylic acid.

in the presence of water as CTA.⁵¹ That is, we have reported a tandem strategy combining an immortal copolymerization reaction of styrene oxide and CO₂ catalyzed by a bifunctional (salen)CoX catalyst with water as CTA, followed by a ring-opening polymerization of lactide in the presence of an organo-catalyst DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Scheme 5 describes this process for synthesizing the diblock polymer.

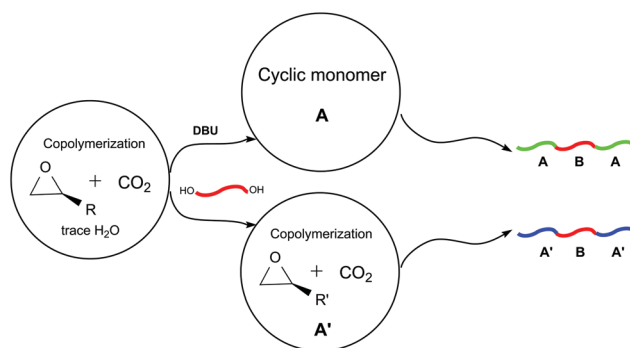
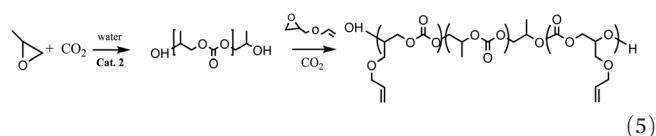
The above study was proceeded by a one-pot synthesis of triblock copolymers from propylene oxide and CO₂, and lactides.⁵² This was accomplished by first copolymerizing propylene and oxide in CO₂ in the presence of a binary (salen)CoO₂CCF₃/PPNO₂CCF₃ catalyst system with added water. The resultant polyol intermediate served as a macroinitiator for the ring-opening of lactide by the organocatalyst, DBU (eqn (4)). If DBU is added in the absence of lactide, the poly(propylene carbonate) degrades *via* a stepwise formation to cyclic styrene carbonate.^{53,54}



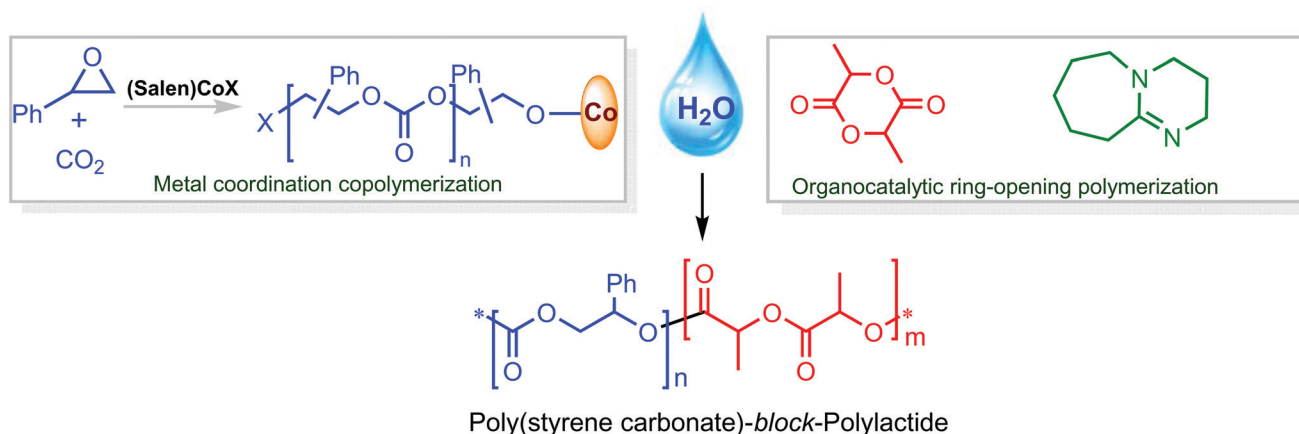
In other analogous studies utilizing a similar tandem synthetic strategy, following the formation of hydroxy end-capped polycarbonates derived from the copolymerization of propylene or cyclohexene oxides and CO₂, a triblock polymer involving a water-soluble cyclic phosphate can be prepared (Scheme 6).⁵⁵ That is, the addition 2-methoxy-2-oxo-1,3,2-dioxaphospholene (monomer A) to the telechelic polymer along with the organo-catalyst (DBU) provides the amphiphilic triblock copolymer. These triblock copolymers were shown to self-assemble into uniform nanostructures in water. As indicated in Scheme 6,

