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Placing Single-Metal Complexes into the Backbone of CO_2-Based Polycarbonate Chains, Construction of Nanostructures for Prospective Micellar Catalysis

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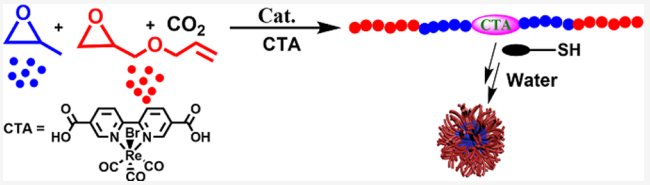
Supporting Information

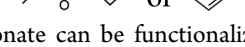
ABSTRACT: The copolymerization of CO_2 and epoxides in the presence of chain-transfer agents (CTAs) has provided a well-controlled route to polycarbonate polyols. Upon employing dicarboxylic acid CTAs which contain discrete metal-binding sites, it is possible to synthesize polycarbonates with a single-metal complex present in the main chain, either during the copolymerization process or in a postpolymerization procedure. In these ways, the (bipy)$Re(CO)_3Br$ complex has been incorporated into the polycarbonate backbone. Furthermore, in a one-pot, two-step synthesis, a second epoxide containing a vinyl substituent can be introduced to afford a triblock **ABA** polycarbonate, where the metal is contained in the **B** block. Subsequent to the thiol−ene click chemistry of HS^COOH and deprotonation, the resulting anionic polymer is shown to self-assemble in deionized water to provide rather uniform, spherical micelles. Since this procedure is modular, it is applicable to a wide variety of CTAs containing metal complexes or metal-binding sites, thereby providing a pathway to synthesize a wide range of micellar catalysts for pursuing organometallic transformations in water.



INTRODUCTION

The synthesis of novel polymers and nanostructures directly from carbon dioxide and cyclic ethers represents an intriguing direction in chemistry for the production of new polymeric materials based in part on nonpetroleum chemical feedstocks. Inoue and co-workers demonstrated the feasibility of copolymerizing epoxides and carbon dioxide to provide (polyether−carbonate)s using a poorly defined heterogeneous zinc catalyst.[1,2] Since that discovery, these researchers along with numerous other research groups have developed catalytic methods for selective and controllable polymerization processes for the production of completely alternating polycarbonates from epoxides and CO_2 under mild reaction conditions.[3−18] These polymerization processes, which are generally catalyzed by well-defined metal complexes, have provided a good working knowledge of the reaction pathways for affording either copolymer or cyclic materials from epoxides and CO_2.[19] With this advancement in catalytic systems and the understanding of their mechanistic aspects, CO_2 and propylene oxide coupling to polycarbonates has been highly commercialized.[20−23] This latter effort is primarily due to the use of poly(propylene carbonate)diols, afforded from propylene oxide and CO_2 in the presence of protic chain-transfer agents (CTAs), and diisocyanates in condensation reactions afford the highly used polymeric materials, polyurethanes.

More recent studies have shown that these poly(propylene carbonate) diols can also serve as macroinitiators in a one-pot coupling reaction with lactides or other epoxides/CO_2, thereby allowing for the subsequent production of ABA triblock copolymers (Scheme 1).[24−27] In instances where the second epoxide added contains a vinyl group, such as



the triblock polycarbonate can be functionalized with various thiols by thiol−ene click chemistry.[28] The thiol−ene reaction for the functionalization of polymer side chains occurs with anti-Markovnikov regioselectivity via azobis(isobutyronitrile) radical initiated addition of thiols.[29] In particular, thiols possessing carboxylic acids or amine groups are important functional substituents for producing amphiphilic polycarbonates.[30]

Nanomaterials derived from biodegradable polymers can serve in a variety of important roles, such as in human diagnostic or therapeutic functions. Alternatively, these polymeric materials can provide a suitable medium for catalytic transformations of organic compounds. Herein, we wish to propose the design of these materials based on amphiphilic polycarbonates derived from carbon dioxide which can serve as catalysts for organic reactions. This study was inspired by earlier studies involving the synthesis of ABA triblock polycarbonates from the terpolymerization of CO_2/propylene oxide/allyl glycidyl ether. These triblock polymers were shown, following functionalization by thiol−ene click chemistry, to

