Macromolecules

Article

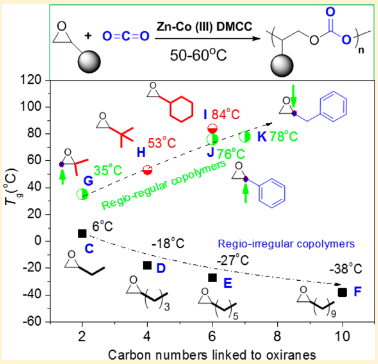
pubs.acs.org/Macromolecules

Carbon Dioxide/Epoxide Copolymerization via a Nanosized Zinc–Cobalt(III) Double Metal Cyanide Complex: Substituent Effects of Epoxides on Polycarbonate Selectivity, Regioselectivity and Glass Transition Temperatures

Xing-Hong Zhang,* Ren-Jian Wei, Ying–Ying Zhang, Bin-Yang Du, and Zhi-Qiang Fan

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China

S *Supporting Information*



ABSTRACT: In this study, we describe the substituent effect of epoxides on CO_2/epoxide copolymerization catalyzed by a nanosized zinc–cobalt(III) double metal cyanide complex [Zn–Co(III) DMCC]. The Zn–Co(III) DMCC catalyzed the copolymerization of CO_2 with 11 epoxides with alkyl or aryl groups at 50–60 °C within 15 h. The reaction afforded various CO_2/epoxide copolymers with high epoxide conversion efficiencies up to 100%. The alternating degree (F_{CO_2}) of the resulting copolymer was solely decided by the steric hindrance of the substituents of the epoxides regardless of their electron-donating or withdrawing properties. Substituents with large steric hindrances (2, 2-dimethyl, *tert*-butyl, cyclohexyl, decyl, and benzyl) led to highly alternating degrees (up to 100%). The regioselective CO_2/epoxide copolymerization was dominated by the electron induction effect of the substituent. The electron-withdrawing substituent such as phenyl and benzyl induced regioselective ring-opening at the methine site of the epoxide. For CO_2/isobutene oxide copolymerization, the regioselective reaction occurred at the methylene site of the isobutene oxide because of the strong electron-donating ability and steric hindrance of the two methyls of the isobutene oxide. The linear alkyl groups of the epoxides could not induce the regioselective reaction during copolymerization. The glass transition temperatures (T_gs) of the CO_2/epoxide copolymers with linear alkyl substituent groups decreased from +6 to −38 °C with increasing alkyl length, but increased from 6 to 84 °C with increasing steric hindrance of the epoxide substituents. Thus, various CO_2/epoxide copolymers with a wide T_g range from −38 to +84 °C were provided and could be applied as elastomers or plastics.

■ INTRODUCTION

Transforming carbon dioxide (CO_2) into polymeric materials by alternating copolymerization of CO_2 with epoxides is incredibly promising. Since the pioneering work of CO_2/propylene oxide (PO) copolymerization catalyzed by $ZnEt_2/H_2O$ system reported by Inoue et al. in 1969,[1] tremendous advances have been made in this field.[2−6] Indeed, CO_2/PO copolymer has been commercialized and shows a bright future for CO_2-based polymeric materials,[7,8] which encouraged us to expand the application of CO_2/epoxide copolymers into the area of plastics or elastomers. Thus, it is a necessity to design and synthesize CO_2/epoxide copolymers with various glass transition temperatures (T_gs) across a wide temperature range. Epoxides with different substituents offer many opportunities to synthesize CO_2/epoxide copolymers with various T_gs; however, the substituent effects of the epoxide on CO_2/epoxide copolymerization (polycarbonate selectivity, regioselectivity and glass transition temperatures) have not yet been systematically investigated.

