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Approach for Introducing a Single Metal Complex into a Polymer Chain: Metallo-Chain Transfer Agents in CO_2 or COS/Epoxide Copolymerization Processes

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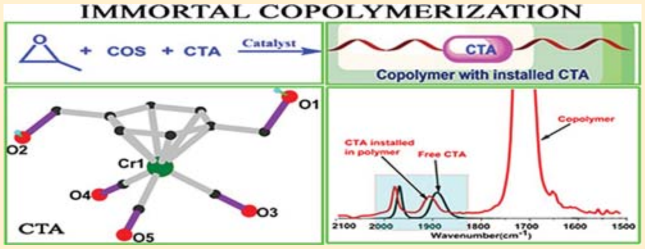
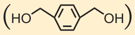
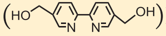
Supporting Information



ABSTRACT: We have designed and synthesized poly(monothiocarbonate)s containing a single well-defined metal complex in the polymers' backbone via the immortal copolymerization of carbonyl sulfide and propylene oxide in the presence of chain transfer agents (CTAs). Our initial studies in this area have involved the utilization of metal carbonyl diols, which serve as CTAs. Included in this investigation are the metal complexes ()$Cr(CO)_3$ and ()$Re(CO)_3Br$. Because of the electron-withdrawing abilities of the metal carbonyl fragments, the CTA afforded catalyst-alkoxide bonds are not sufficiently nucleophilic to react with CO_2; hence, the more reactive carbonyl sulfide analog was employed. As anticipated, the molecular weights of the resulting copolymers decreased with increasing quantities of added metal complexes. The incorporation of the metal complexes directly into the polymers' backbone was noted by ν_{co} infrared and ^{1}H NMR spectroscopies. Estimates of metal loading were obtained using calibration curves of the pure metal complexes based on ν_{co} infrared or electronic spectra. Thermal decomposition of the copolymers occurred above 180 °C.

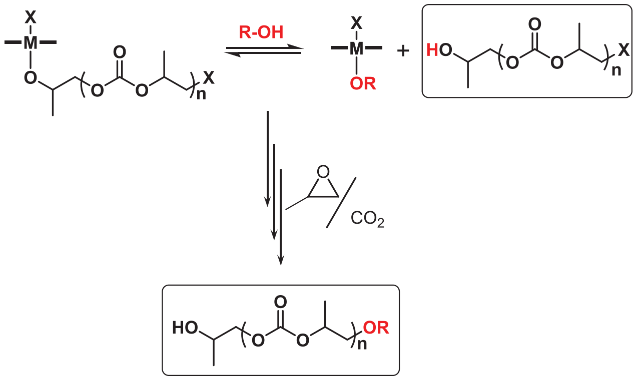
INTRODUCTION

The utilization of carbon dioxide as a feedstock for producing value-added chemicals and materials remains a challenging endeavor.[1−3] Nevertheless, much research activity is being directed at addressing this issue. The importance of these efforts is that they advance attempts to transform the readily available, nontoxic, greenhouse gas, as well as providing a potentially greener and more sustainable approach to chemical synthesis. Among the most promising transformations currently achieving these desirable attributes are the coupling reactions of CO_2 and epoxides to provide polycarbonates.[4−17] Progress in this area has been greatly aided by the development and availability of well-defined and highly selective metal catalysts.

Although the copolymerization of epoxides and carbon dioxide catalyzed by metal complexes have many of the features of a living polymerization process, because of rapid and reversible chain transfer reactions, the molecular weight of the resulting polymer is difficult to control. That is, in the presence of protic compounds, e.g., adventitious water, a single catalyst site can lead to several polymer chains.[18−20] This, in turn, leads to poor control of the copolymer's molecular weight. Scheme 1 summarizes the reaction pathways, which take place during the copolymerization of propylene oxide and CO_2 in the presence of a monofunctional chain transfer agent.