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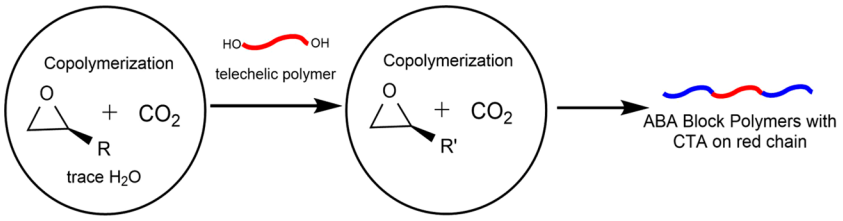
Scheme 1. Production of ABA Triblock Copolymers



self-assemble into micellar nanostructures in water.[24] This approach for encompassing a metal species differs from side-group organometallic polymers (SGOPs) as described by Bielawski and co-workers.[31] That is, SGOPs refer to polymers containing an all organic backbone with an attachment at *each* repeating unit for metal binding as depicted below. As seen in Figure 1, there is one metal complex for a repeating polymer

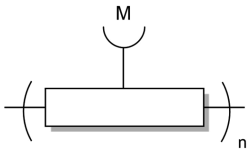
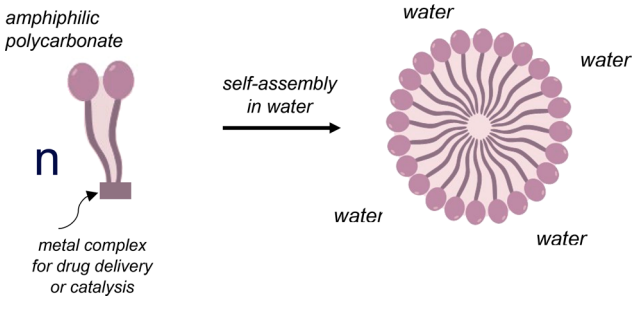


Figure 1. Side-group organometallic polymers.

unit, where the metal and polymer chain maintain structural integrity. Alternatively, our methodology provides a single-metal complex in the organic backbone of an amphiphilic polymeric material. Similar to SGOPs, in some instances metal incorporation can be accomplished during polymer synthesis or postpolymerization. Our concept is based on the designing of bifunctional alcoholic or carboxylic acid CTAs which contain strong metal-binding sites for the incorporation into the backbone of polycarbonate chains during immortal copolymerization of epoxides and carbon dioxides (Scheme 2).

Scheme 2. Metal Complex Containing Amphiphilic Polycarbonate Chains for Self-Assembly into Micelles in Water



Related to these studies is the observation that numerous organic reactions are capable of being carried out in water.[32] Nevertheless, in general, this inexpensive and environmentally benign solvent is not compatible with many metal-catalyzed organic transformations. On the contrary, the low solubility of oxygen in water can enable air-sensitive transition metal catalysis under aerobic conditions. Pioneering studies by Lipshutz and co-workers have demonstrated the use of "designer" surfactants in water for metal-catalyzed reactions. For example, his group has utilized several amphiphiles, including the commercially available TPGS-750-M, as effective nanomicelles forming species in a wide variety of metal-catalyzed cross-coupling reactions in water (Figure 2).[33]

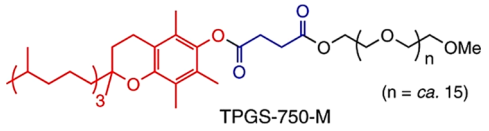
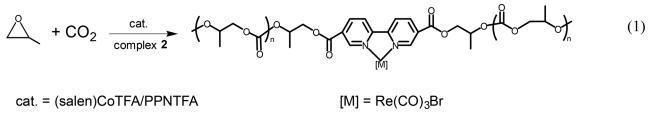


Figure 2. Surfactant for micellar catalysis.

RESULTS AND DISCUSSION

Unlike the unsuccessful immortal copolymerization of propylene oxide and CO_2 using complex **1** as CTA, the analogous process in the presence of complex **2** readily affords the triblock copolymer as indicated in eq 1.[34]



Derivatives of $(bipy)Re(CO)_3Br$ were chosen for our preliminary studies because of their stability and importance to the CO_2 reduction process.[35,36] The X-ray structure of the chloride analog of complex **2** is illustrated in Figure 3.