this procedure in principle should apply to the formation of various ABA triblock copolymers in a one-pot process dependent on the nature of the cyclic monomer (A) involved in the ROP process.

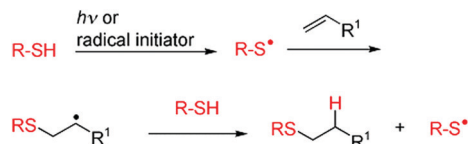
As illustrated in Scheme 6 the macro-diol afforded by immortal copolymerization of propylene oxide (R = Me) and CO₂ can be easily coupled in a one-pot process to produce triblock polycarbonates composed of two different epoxide monomers. The importance of this procedure is that it allows for the synthesis of a polymeric material containing two quite different regions, *e.g.*, hydrophobic and hydrophilic regions. Eqn (5) describes the preparation of a triblock polycarbonate, where the initially synthesized telechelic polymer derived from propylene oxide and CO₂ in the presence of water, is coupled to the copolymer resulting from allylglycidylether (AGE) and carbon dioxide.⁵⁶ These reactions are carried out consecutively in a one-pot reaction following the removal of any unreacted epoxide monomer from the first step.



Scheme 6 One-pot, two steps synthesis of designer block polymers.



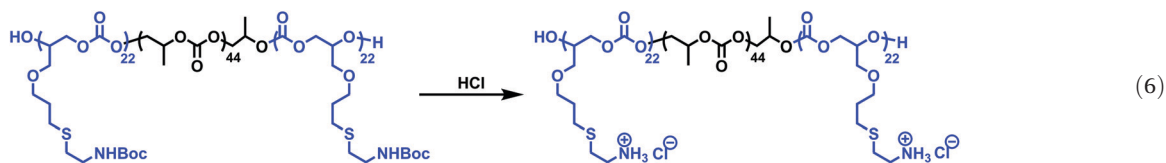
Scheme 5 Preparation of poly(styrene carbonate)-*block*-Polylactide Copolymer.



Scheme 7 Thiol-ene coupling to vinyl group pathway.

The presence of the vinyl group in the AGE enchaind monomer can be taken advantage of by the addition of thiols (thiol-ene coupling) to provide functionality to the polycarbonate.⁵⁷ The thiol-ene coupling reaction is either photochemically- or thermally-induced, proceeding *via* a radical mechanism as indicated in Scheme 7 to afford an anti-Markovnikov thioether.

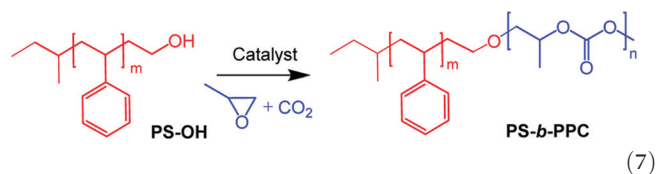
The triblock polymers synthesized between the polyol produced from propylene oxide and CO₂ in the presence of trace quantities of water as CTA, and the AGE and CO₂ copolymer as described in eqn (5) upon reacting with a series of thiols afford polymers with $-S-CH_2-CH_2-COOH$, $-S-CH_2-CH_2-NHBoc$, and $-S-CH_2-CH_2-COOH$ functionalities. Further reactions of these polymers with NH₄OH or HCl have provided amphiphilic polymers, see for example eqn (6). Furthermore, the functionalized polymer shown in eqn (6) when deprotonated with HCl affords a polymer which self-assembles in water to provide nanoparticle micelles. It can be anticipated that these polymeric materials will have a variety of biomedical applications, such as drug delivery or tissue engineering. Using this approach, Lu and coworkers have prepared micelles of polycarbonates conjugated with gadolinium (Gd³⁺) for imaging cancer cells.⁵⁸ These degradable polymer-Gd conjugates displayed higher MRI signal in tumor regions due to EPR (enhanced permeability and retention) effects.