The products of the chain transfer process in the instance where R = H and X represents an easily hydrolyzable initiator, e.g., trifluoroacetate, are nearly 100% macropolyols.[21−23] Because of the use of these polyols in the synthesis of thermoplastic polyurethanes, the incorporation of CO_2 has the potential to reduce the petrochemical-based content of these high-volume commercial materials. Indeed, Covestro is currently marketing polyurethanes based on CO_2-derived polyols for the synthesis of flexible foam materials.[24] Other companies are similarly exploring applications based upon this technology, including Aramco, SK Energy, and Econic.[25−27]

Scheme 1. Immortal Polymerization of the Copolymerization of Epoxides and CO_2



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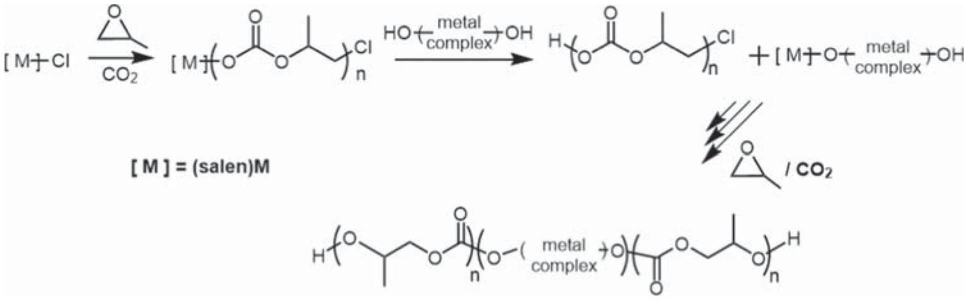
Scheme 2. Installing Metal Complexes into the Backbone of Polycarbonates



The above applications generally utilize difunctional chain transfer agents (CTAs), such as poly(ethylene glycol), polypropylene glycol, or dicarboxylic acids. These CTAs allow for the synthesis of triblock copolymers, which display emerging areas for the use of CO_2-derived copolymers. For example, a green flame-retarding polyurethane has been prepared from the reaction of a poly(propylene carbonate)-diol and diisocyanate, where the poly(propylene carbonate)-diol was synthesized by the copolymerization of propylene oxide and CO_2 in the presence of the CTA, phenylphosphonic acid.[28] In a one-pot synthesis, a triblock polycarbonate was prepared from the polyol derived from propylene oxide and CO_2 in the presence of water followed by the polymerization of allylglycidyl ether and CO_2. Subsequent thiol−ene click chemistry was carried out on these triblock polymers to afford amphiphilic polymers, which self-assembled in water to provide nanoparticles.[29] This approach was employed to prepare micelles of polycarbonates conjugated with gadolinium for imaging cancer cells.[30] Additionally, the ionic liquid CTA, 1,3-bis(3-carboxypropyl)imidazolium tetrafluoroborate, was utilized in the immortal copolymerization of propylene oxide and CO_2 to provide ion-containing polycarbonates and eventually ion-containing polyurethanes.[31]

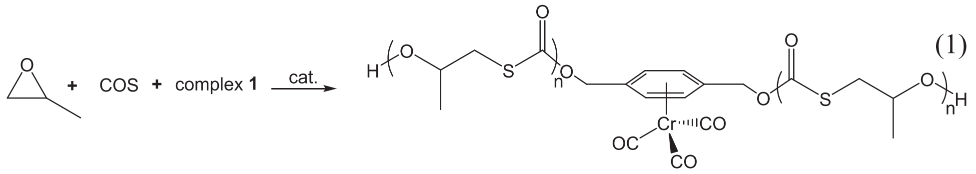
Although we have shown that it is possible to bind metal conjugate to the side chains of CO_2-based polycarbonates, there are no reports of polycarbonates containing metal complexes rigidly held in the polymer's backbone structure.[32] At this time, we wish to describe our initial studies representing a novel approach for inserting a single metal complex into the polymer backbone via a chain transfer process. Scheme 2 illustrates our strategy for incorporating a metal complex into the copolymer's backbone in a one-step process. Note, the metal complex is part of the linear polycarbonate chain, where the metal fragment is bound to the CTA by way of strong coordinate covalent bonds. That is, the metal center is not part of the polymer's backbone.

A major benefit of this technique is that, as stated above, it ultimately allows for the easy production of amphiphilic polymers, which spontaneously self-assemble into nanostructures in water. These nanomaterials can be used in various important applications, including drug delivery. For example, many metal complex delivery agents may be unstable in an aqueous environment, such as NO or CO slow-release complexes.[33−37] Alternatively, these amphiphiles can provide micelle-forming metal catalytic species for performing a wide variety of organic transformations in aqueous media.[38,39]

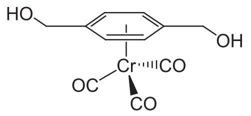
Figure 1. X-ray structure of complex **1** determined at 100 K.