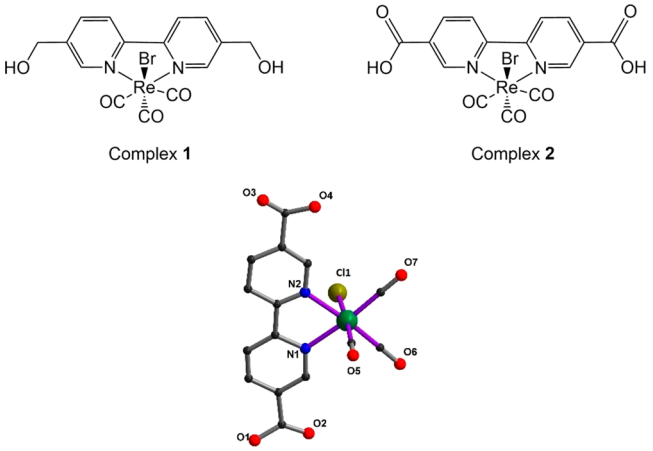


Figure 3. X-ray single-crystal structure of chloride analog of complex **2**.

As indicated in eq 1, the very efficient binary (salen)CoX/PPNX catalyst system was employed in this polymerization process. We attribute the difference in behavior of these two metallo-CTAs due to the manner in which each initiates the new chain growth following chain transfer. It is relevant to note that the growing polymer chain initially instigated by the anion (X) is terminated by a chain-transfer process involving the protic CTA. That is, in the instance of the CTA being complex

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1, the resulting cobalt-alkoxide bond is not sufficiently nucleophilic to effect the insertion of CO_2 due to the electron-withdrawing {Re(CO)$_3$Br}fragment, thereby inhibiting chain growth. However, insertion of the more electrophilic COS molecule readily occurs.[37] In contrast, following chain transfer by complex **2**, the carboxylate−cobalt bond is effective at ring-opening an epoxide, thereby allowing for chain growth.

Table 1 contains a summary of the copolymerization of propylene oxide and carbon dioxide in the presence of various quantities of CTA complex **2**. The infrared spectra of the purified copolymers from this process are depicted in Figure 4,

Table 1. Copolymerization of Propylene Oxide and CO_2 in the Presence of Complex 2[a]

entry	[monomer]/[initiator][b]	M_n(GPC) (g/mol)	$Đ$	M_n (H NMR) (g/mol)	calcd (g/mol)[c]
1	500	25800	1.28	53200	51594
2	333	21200	1.51	35500	34560
3	250	12700	1.20	16900	26094
4	200	9500	1.28	14600	20994
5	167	7550	1.00	12500	17628

[a]All crude ^{1}H NMR spectra of copolymers showed CTA loading was 100%. [b]Reaction conditions: cat./PPNTFA/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 22h. [c]Calculation based on number of initiators = no. of CTAs + 1. The initial chain initiated by Cl^- does not contain the CTA; hence, the calculated M_n are approximate only.

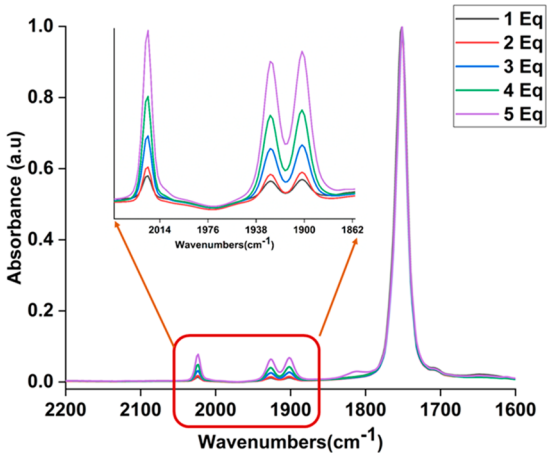

Figure 4. Infrared spectra of metal conjugated copolymer as a function of [complex **2**].