The copolymerization of CO_2 with the epoxides containing long linear alkyl groups could create copolymers with T_gs below room temperature.[9−11] Such CO_2/epoxide copolymers with low T_g could serve as biodegradable elastomers—a new application of CO_2-based polymers.[8a,c] However, the copolymerization of CO_2 with epoxides containing long linear alkyl groups have rarely been reported likely because of the relatively low reactivity of these epoxides. Coates and co-workers reported CO_2/1,2-butene oxide copolymerization using a zinc β-diiminate complex catalyst at 25 °C and 300 psi CO_2. This produced 15% cyclic carbonate.[9] The turnover frequency (TOF) of this copolymerization had <50% the activity of CO_2/PO copolymerization with the same catalyst. The alternating copolymerization of 1, 2-butene oxide, 1,2-hexene oxide and 1,2-octene oxide with CO_2 were reported by the Lu group using a (Salen)Co(III) complex with (PPN)Cl, [bis(triphenylphosphine)iminium] chloride, at 25–40 °C for 3–4 h. This gave copolymers with polycarbonate selectivity of 97–99%,[10] while the TOFs of these copolymerizations also decreased dramatically versus the CO_2/PO copolymerization with the same catalyst.

Received: November 24, 2014
Revised: January 16, 2015

DOI: 10.1021/ma5023742

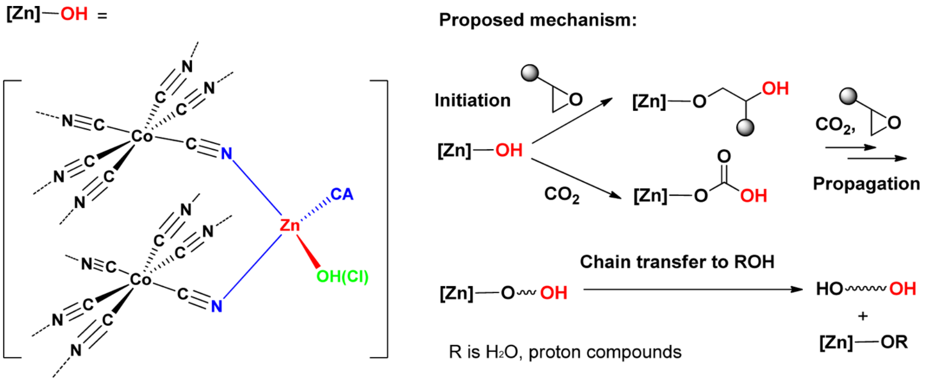


Figure 1. Possible ground-state structure of the active site of Zn−Co(III) DMCC catalyst (left) and mechanism for CO_2/epoxide copolymerization (right). Herein, two CN^- groups are shared by Zn^{2+} and Co^{3+} ions. They contain one negative charge in one tetrahedral Zn^{2+} structure. Thus, the structure meets the electroneutrality principle because of the existence of OH^- (and Cl^-) based on the elemental results, FT-IR spectrum and characterization of the polymer end groups.[28] CA is the complexing agent (generally H_2O and *t*-BuOH).

Nozaki et al. reported the copolymerization of 1,2-hexene oxide with CO_2 using a Co(III) complex with a piperidinium end-capping arm at 25 °C within 48 h. This afforded a copolymer with 98% polycarbonate selectivity.[11] Nevertheless, the copolymerization of CO_2 with epoxides with long linear alkyl chain is still a big challenge. Moreover, the copolymerization of CO_2 and epoxides with bulky branched alkyl groups such as isobutene oxide[12] and 2-*tert*-butyloxirane has not yet been reported. A recent attempt to copolymerize of isobutene oxide with CO_2 via a (Salen)Cr(III) complex with PPN azide as the catalyst promoter led to an exclusive cyclic carbonate.[12] The copolymers from CO_2 and the epoxides with branched alkyl groups produce copolymers with high T_gs, and thus this is also an attractive topic in the field.

On the other hand, the copolymerization of CO_2 with epoxides with anchoring aryl groups is equally rare,[13−17] although the resulting copolymers from CO_2 and these epoxides had a relatively high T_gs and strong intermolecular interactions that could improve the mechanical properties of the materials. Lu and Daresnbourget al.[13] reported a perfect alternating CO_2/styrene oxide (SO) copolymerization using a (Salen)Co(III) complex anchoring 1,5,7-triabiabicyclo[4,4,0]dec-5-ene and (Salen)Cr(III)/(PPN)Cl at 25 °C, which afforded a fully alternating poly(styrene carbonate) (PSC). Recently, our group reported an alternating and regioregular PSC with an alternating degree of 99.4% and 96% head-to-tail (HT) connectivity using nanosized zinc−cobalt(III) double metal cyanide complex [Zn−Co(III)DMCC] catalysts without introducing any cocatalysts or catalyst promoters.[14] Such PSC presented a T_g of 82 °C, which was higher than that of CO_2/PO copolymer (ca. 35−42 °C) and could be used as a plastic with good thermal properties.