■ RESULTS AND DISCUSSION

In our "proof-of-concept" studies, an (arene)$Cr(CO)_3$ diol, complex **1**, has been utilized as a bifunctional CTA during the copolymerization of propylene oxide and CO_2 or carbonyl sulfide (COS) (Figure 1).[40] This chain transfer agent was chosen because it contains a strongly η^6 bound $Cr(CO)_3$ fragment with intense ν_{co} probes. Unfortunately, reactions involving CO_2, propylene oxide, and complex **1** in the presence of the binary catalyst system (salen)CrCl/PPNCl afforded as the major product, cyclic carbonate, with only a small quantity of low-molecular-weight polycarbonates. Nevertheless, the copolymer produced upon purification clearly indicated the



(1)



Complex **1**

incorporation of complex **1**, as evidenced via infrared spectroscopy in the ν_{co} region, which exhibited a decrease in molecular weight with an increase in the concentration of **1**. This behavior is attributed to the electron-withdrawing ability of the $Cr(CO)_3$ unit, which reduces the nucleophilicity of the oxygen atom and thereby the rate of insertion of the poorly electrophilic CO_2 molecule. A similar response has been noted previously for the insertion of CO_2 into the W−O bond of $W(CO)_5O{-}(arene)Cr(CO)_3{}^{-1}$.[41] Attempts to overcome the electron-withdrawing ability of the $Cr(CO)_3$ unit by adding four methyl groups to the arene ligand of complex **1** were ineffective. It should be recognized that utilizing the analogous diol without the $Cr(CO)_3$ fragment readily serves as a CTA for the polymerization of propylene oxide and CO_2 under identical conditions.

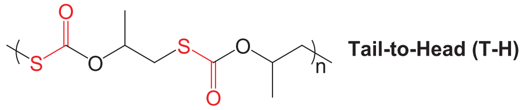


Figure 2. Diad of the PO/COS copolymer.

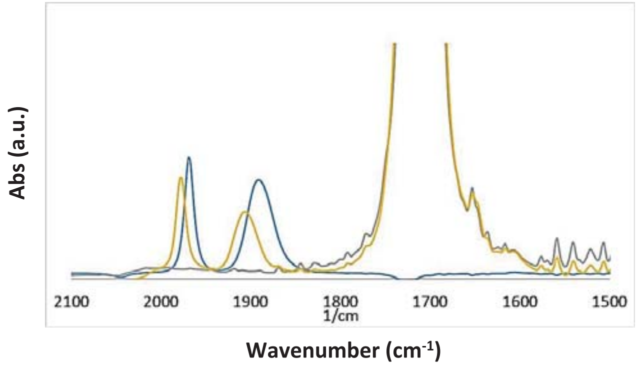
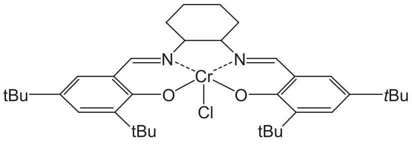


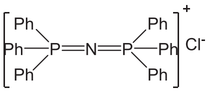
Figure 4. Infrared spectra in ν_{co} region: complex **1** in blue (ν_{co} 1970, 1889 cm^{-1}), complex **1** conjugated in polymer yellow (ν_{co} 1979, 1903 cm^{-1}), and metal-free polymer in gray.