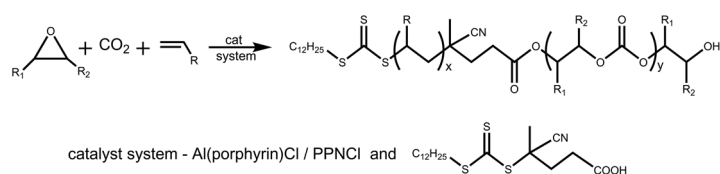
An alternative approach for preparing diblock polymers of quite different polymeric materials can be achieved by carrying out the propylene oxide/CO₂ copolymerization process in the presence of polymeric CTA which contains a single hydroxyl or carboxylic acid end group. For example, Wang, Lu and co-

workers have functionalized carbon nanotubes by a surface-initiated copolymerization of propylene oxide and CO₂ on the sidewalls of carbon nanotubes.⁵⁹ In addition, Xie and Wang have recently prepared CO₂-based diblock copolymers in a one-step process by the alternating copolymerization of CO₂ and an epoxide followed by RAFT polymerization of vinyl monomers using a trithiocarbonate compound bearing a carboxylic group (TTC-COOH) as a bifunctional CTA (Scheme 8).⁶⁰

In other studies, diblock copolymers between polystyrene and poly(propylene carbonate) were synthesized by the reaction sequence shown in eqn (7).⁶¹ These easily synthesized in a controlled process diblock copolymers of polystyrene-*b*-polypropylene carbonate were found to display high Flory-Huggins interaction parameters (χ), thereby qualifying them to fill key positions on direct self-assembly strategy for the next-generation lithography. That is, they were shown to have the ability to afford perpendicular sub-10 nm morphologies *via* thermal annealing.

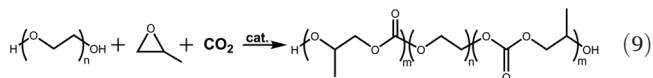
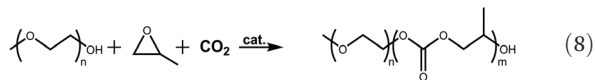


In another report, Frey and coworkers have utilized the copolymerization process of propylene oxide and CO₂ to provide amphiphilic polycarbonate block copolymers with a hydrophilic poly(ethylene glycol) block.^{62,63} That is, CO₂ based non-ionic surfactants have been synthesized by way of an immortal copolymerization of propylene oxide and CO₂ using poly(ethylene glycol) (PEG) and poly(ethylene glycol methyl ether) (mPEG) as macroinitiators. These chain-transfer agents allowed for both AB diblock and ABA triblock copolymer syn-



Scheme 8 Synthesis of diblock copolymers by a one-step terpolymerization of CO₂, epoxide, and vinyl monomers.

solutions and were used in the mini-emulsion polymerization to generate stable poly(styrene) nanoparticles.



A similar reaction to that depicted in eqn (7) was employed in the synthesis and self-assembly of cocontinuous network structures of polyisoprene-*b*-polystyrene-*b*-poly(propylene carbonate) by Coates and coworkers.⁶⁴ These polymeric materials were utilized in the preparation of three component polymer-inorganic hybrid materials following the orthogonal degradation of the polyisoprene and poly(propylene carbonate) blocks. Subsequently, the resulting mesopores were backfilled with metals to provide the polymer hybrids.