Thus, far, a considerable number of catalyst systems[2,3,5,6,18] have been developed to synthesize CO_2/epoxide copolymers, but few of these can catalyze the copolymerization of CO_2 with many kinds of epoxides with different substituents. This is likely due to limitations in structural matching of the catalysts and epoxides with respect to their steric/electronic effects. To date, two kinds of catalyst systems could catalyze the copolymerization of CO_2 with many kinds of epoxides with good efficiency. One is the (Salen)M(III) (M = Co, Cr) complex/catalyst promoter systems[6] including both bifunctional[19−21] and two component[22−26] systems. These are highly active due to the perfectly alternating copolymerization of CO_2 with many epoxides. The CO_2/epoxide copolymerization could be precisely tuned by subtle design of the organic backbone of the catalyst. However, these syntheses are complex with multistep operations. In most cases, low temperature polymerizations are required to avoid cyclic carbonate generation.

The other catalyst is nanosized Zn−Co(III) DMCC,[27] which is a highly efficient catalyst for CO_2/epoxide copolymerization without any cocatalyst or catalyst promoters.[14,16,28,29] Recently, a nanolamellar Zn−Co(III) DMCC was observed to effectively catalyze the alternating copolymerization of CO_2 with epoxides with long side alkyl groups.[30] These results led us to systematically study the substituent effects of the epoxides on the alternating copolymerization of CO_2/epoxide using this catalyst. We obtained CO_2/epoxide copolymers with various T_gs across a wide range of temperatures. A regioselective CO_2/epoxide copolymerization style induced by bulky and electron-donating substituents via Zn−Co(III) DMCC catalysis was also proposed.

■ RESULTS AND DISCUSSION

Brief Introduction of Zn−Co(III) DMCC Catalyst. Zn−Co(III) DMCC was early discovered to be an efficient catalyst for ring-opening polymerization of epoxides, especially PO.[31,32] It is still industrially used to produce poly(propylene oxide) polyols with moderate and high molecular weights, which are widely used for making soft polyurethanes. In 1985, Kruper et al. applied Zn−Co(III) DMCC to CO_2/epoxide copolymerization for the first time.[33] Many research groups subsequently studied its preparation and application for synthesizing CO_2-based copolymers.[34−38] The traditional preparation of Zn−Co(III) DMCC involves room temperature schemes via a precipitation reaction with excess $ZnCl_2$ and $K_3Co(CN)_6$ in water/*tert*-butanol (*t*-BuOH) solution.[39] The resulting catalyst presents irregular lumps with several to dozens of micrometers and showed moderate productivity and low polycarbonate selectivity toward CO_2/epoxide copolymerization. The empirical formula of this catalyst is $Zn_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot yCA \cdot zH_2O$ (CA is the complexing agent). It is nonstoichiometric because *x, y*, and *z* varied with the methods and batches of the preparation. The basic bulk structure of this catalyst shows that the cyanide bridges link zinc and cobalt atoms, but the catalytic center has not yet been disclosed. Changes in either the cobalt ion or zinc ion, e.g., $Zn[Ni(CN)_4]$[40] and $Co[Ni(CN)_4]$,[41] and substitution of one of the cyanide ions results in a dramatic change in the catalytic activity and polycarbonate selectivity.[40] The Zn−Co(III)

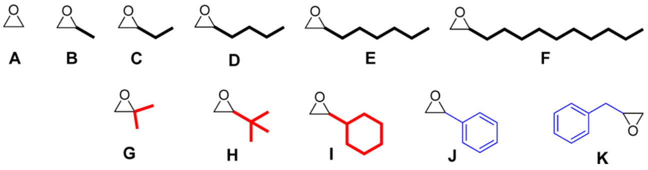
DMCC prepared using *t*-BuOH as a CA remains the best for epoxide-involved polymerizations.[42]

We proposed a hydrothermal method to synthesize Zn−Co(III) DMCC for highly active and selective CO_2/epoxide copolymerization.[27] The resulting catalyst was thermally stable, air and moisture insensitive and had unique nanolamellar and nanoporous structures with high a BET surface area of >500 m^2/g. Such nanosized structure could accommodate more catalytic sites on the surface of the catalyst and thus improved the catalytic activity toward CO_2/epoxide copolymerization.[27]