In further studies reported upon herein, the use of the more electrophilic and reactive carbonyl sulfide congener will be investigated. The copolymerization of propylene oxide and COS in the presence of complex **1** was carried out at ambient temperature in dichloromethane/toluene solvent (eq 1). As reported previously, the copolymerization was found to be completely alternating and regioselective (Figure 2).[42−44] That is, COS inserts into the M−OR bond to afford exclusively the M−S derivative, and the afforded monothiocarbonate ligand ring opens the propylene oxide regioselectivity at the less-hindered methylene carbon center. Figure 3 displays the purified copolymers afforded in the presence and absence of $Cr(CO)_3$-bound diol. The ν_{co} infrared spectra in dichloromethane of the metal-conjugated and metal-free copolymers are illustrated in Figure 4. As indicated, assuming true C_{3v} symmetry, the A_1 and E ν_{co} vibrations of complex **1** increase by 9 and 4 cm^{-1} upon copolymer incorporation, respectively. Copolymerization reactions of propylene oxide and COS in the presence of varying quantities of a chain transfer agent, complex **1**, are summarized in Table 1. Figure 5 clearly illustrates the relationship between the complex **1** loading and M_n, with a decrease in M_n with an increase in **1** being linear. It is also noteworthy that, in general, there is good agreement between the M_n values determined by gel permeation chromatography (GPC) and ^1H NMR measurements. Efforts to prepare the metal-conjugated polymer by the postpolymerization of the copolymer prepared from propylene oxide and carbonyl sulfide in the presence of bis-hydroxymethyl-substituted benzene with a 25-fold excess of $Cr(CO)_3(NH_3)_3$ were only modestly successful, with only a low level of $-Cr(CO)_3$ incorporation after refluxing in dioxolane for 5 h. The average metal loadings as predicted based on the copolymers' molecular weights were estimated by comparing the ν_{co} absorbances to those obtained from a calibration curve of the pure complex **1** ν_{co} absorbances in the infrared (Figure S20).

Similar results were obtained using the rhenium tricarbonyl complex **2** as a CTA in the copolymerization of propylene oxide and COS. Equation 2 proceeded smoothly to copolymer at ambient temperature. The bright yellow metal-conjugated purified copolymer is illustrated in Figure 6, alongside its unmetallated analog. It is noteworthy that in this instance the copolymer in eq 2 can be produced in a postpolymerization manner from $BrRe(CO)_5$ and the unmetallated polymer. Spectroscopic infrared data are provided in Figure 7 for the free complex and conjugated polymers, respectively. Table 2 summarizes the copolymerization data for the reaction of propylene oxide and COS in the presence of complex **2**. As noted for CTA complex **1**, the molecular weight of the copolymer decreases with an increase in [CTA] (Figure 8). Also illustrated in Table 2, there is reasonable consistency between the observed M_n and the calculated M_n based on the monomer-to-initiator ratio. The % metal loading was determined to be in reasonable agreement with that expected from the copolymer molecular weight based on a calibration curve in the visible electronic spectra of the pure complex **2**. It is noteworthy that the polymer-incorporated complex **2** displays a significant red shift in the low-energy charge transfer bond in the visible region from the free metal complex. For



Catalyst



[PPN]Cl

Figure 3. Purified copolymers from reaction in eq 1, with and without $-Cr(CO)_3$ unit.

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Table 1. Copolymerization of Propylene Oxide and COS in the Presence of Complex 1[a]

entry	[monomer]/[initiator][b]	M_n (GPC)[c] g/mol	$Đ$	M_n (H NMR) g/mol	calcd[d] g/mol
1	200 (no metal)	18 000	1.20	21 054	23 874
2	200	15 700	1.32	18 182	23 874
3	143	18 900	1.27	13 778	17 131
4	90.9	8900	1.46	9204	11 001
5	52.6	6400	2.10	7525	6484

[a] All crude ^{1}H NMR spectra of copolymers showed that the CTA loading was 100%, i.e., there was no free CTA following polymerization. [b] Reaction conditions: cat./PPNCl/PO/CTA = 1:1:1000: CTA, where CTA was 4, 4, 6, 10, and 18. Ambient temperature in dichloromethane (DCM)/toluene at 1.0 MPa for 22 h. [c] All GPC traces were bimodal or higher. Tetrahydrofuran (THF) was used as an eluent, and polystyrene standards were used to calibrate the system. [d] Calculation based on the number of initiators = no. of CTAs + 1. The initial chain initiated by Cl^- does not contain the CTA; hence, the M_n calculated are approximate only. M_n = [monomer]/[initiator] × 118 + 274.

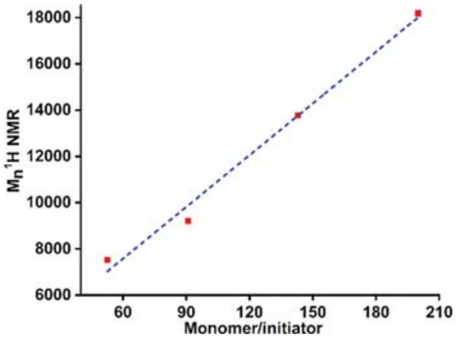


Figure 5. Copolymer's measured molecular weight (M_n) by H NMR versus [monomer]/[initiator] for **1**.