As noted in both the patent and open literature, immortal copolymerization reactions of epoxides and carbon dioxide using macro-CTAs are efficient methods for preparing CO₂-based block copolymers for the production of value-added materials. Nevertheless, many of the consequences dealing with the preparation of these polycarbonates in the presence of a wide variety of macro-CTAs are insufficiently understood. Initial investigations on this subject have been carried out in recent studies by Wu and coworkers.⁶⁵ That is, the copolymerization rates and blocking efficiencies were systematically examined employing several macro-CTAs (*e.g.*, PPG, PEG, and PS) in the presence of two long-established catalyst systems ((BDI)ZnOAc and (salen)CoTFA/PPNTFA). These studies were accomplished by analysis of the gel permeation chromatograms *via* mathematical deconvolution (Scheme 9).

These investigations clearly reveal that the size, nature, and ratio of [macro-CTA] to [catalyst] strongly influence the catalytic activity of the reaction and blocking efficiency for the resultant block copolymers. For example, for the (BDI)ZnOAc catalyzed copolymerization of cyclohexene oxide and CO₂ the TOF of the reaction decreased upon adding a 1 : 1 PPG_{2k} (CTA) from 160 to 149 h⁻¹, with additional decrease when adding a 5 : 1 PPG_{2k}

to 85 h⁻¹. There was a further decrease in catalytic activity upon increasing the molecular weight of the macro-CTA to PPG_{4k}. Similar but more significant changes in catalytic activity were seen utilizing PEG and PSOH as chain transfer agents.

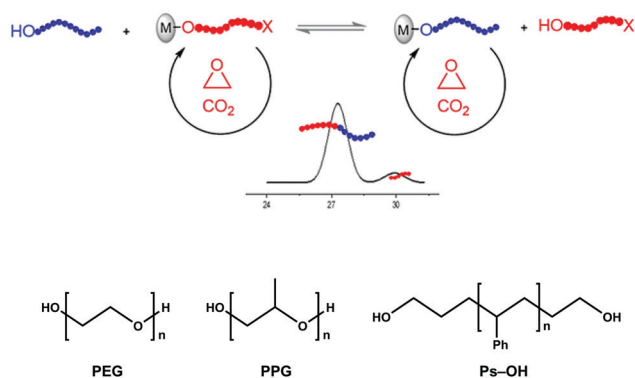
The blocking efficiencies were also notably impacted by changes in the macro-CTA, where the blocking efficiency is defined by the measured chain-transfer efficiency (E_{cal}) to the theoretical efficiency (E_{theo}). E_{theo} is calculated by the equation below,

$$E_{\text{theo}} = \frac{N_{\text{OH}}}{N_{\text{OH}} + N_{\text{X}}},$$

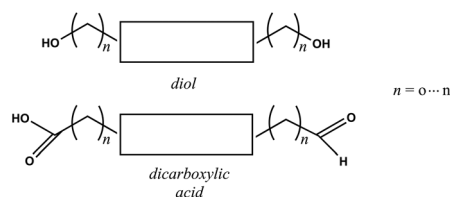
where N_{OH} represents the mole number of -OH groups in the macro-CTA and N_{X} is the corresponding value of the anion (X^-) on the catalyst. For instance, the blocking efficiencies for the copolymerization of propylene oxide and CO₂ reaction catalyzed by (salen)CoTFA/PPNTFA varied with the ratio of [PEG_{4k}] to [catalyst]. That is, for ratios of 1 : 1, 5 : 1, and 10 : 1, the E_{theo} values are 50, 83, and 91; whereas, the determined E_{cal} percentages were 38, 60, and 78. Alternatively, for a macro-CTA of higher molecular weight, *i.e.*, [PEG_{8k}]/[catalyst] of 5 : 1, E_{cal} was reduced to 50. By comparison, using the macro-CTA PPG_{4k} in ratios of 1 : 1 and 10 : 1, E_{cal} values of 45 and 86 were determined.

In summary, closely correlated trends in activities and blocking efficiencies were observed employing the two distinctly catalyzed copolymerization systems. Notwithstanding, this is an area where studies of immortal copolymerization reactions involving a wide variety of chain-transfer agents is greatly needed.