where the rhenium carbonyl complex ν_{co} bands are shown to increase in intensity as the equivalents of complex **2** are increased. As anticipated, the average molecular weight (M_n) of the copolymers decreased with increasing equivalents of CTA (Figure 5). A systematic study of the influence of the concentration of the metal-containing CTA on the nature of the afforded polycarbonate is summarized in Figure 6. In Figure 6, the low molecular weight material initially observed in the chromatograms is assigned to the propylene oxide/CO_2 copolymer initiated by the trifluoro-acetate ion, whereas the high molecular weight copolymer designates the polymer containing the CTA due to its increased hydrodynamic volume. As noted, the polymeric material containing the

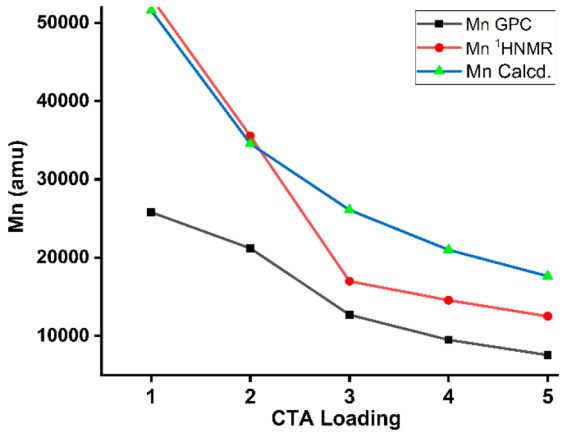

Figure 5. Copolymer's measured molecular weight (M_n) GPC and (M_n) HNMR versus the CTA loading.

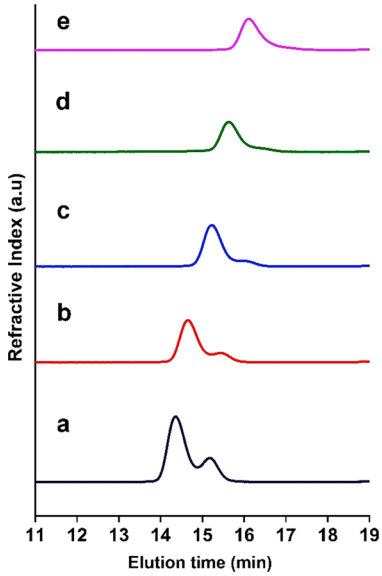

Figure 6. GPC traces of the copolymerization process as a function of added CTA: (a) 1 equiv, (b) 2 equiv, (c) 3 equiv, (d) 4 equiv, and (e) 5 equiv of (salen)CoTFA/PPNTFA/CTA.

CTA decreases in molecular weight with increasing equivalents of CTA.

In order to better assess the nature of the polymers produced by this process, copolymer samples were subjected to MALDI-ToF analysis. The MALDI-ToF spectrum (Figure 7) of the copolymer produced in entry 5 of Table 1 revealed two series of peaks indicative of a bimodal molecular weight distribution as noted in the GPC traces in Figure 6. Each series of peaks showed a separation of 102 m/z corresponding to the repeated addition of propylene oxide/CO_2 units. Of the possible architectures expected from this immortal copolymerization process indicated in Figure 8, polymer **II** was shown to be the major component. The minor series of peaks are assigned to the copolymer initiated by the $CF_3CO_2^-$ anion. Hence, there are no polymer chains with CTA end groups or no polymer chains resulting from water/propylene diol as chain transfer agents. These would appear as polymers **III** and **IV**, respectively. It would be anticipated upon employing smaller quantities of CTA (complex **2**), the percentage of copolymer initiated by the trifluoroacetate anion would be increased. This is consistent with the observed MALDI-ToF

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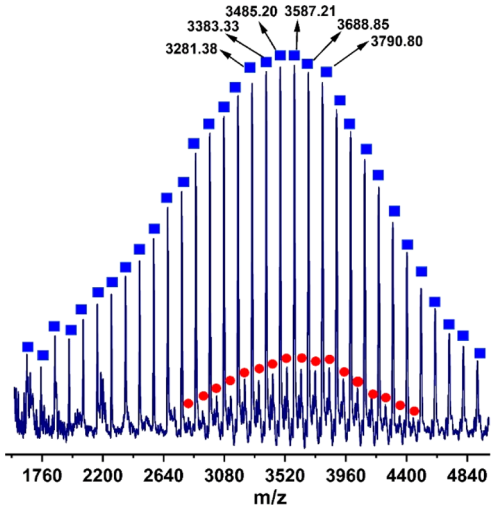