Figure 6. Poly(monothiopropylene carbonate) with and without $-ReBr(CO)_3$ fragment.

example, the copolymer prepared in entry 5 (Table 2) was found to contain 0.021 mmol of complex **2**, whereas 0.030 mmol was the expected value. This would be anticipated to be low since the initially generated polymer contains no CTA, and the blocking efficiently is, in general, less than 100%.[45]

The thermogravimetric analysis (TGA) curves of the propylene oxide/COS copolymers derived in the presence of the CTA with and without the metal fragment were shown to differ slightly with T_{d5} (°C) of 180 and 210 and T_{d50} (°C) of 250 and 255, respectively (Figure 9). These results are higher than that provided for the pure poly(monothiocarbonate) reported in the literature, where decomposition began at 137 °C.[42]

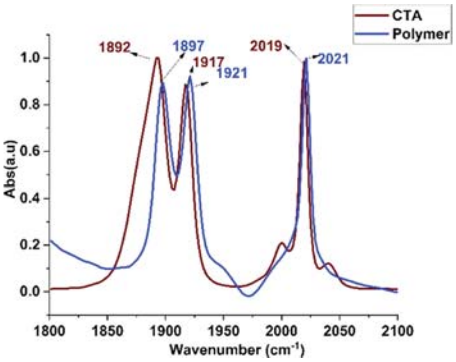
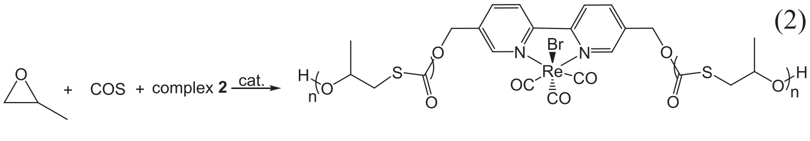


Figure 7. Free complex **2** and conjugated to a polymer.

SUMMARY AND PROSPECTUS

It is reported upon herein that although copolymers of propylene oxide and CO_2 are not easily synthesized in the presence of metal carbonyl complexes **1** and **2** as chain transfer agents, the corresponding copolymers prepared from the more reactive carbonyl sulfide are easily afforded in a regioselective and completely alternating manner under mild reaction conditions. Hence, this approach provides a facile method for incorporating a single metal complex into the copolymer's backbone chain. This procedure affords an accessible route for installing appropriate metal derivatives into polymers for catalysis or drug delivery. This is especially the case in light of the ability of these polymeric materials to be made amphiphilic via functionalization using thiol−ene click chemistry and thereby of use in applications in micellar catalysis. It is worthy of comment here that when alcoholic metallo-CTAs are replaced with their carboxylic acid metallo-CTA analogs, the immortal copolymerization of propylene oxide and CO_2



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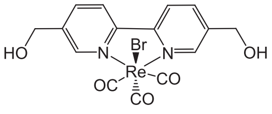

Complex **2**

Table 2. Copolymerization of Propylene Oxide and COS in the Presence of Complex 2[a]

entry	[monomer]/[initiator][b]	M_n (GPC)[c] g/mol	Đ	M_n (H NMR) g/mol	calcd[d] g/mol
1	500	21 000	1.43	53 729	59 564
2	333	37 900	1.32	37 144	39 897
3	250	27 800	1.56	31 598	30 064
4	200	34 200	1.48	28 962	24 164
5	167	19 600	1.32	24 557	20 231

[a] All crude ^{1}H NMR spectra of copolymers showed that the CTA loading was 100%, i.e., there was no free CTA following polymerization. [b] Reaction conditions: cat./PPNCl/PO/CTA = 1:1:1000:CTA, where CTA was 1, 2, 3, 4, and 5. Ambient temperature in DCM/toluene at 1.0 MPa for 22 h. [c] All GPC traces were bimodal or higher. THF was used as an eluent, and polystyrene standards were used to calibrate the system. [d] Calculation based on the number of initiators = no. of CTAs + 1. The initial chain initiated by Cl^- does not contain the CTA; hence, the M_n calculated are approximate only. M_n = [monomer]/[initiator] × 118 + 564.