Related to this matter, chemical composition of the chain-transfer agent represented by the rectangular boxes in Scheme 10 can provide functionality to the resulting copolymer upon copolymerization of epoxides and CO₂ in their presence. For example, we have recently reported the synthesis of ion-containing polycarbonates *via* the (salen)CoO₂CCF₃/onium salt catalyzed immortal copolymerization of propylene oxide and CO₂ utilizing protic ionic liquids as CTAs.⁶⁶ In this study, several protic ionic liquids were examined for their effectiveness as CTAs. These included 1,3- bis (3-carboxypropyl)imidazolium chloride or tetrafluoroborate. Of importance, when the IL contained a chloride anion, the chloride acted as a good nucleophile to initiate ring-opening which did not allow for the cation to serve as a CTA, thereby it not being incorporated significantly into the copolymer chain.^{67,68} By way of contrast,

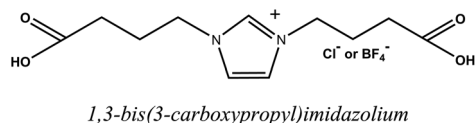


Scheme 9 Immortal copolymerization of epoxides and CO₂ in presence of macro-CTAs.

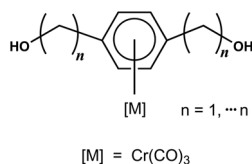


Scheme 10 Chain-transfer agents easily functionalized.

exchange of chloride for the non-nucleophilic BF_4^- anion led to complete incorporating of the CTA to afford ion-containing polycarbonates. These in turn could be employed in synthesizing ion-containing polyurethanes.^{69,70} Postpolymerization exchange of BF_4^- with a halide anion is readily achievable.



The rectangular boxes depicted in Scheme 10 as part of the CTAs can represent a procedure for introducing metal complexes into the backbone of polycarbonate structures. For example, polymeric materials resulting from the use of metal complexes as CTAs during the immortal copolymerization of CO_2 or COS with epoxides have been successfully synthesized in our laboratory.⁷¹ Exploitation of processes of this type constitutes an emerging area of study in our investigations of chain-transfer reactions in the synthesis of polycarbonates and their thio-analogs. An added advantage of this methodology is that these copolymers can be readily functionalized by utilization of the appropriate epoxide coupled with thiol-ene click chemistry as described earlier. In this manner, the metallopolymers can be designed to be water soluble or to self-assemble into micelles in water. Suitable CTAs containing strong binding sites for metals are depicted below, and numerous other examples are possible.



A major impetus for developing this chemistry is that metal complexes incorporated into polymeric materials can serve as catalysts for a variety of important processes. In a germane study, $[\text{FeFe}]$ -hydrogenase metallopolymers derived from an atom-transfer radical polymerization pathway have exhibited enhanced catalytic activity for hydrogen production in water.^{72–74}

Conclusions and prospectus

Early studies on the copolymerization of epoxides and carbon dioxide utilizing well-defined metal complexes as catalysts revealed that although the copolymers produced were of low polydispersity, there was no correlation between their molecular weight and monomer/initiator ratio. This behavior has been recognized as being due to adventitious water present during the polymerization process. In support of this interpretation, polymerization reactions performed under meticulously dry conditions greatly enhanced the agreement between the copolymer's molecular weight and the monomer/initiator ratio. In previous closely related studies of the polymerization of epoxides to polyethers in the presence of metal catalysts,

Inoue has referred to this behavior as *immortal polymerization*, where rapid and reversible chain transfer reactions involving protic additives are occurring. This effect is currently being utilized to produce polyols industrially for the incorporation of CO_2 into polyurethanes.

Additionally, the production of CO_2 -based polyols is being developed for the synthesis of di- and tri-block copolymers using different monomers, e.g., two different epoxides, epoxides and lactides, epoxides and polyolefins, etc. It is apparent that the future use of CTAs will provide for the synthesis of polycarbonates containing a wide variety of functionalities including charged species and metal complexes. Hence, this area of research has a bright future in the evolution of synthetic methods for the production of novel polymeric materials.

Conflicts of interest

There are no conflicts of interest to declare.

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