Figure 7. MALDI-ToF spectrum of copolymer produced in entry 5 of Table 1. Molecular weight of polymer **I** (red circles) = $M_{[CF_3CO_2^-]}$ + $nM_{[PO+CO_2]}$ + $M_{[K^+]}$ and molecular weight of polymer **II** (blue squares) = $M_{[CTA]}$ + $nM_{[PO+CO_2]}$ + $M_{[K^+]}$.

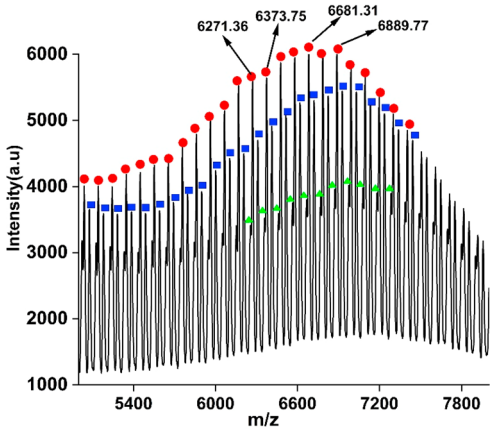

Figure 9. MALDI-ToF spectrum of copolymer produced in entry 1 of Table 1. Polymer **I** (red circles), polymer **II** (blue squares), and polymer **IV** (green triangles).

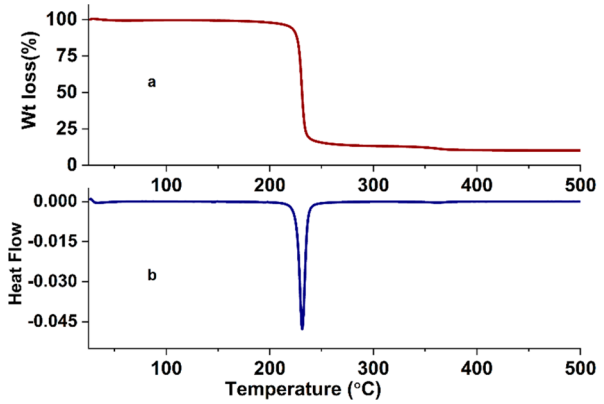

Figure 10. (a) TGA and (b) DTA curves for the copolymer derived from propylene oxide and CO_2 in the presence of 5 equiv of complex **2**.

spectrum of the copolymer sample produced in entry 1 of Table 1 (Figure 9).

The thermal gravimetric analysis (TGA) plot of the propylene oxide/CO_2 copolymer derived in the presence of 5 equiv of complex **2** is shown in Figure 10a, along with the differential thermal analysis (DTA) curve in Figure 10b. As noted in Figure 10, the T_{d50} (°C) is found at 230, which is lower than that of its COS copolymer counterpart of 250 (*vide infra*).

In order to functionalize these metal-containing polycarbonates in a postpolymerization process, a one-pot synthesis of the triblock terpolymer of propylene oxide, allyl glycidyl ether, and CO_2 was carried out in the presence of complex **2** using the (salen)CoCl/PPNCl binary catalyst system (Scheme 3). Following thiol−ene click chemistry of these ABA triblock polycarbonates with HS^COOH and deprotonation with NH_4OH, the terpolymer was found to self-assemble in water into nanoparticles.