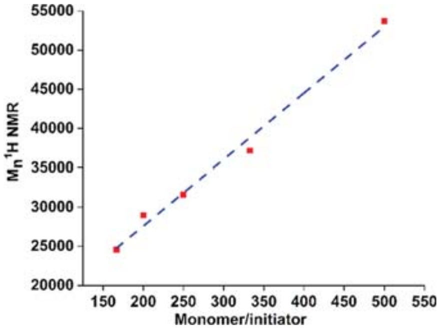

Figure 8. Copolymer's measured molecular weight (M_n) by H NMR versus [monomer]/[initiator] for 2.

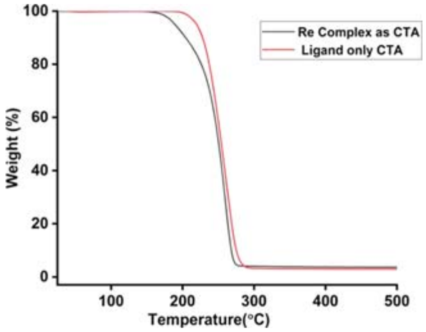

Figure 9. TGA curve for propylene oxide/COS copolymer with and without metal fragment, {Re(CO)$_3$Br}.

readily occurs. This is the result of the hydroxyl groups providing metal alkoxides upon chain transfer, which are not nucleophilic enough for the insertion of CO_2 due to the electron-withdrawing metal carbonyl fragments, whereas the carboxylic acid-initiating groups are capable of ring-opening a metal-bound epoxide, leading to polymer chain growth. We will provide a detailed report of the dicarboxylic acid metallo-CTAs in the future, along with other properties of these metal-conjugated copolymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.9b00906.

Methodology for M_n by ^{1}H NMR; NMR spectrometry data; FTIR spectroscopy data; ESI mass spectrometry data; gel permeation chromatography data; thermal gravimetric analysis data; calibration curve data; and X-ray crystallography data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the Valorization of Exhaust Carbon: from CO_2 to Chemicals, Materials, and Fuels. Technological Use of CO_2. *Chem. Rev.* **2014**, *114*, 1709−1742.

(2) Sakakura, T.; Choi, J.-C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365−2387.

(3) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using carbon dioxide as a building block in organic synthesis. *Nat. Commun.* **2015**, *6*, No. 5933.

(4) Darensbourg, D. J.; Holtcamp, M. W. Catalytic Activity of Zinc(II) Phenoxides Which Possess Readily Accessible Coordination Sites. Copolymerization and Terpolymerization of Epoxides and Carbon Dioxide. *Macromolecules* **1995**, *28*, 7577−7579.

(5) Coates, G. W.; Moore, D. R. Discrete metal-based catalysts for the copolymerization of CO_2 and epoxides: discovery, reactivity, optimization, and mechanism. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618−6639.

(6) Sugimoto, H.; Inoue, S. Copolymerization of carbon dioxide and epoxide. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5561−5573.

(7) Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaux, D. R. The Copolymerization of CO_2/Epoxides Catalyzed by Metal Salen Complexes. *Acc. Chem. Res.* **2004**, *37*, 836−844.

(8) Chisholm, M. H.; Zhou, Z. New generation polymers: the role of metal alkoxides as catalysts in the production of polyoxygenates. *J. Mater. Chem.* **2004**, *14*, 3081−3092.

(9) Darensbourg, D. J. Making Plastics from Carbon Dioxide. Salen Metal Complexes as Catalysts for the Production of Polycarbonates from Epoxides and CO_2. *Chem. Rev.* **2007**, *107*, 2388−2410.

(10) Klaus, S.; Lehenmeier, M. W.; Anderson, C. W.; Rieger, B. Recent advances in CO_2/epoxide copolymerization—New strategies and cooperative mechanisms. *Coord. Chem. Rev.* **2011**, *255*, 1460−1479.

(11) Kember, M. R.; Buchard, A.; Williams, C. K. Catalysts for CO_2/epoxide copolymerisation. *Chem. Commun.* **2011**, *47*, 141−163.

(12) Lu, X.-B.; Darensbourg, D. J. Cobalt Catalysts for the Coupling of CO_2 and Epoxides To Provide Polycarbonates and Cyclic Carbonates. *Chem. Soc. Rev.* **2012**, *41*, 1462−1484.