The Zn/Co molar ratio of the initial Zn−Co(III) DMCC varied depending on the preparation conditions, while the Zn/Co molar ratio of the nanosized Zn−Co(III) DMCC via hydrothermal process was ca. 2.0 and was constant across different conditions.[14,27,29] Therefore, the molar ratio of Zn^{2+}:Co^{3+}:CN^- was 2:1:6 based on the perfect coordination reaction of Zn^{2+} with $Co(CN)_6^{3-}$ via $K_3Co(CN)_6$. The $Zn_2[Co(CN)_6](OH)_aCl_b{\cdot}y\mathrm{CA}{\cdot}zH_2O$ ($a + b = 1$) structure of Zn−Co(III) DMCC meets the electroneutrality principle because Cl^- was observed by elemental analysis and OH^- was confirmed by FT-IR spectrum (samples with CA and water removed by heat).[28] The catalytic center of this species was a zinc−hydroxyl bond (Zn−OH) based on the fact that the resulting polymers had two terminal −OH groups. In structure, the Zn−OH bond could be regarded as a Lewis acid (Zn^{2+})-base (OH^-) center, which could activate the epoxide and CO_2 collaboratively.[28] The proposed mechanism for the chain initiation, propagation and transfer reaction for Zn−Co(III) DMCC-catalyzed CO_2/epoxide copolymerization is shown in Figure 1.[28] Note that the complexes, $Zn_2[Co(CN)_6]OH$[43] and $Zn_2[Co(CN)_6]Cl$ had no any catalytic activity toward CO_2/epoxide copolymerization. This demonstrates that the activity of this catalyst might be originated from $Zn_2[Co(CN)_6](OH)_aCl_b$, although its real structure still needs ongoing investigation. Herein, we present our continued investigation concerning the CO_2/epoxide copolymerization via nanosized Zn−Co(III) DMCC catalysts for improved understanding of the substituent effects of epoxides.

Copolymerization of CO_2 with Selected Epoxides. Eleven epoxides (Scheme 1) with various substituents were successfully copolymerized with CO_2 using nanosized Zn−Co(III) DMCC. Thereof, the copolymerization of CO_2 with epoxides **A**, **C**−**E** and **G**−**I** were reported for the first time with our Zn−Co(III) DMCC catalyst. Species **B**, **C**, **D**, **E** and **F** were the epoxides with pendant linear alkyl groups with carbon numbers of 1, 2, 4, 6 and 10, respectively. **J** and **K** were epoxides with the pendant electron-withdrawing aryl groups.[14] **G**, **H**, and **I** were the epoxides with branched alkyl groups with carbon numbers of 2, 4 and 6, respectively.

Scheme 1. Selected Epoxides with Alkyl and Aryl Groups for the Copolymerization with CO_2 with Nanosized Zn−Co(III) DMCC Catalysts[a]



[a]Key: **A**, ethylene oxide, **B**, propylene oxide, **C**, 2-ethyloxirane (1,2-butene oxide), **D**, 2-butyloxirane (1,2-hexene oxide), **E**, 2-hexyloxirane (1,2-octene oxide), **F**, 2-decyloxirane (1,2-epoxydodecane), **G**, isobutene oxide, **H**, 2-(*tert*-butyl)oxirane, **I**, 2-cyclohexyloxirane, **J**, styrene oxide; **K**, 2-benzyloxirane. The syntheses of **I** and **K** are given in the Supporting Information part (see Figures S1 and S2).

The copolymerization data for the above-mentioned epoxides and CO_2 catalyzed by Zn−Co(III) DMCC are summarized in Table 1. The minimum reaction temperature was 50 °C for activating the copolymerization of CO_2 with most of the selected epoxides. However, the minimum temperature for activating the copolymerization of the epoxides **H**, **I**, and **K** with CO_2 within 15 h was 60 °C (Table 1, entries 8−9 and 11). Moreover, relatively more amounts of the catalyst (10.0 mg for 3.0 mL epoxide) was loaded for each polymerization to ensure activation of all the epoxides.