Polymer **C** was dispersed in deionized water by sonication at ambient temperature, and the morphology of the resulting material was characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Figure 11 displays the results of DLS and TEM measurements of negatively charged (zeta potential −18.4 ± 7.41) triblock amphiphilic polycarbonate **C**. As noted in Figure 11b, anionic polymer **C** underwent self-assembly to form nanoparticles with

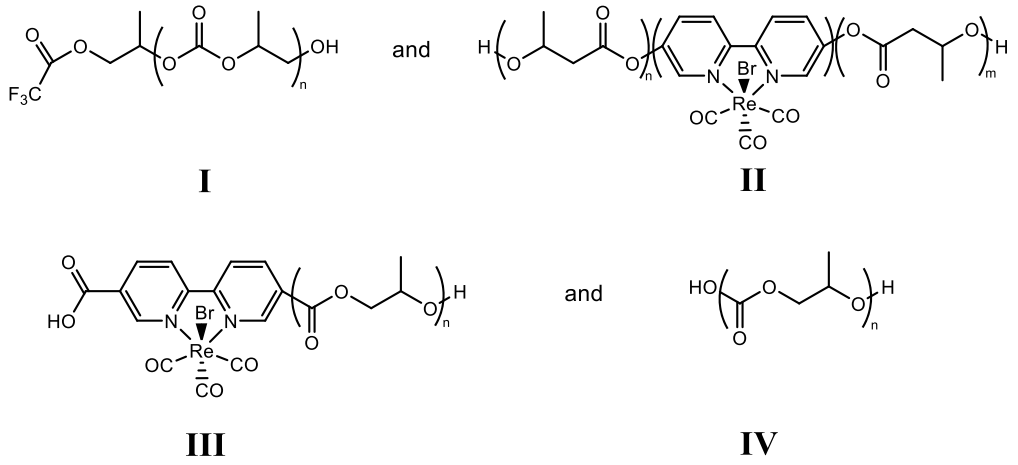

Figure 8. Possible copolymer architectures afforded by the copolymerization of propylene oxide and CO_2 in the presence of complex **2** using the (salen)Co(CF_3CO_2)/[PPN][CF_3CO_2] catalyst system.

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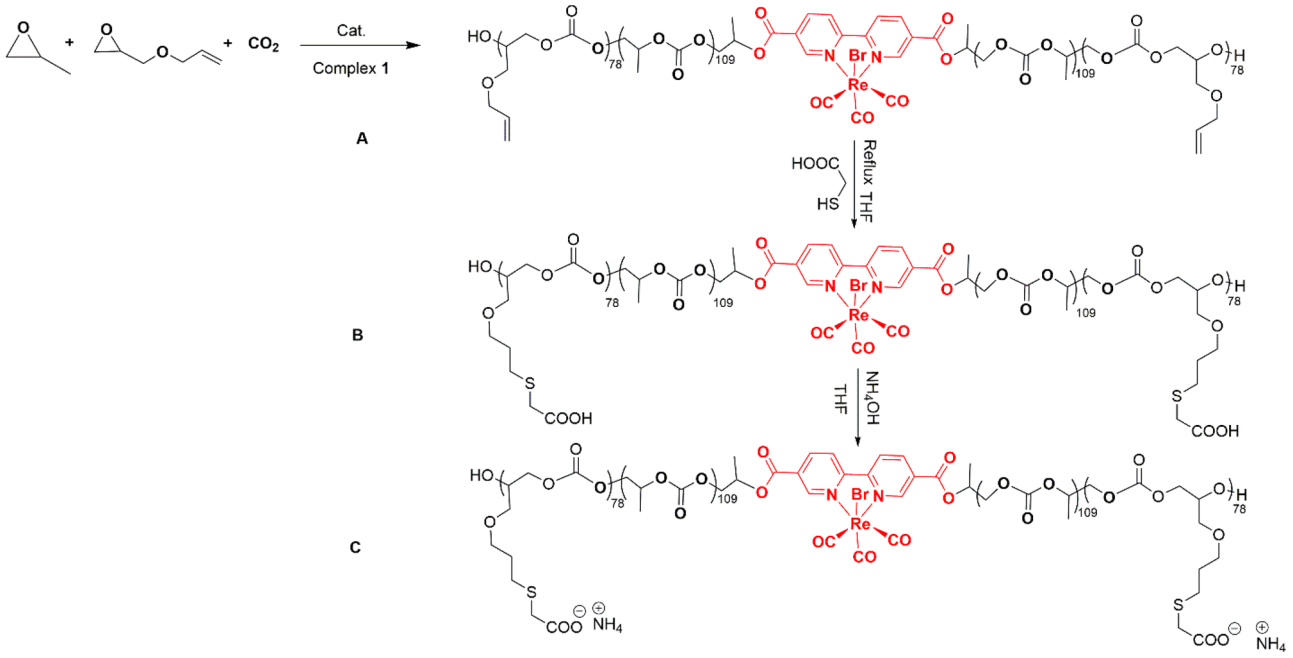
Scheme 3. Synthesis of Metal-Containing Triblock Polycarbonate and Postpolymerization Functionalization