(13) Lu, X.-B.; Ren, W.-M.; Wu, G.-P. CO_2 Copolymers from Epoxides: Catalyst Activity, Product Selectivity, and Stereochemistry Control. *Acc. Chem. Res.* **2012**, *45*, 1721−1735.

(14) Darensbourg, D. J.; Wilson, S. J. What's New with CO_2? Recent Advances in its Copolymerization with Oxiranes. *Green Chem.* **2012**, *14*, 2665−2671.

(15) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. Ring-opening copolymerization (ROCOP): synthesis and properties of polyesters and polycarbonates. *Chem. Commun.* **2015**, *51*, 6459−6479.

(16) Trott, G.; Saini, P. K.; Williams, C. K. Catalysts for CO_2/epoxide ring-opening copolymerization. *Philos. Trans. R. Soc., A* **2016**, *374*, No. 20150085.

(17) Poland, S. J.; Darensbourg, D. J. A quest for polycarbonates provided via sustainable epoxide/CO_2 copolymerization processes. *Green Chem.* **2017**, *19*, 4990−5011.

(18) Sugimoto, H.; Ohtsuka, H.; Inoue, S. Alternating copolymerization of carbon dioxide and epoxide catalyzed by an aluminum Schiff base−ammonium salt system. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4172−4186.

(19) Nakano, K.; Nakamura, M.; Nozaki, K. Alternating Copolymerization of Cyclohexene Oxide with Carbon Dioxide Catalyzed by (salen)CrCl Complexes. *Macromolecules* **2009**, *42*, 6972−6980.

(20) Cohen, C. T.; Chu, T.; Coates, G. W. Cobalt catalysts for the alternating copolymerization of propylene oxide and carbon dioxide: combining high activity and selectivity. *J. Am. Chem. Soc.* **2005**, *127*, 10869−10878.

(21) Kember, M. R.; Copley, J.; Buchard, A.; Williams, C. K. Triblock copolymers from lactide and telechelic poly(cyclohexene carbonate). *Polym. Chem.* **2012**, *3*, 1196−1201.

(22) Kember, M. R.; Williams, C. K. Efficient Magnesium Catalysts for the Copolymerization of Epoxides and CO_2; Using Water to Synthesize Polycarbonate Polyols. *J. Am. Chem. Soc.* **2012**, *134*, 15676−15679.

(23) Darensbourg, D. J. Chain transfer agents utilized in epoxide and CO_2 copolymerization processes. *Green Chem.* **2019**, *21*, 2214−2223.

(24) Carbon Dioxide is revolutionizing plastics production. 2018, https://www.co2-dreams.covestro.com/en (accessed December 12, 2018).

(25) Tullo, A. H. Aramco Buys Novomer's CO_2-Based Polyols Business. *Chem. Eng. News* **2016**, *94*, 14.

(26) Ok, M.-A.; Jeon, M. In *Properties of Poly(propylene carbonate) Produced via SK Energy's Greenpol Technology*, ANTEC-Conference Proceedings; Society of Petroleum Engineers: Richardson, TX, 2012; pp 2134−2139.

(27) Econic Technologies Ltd., Nether Alderley 2018. http://www.econic-technologies.com/ (accessed December 12, 2018).

(28) Lee, S. H.; Cyriac, A.; Jean, J. Y.; Lee, B. Y. Preparation of thermoplastic polyurethanes using *in-situ* generated poly(propylene carbonate)-diols. *Polym. Chem.* **2012**, *3*, 1215−1220.

(29) Wang, Y.; Fan, J.; Darensbourg, D. J. Construction of Versatile and Functional Nanostructures Derived from CO_2-based Polycarbonates. *Angew. Chem., Int. Ed.* **2015**, *54*, 10206−10210.

(30) Li, Y.; Liu, S.; Zhao, X.; Wang, Y.; Liu, J.; Wang, X.; Lu, L. CO_2-based amphiphilic polycarbonate micelles enable a reliable and efficient platform for tumor imaging. *Theranostics* **2017**, *7*, 4689−4698.

(31) Huang, Z.; Wang, Y.; Zhang, N.; Zhang, L.; Darensbourg, D. J. One-Pot Synthesis of Ion-Containing CO_2-Based Polycarbonates Using Protic Ionic Liquids as Chain Transfer Agents. *Macromolecules* **2018**, *51*, 9122−9130.