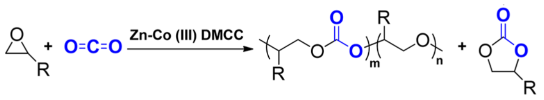
In a typical polymerization process, 3.0 mL epoxide was nearly completely converted to products (including the cyclic carbonate) with 10.0 mg Zn−Co(III) DMCC at 50 °C and 4.0 MPa CO_2 pressure within 15 h as indicated by the ^{1}H NMR spectra of the crude products (Figures S3−S5). This indicated the highly effective catalytic activity of Zn−Co(III) DMCC for these CO_2/epoxide copolymerizations. The productivities for CO_2 with epoxides **C**, **D**, **E**, and **F** were 1328, 1070, 1120, and 1184 g polymer/g Zn, respectively—values closer to that of CO_2/**B** (i.e., PO) copolymerization. A previously reported Zn−Co(III) DMCC catalyst prepared with poly(tetramethylene ether glycol) as a complexing agent presented no activity to CO_2/**D** copolymerization at 50 °C within 24 h.[44] Clearly, nanosized Zn−Co(III) DMCC presented higher catalytic ability toward the copolymerization of CO_2 with epoxides containing long linear alkyl groups than those with reported analogues.

The productivities of CO_2/**G** and CO_2/**H** copolymers were lower than that of CO_2/**B** copolymer because of the production of relatively more amounts of cyclic carbonate (entries 7 and 8 in Table 1). Moreover, the productivity of CO_2/**J** copolymer was 752 g of polymer/g of Zn—much less than that of CO_2/**B** copolymer because of the low reactivity of **J** under Zn−Co(III) DMCC catalysis.[14] Long linear alkyl groups could lead to a CO_2/epoxide copolymer with high number-average molecular weight (M_n) because the long linear alkyl group could suppress the chain transfer reaction to trace water in the system along as well as backbiting reactions that decrease M_n. We found that the branched alkyl groups and aryl groups of the epoxides also resulted in CO_2/epoxide copolymers with relatively low M_ns (Table 1) and relatively more amounts of cyclic carbonates.

The alternating degree (F_{CO_2}) of the resulting CO_2/epoxide copolymers and the weight percentage of the cyclic carbonate in the total products (W_{CC}) were then used to evaluate the polycarbonate selectivity of the catalyst. Moreover, the selective ring-opening reaction of the epoxide produced a regioregular copolymer. Such regioselectivity could be evaluated by the content of the head-to-tail (HT) connectivity of the resulting copolymer based on the ^{13}C NMR spectrum.[45] Herein, the substituent effects of the epoxides on CO_2/epoxide copolymerization were illustrated with the above parameters.

Alternating Degree (F_{CO_2}). The increase in the length of the pendant linear alkyl group of the epoxide led to a high F_{CO_2} of the resulting copolymers. As shown in Figure 2, the longer the pendent alkyl groups, the higher F_{CO_2} was achieved. Ethylene oxide (**A**)/CO_2 copolymer showed an F_{CO_2} of 55.3% (entry 1 in Table 1, spectrum 1 in Figure 2). For the copolymer of CO_2/**B** with a side methyl group, the F_{CO_2} increased to 73.2% under the same experimental conditions (entry 2 in Table 1). The F_{CO_2}

Table 1. Copolymerization of CO_2 with Various Mono-Substituted Epoxides Using Zn−Co(III) DMCC Catalyst (R Represents the Substituent of the Epoxide)[a]



entry	epoxides	temp (°C)	F_{CO_2} (%)[b]	W_{CC} (wt %)[b]	M_n (kg/mol)[c]	PDI[c]	productivity[d] (g polymer/g Zn)	convn (%)[e]	T_g (°C)
1	**A**	50	55.3	14.2	0.9	2.3	925	98	−1
2	**B**	50	73.2	5.7	21.2	2.4	1215	88	14
3	**C**	50	91.5	4.8	24.6	4.6	1328	100	6
4	**D**	50	95.6	2.7	19.2	5.0	1070	100	−18
5	**E**	50	98.6	2.0	48.7	4.0	1120	100	−27
6	**F**	50	>99.0	1.1	93.2	4.5	1184	100	−38
7	**G**	50	>99.0	20.0	6.6	2.0	993	100	35
8	**H**	60	>99.0	13.0	44.6	2.5	750	86.5	53
9	**I**	60	>99.0	1.5	20.0	2.9	1210	100	84
10	**J**	50	94.2	3.0	12.7	3.0	752	80.6	76
11	**K**	60	99.0	1.8	16.1	3.9	1094	100	78