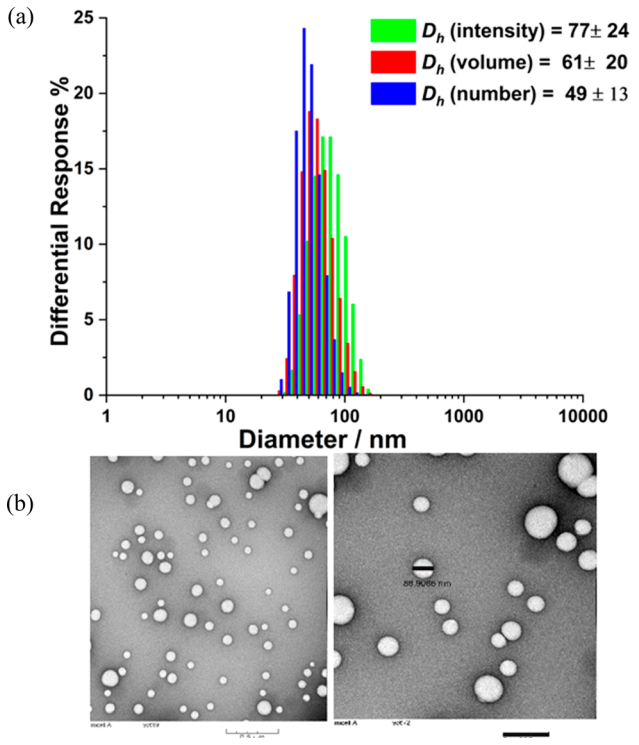


Figure 11. (a) DLS results of anionic nanoparticle of **C**. (b) TEM images of anionic nanoparticles of **C**.

good uniformity, providing an intensity-averaged hydrodynamic diameter of 77 ± 24 nm. The morphology of these nanoparticles are shown in Figure 11b to be spherical.

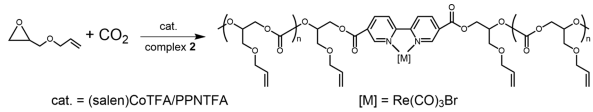
The copolymerization of carbon dioxide and allyl glycidyl ether alone was accomplished in the presence of complex **2**. The procedure for describing copolymer formation is depicted in eq 2. A summary of the results of the process can be found in Table 2. A plot of the measured molecular weights by ^{1}H NMR versus the [monomer]/[initiator], along with the GPC

Table 2. Copolymerization of AGE and CO_2 in the Presence of Complex 2

entry	[monomer]/[initiator][b]	M_n(GPC) (g/mol)	Đ	M_n(H NMR) (g/mol)	calcd (g/mol)[c]
1	500	60100	1.15	57100	79594
2	333	51400	1.68	39200	53208
3	250	43700	1.26	24400	40094
4	200	40100	1.26	14800	32194

[a]All crude ^{1}H NMR spectra of copolymers showed CTA loading was 100%. [b]Reaction conditions: cat./PPNTFA/AGE/CTA = 1:1:1000:CTA, where CTA was 1, 2, 3, and 4. Ambient temperature in DCM/toluene at 1.0 MPa for 48h. [c]Calculation based on number of initiators = no. of CTAs + 1. The initial chain initiated by TFA^- does not contain the CTA, hence the M_n calculated are approximate only.

traces for these reactions are included in Figures S1 and S2. It is worth emphasizing here that the behavior of this copolymerization reaction was total consistent with that previously described for the case of propylene oxide.



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Upon postpolymerization functionalization of the AGE/CO_2 copolymer shown in eq 2 as described in Scheme 3, the corresponding carboxylic anionic polymer consequent to DLS analysis displayed *no* hydrodynamic diameter distribution in aqueous solutions illustrating the polymer to be completely water-soluble. Hence, the procedure described herein for synthesizing functional polycarbonates containing metal complexes in their main chains can provide either nanostructured micelles or water-soluble polymeric materials.