(32) Tsai, F.-T.; Wang, Y.; Darensbourg, D. J. Environmentally Benign CO_2-Based Copolymers: Degradable Polycarbonates Derived from Dihydroxybutyric Acid and Their Platinum-Polymer Conjugates. *J. Am. Chem. Soc.* **2016**, *138*, 4626−4633.

(33) Cabral, H.; Miyata, K.; Osada, K.; Kataoka, K. Block Copolymer Micelles in Nanomedicine Applications. *Chem. Rev.* **2018**, *118*, 6844−6892.

(34) Heinemann, S. H.; Hoshi, T.; Westerhausen, M.; Schiller, A. Carbon Monoxide-physiology, detection and controlled release. *Chem. Commun.* **2014**, *50*, 3644−3660.

(35) Kim, H. P.; Ryter, S. W.; Choi, A. M. K. CO as cellular signaling molecule. *Annu. Rev. Pharmacol. Toxicol.* **2006**, *46*, 411−449.

(36) Chupik, R.; Pulukkody, R.; Montalvo, S.; Khan, S.; Bhuvanesh, N.; Lim, S.-M.; Darensbourg, M. Y. Towards Biocompatible Dinitrosyl Iron Complexes: Sugar Appended Thiolates. *Chem. Commun.* **2017**, *53*, 1180−1183.

(37) Kang, Y.; Kim, J.; Lee, Y. M.; Im, S.; Park, H.; Kim, W. J. Nitric oxide-releasing polymer incorporated ointment for cutaneous wound healing. *J. Controlled Release* **2015**, *220*, 624−630.

(38) Lipshutz, B. H.; Taft, B. R. Heck Couplings at Room Temperature in Nanometer Aqueous Micelles. *Org. Lett.* **2008**, *10*, 1329−1332.

(39) Lipshutz, B. H.; Ghorai, S.; Abela, A. R.; Moser, R.; Nishkata, T.; Duplais, C.; Krasovskiy, A.; et al. TPGS-750-M: A Second-Generation Amphiphile for Metal-Catalyzed Cross-Couplings in Water at Room Temperature. *J. Org. Chem.* **2011**, *76*, 4379−4391.

(40) Christofi, A. M.; Garratt, P. J.; Hogarth, G.; Steed, J. W. Synthesis and structures of chromium tricarbonyl complexes of benzylic halides and benzylic alcohols. *J. Chem. Soc., Dalton Trans.* **2000**, 2137−2144.

(41) Darensbourg, D. J.; Mueller, B. L.; Reibenspies, J. H. The synthesis and X-ray structure of a phenoxide-bridged heterobimetallic anion, $W(CO)_5OPh(Cr(CO)_3)^-$, and its reactivity with carbon dioxide and carbonyl sulfide. *J. Organomet. Chem.* **1993**, *451*, 83−87.

(42) Luo, M.; Zhang, X.-H.; Du, B.-Y.; Wang, Q.; Fan, Z.-Q. Regioselective and Alternating Copolymeriztaion of Carbonyl Sulfide with Recemic Propylene Oxide. *Macromolecules* **2013**, *46*, 5899−5904.

(43) Darensbourg, D. J.; Mueller, B. L.; Bischoff, C. J.; Chojnacki, S. S.; Reibenspies, J. H. Investigations into the steric influences on the reaction mechanism of carbon dioxide insertion into metal-oxygen bonds. Carbonyl sulfide activation as a model for CO_2. *Inorg. Chem.* **1991**, *30*, 2418−2424.

(44) Luo, M.; Zhang, X.-H.; Darensbourg, D. J. An Examination of the steric and Electronic Effects in the Copolymerization of Carbonyl Sulfide and Styrene Oxide. *Macromolecules* **2015**, *48*, 6057−6062.

(45) Zhang, Y.-Y.; Yang, G.-W.; Wang, Y.; Lu, X.-Y.; Wu, G.-P.; Zhang, Z.-S.; Wang, K.; Zhang, R.-Y.; Nealey, P. F.; Darensbourg, D. J.; Xu, Z.-K. Synthesis of CO_2-Based Block Copolymers via Chain Transfer Polymerization Using Macroinitiators: Activity, Blocking Efficiency, and Nanostructure. *Macromolecules* **2018**, *51*, 791−800.

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