Similar copolymerization processes were performed using carbonyl sulfide (COS) as a substitute monomer for CO_2; in these instances where sulfur is incorporated into the polymer's backbone, the copolymers often exhibit significantly different

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physical properties. Table 3 summarizes the results from the copolymerization of propylene oxide and COS in the presence

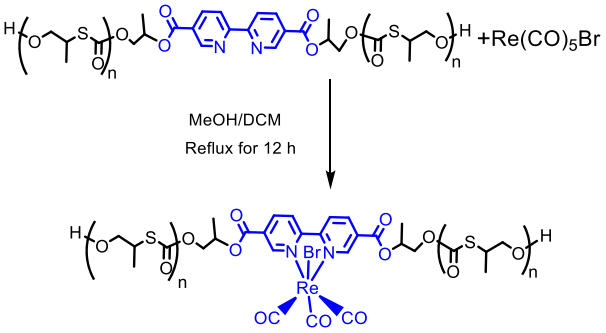
Table 3. Copolymerization of Propylene Oxide and COS in the Presence of Complex 2[a]

entry	[monomer]/[initiator][b]	M_n(GPC)[c]	$Đ$	M_n(H NMR)	calcd (g/mol)[d]
1	500	25800	1.39	55700	59594
2	333	18100	1.40	41300	39888
3	250	27700	1.38	36200	30094
4	200	28600	1.35	23000	24194
5	167	11700	1.29	16700	20300

[a]All crude ^{1}H NMR spectra of copolymers showed CTA loading was 100%. [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 22h. [c]All GPC traces were bimodal. [d]Calculation based on number of initiators = no. of CTAs + 1. The initial chain initiated by Cl^- does not contain the CTA, hence the calculated M_n are approximate only.

of complex **2** employing the (salen)CrCl/PPNCl catalyst system. As previously noted for the analogous copolymerization process involving CO_2, the intensities of the ν_{co} stretching frequencies increased with an increase in the concentration of complex **2** utilized in the reaction, while the average molecular weight (M_n) decreased (Supporting Information). There was a good correlation of the observed M_n values with those calculated based on the [monomer]/[initiator] ratio.

An identical copolymerization reaction of propylene oxide and COS in the presence of 10 equiv of the CTA, a dicarboxylic acid derivative of 2,2′-bipyridine, was carried out to provide the copolymer with a single bipy ligand in its backbone. To this copolymer ($M_w \approx 10\,000$ g/mol) in dichloromethane was added 2 equiv of $Re(CO)_5Br$ in methanol, and the reaction mixture was refluxed for 12 h. During this period, the reaction solution underwent a prominent color change from colorless to red, indicative of $Re(CO)_3Br$ being incorporated into the copolymer (eq 3). Complete postpolymerization metalation of the purified copolymer was ascertained by spectral (IR and NMR) comparison with the polymer sample prepared by copolymerization of propylene oxide and COS in the presence of complex **2**.



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CONCLUDING REMARKS

Our investigations into the copolymerization of epoxides and CO_2 in the presence of CTAs containing metal complexes have provided a straightforward, modular route for preparing polycarbonates with a single-metal complex in the backbone of the copolymer. It was further shown that the metal fragment could be incorporated into the polymer chain either during polymer synthesis or in a postpolymerization process. This latter feature allows for the capability of introducing various metal derivatives which possess common binding sites in polymeric materials, assuming the metal fragment substitution process occurs below the T_{ds} of the copolymer. For example, the {$Re(CO)_3Br$}fragment has been readily incorporated into the copolymer containing the bipyridine ligand in a postpolymerization process. We have also recounted a procedure for carrying out a one-pot, two-step process followed by functionalization using thiol−ene click chemistry to provide a metal complex sequestered in the hydrophobic portion of the nanostructured micelle afforded upon the polymer's self-assembling in water. This process is proposed to provide a pathway for performing organic transformation catalytically in aqueous solutions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00704.

Experimental details, including all synthesis and characterization data, i.e., ^{1}H and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 1962552 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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