[a] Reaction conditions: Zn−Co(III) DMCC, 10.0 mg; epoxide, 3.0 mL; CO_2, 4.0 MPa; 50 °C; 15 h. [b] Calculated from ^{1}H NMR spectroscopy, $F_{CO_2} = (A_{\text{carbonate linkage}})/[(A_{\text{carbonate linkage}} + A_{\text{ether linkage}}), W_{cc} = A_{\text{cyclic carbonate}}M_{\text{cyclic carbonate}}/[M_{\text{cyclic carbonate}}(A_{\text{cyclic carbonate}} + A_{\text{carbonate linkage}}) + M_{\text{ether unit}}A_{\text{ether linakes}}]$. Term A represents the integral area, and M represents the molecular weight. [c] Determined by gel permeation chromatography (GPC) calibrated with monodisperse polystyrene standards in THF at 40 °C. [d] The productivity was defined as g polymer/g Zn. [e] Including the copolymer and cyclic carbonates, EO conversion from ^{1}H NMR determination might be on the high side due to its low boiling point of 10.4 °C.

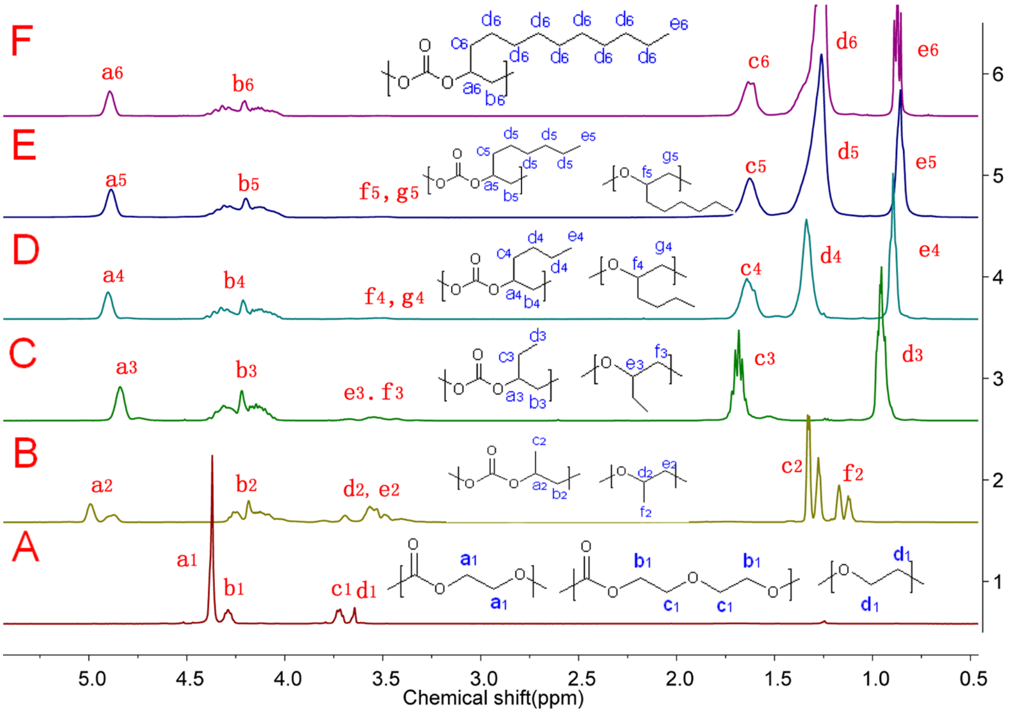


Figure 2. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of the purified CO_2/epoxide copolymers from **A-E** via Zn−Co(III) DMCC catalysis at 50 °C, 4.0 MPa CO_2 pressure and 15 h.

values of CO_2/**C**, CO_2/**D**, CO_2/**E** and CO_2/**F** copolymers were 91.5%, 95.6%, 98.6%, and >99%, respectively (entries 3−6 in Table 1). They increased with increasing number of carbons on the pendant alkyl group. This result could be explained by intramolecular steric repulsion effects through the formation of two neighboring CO_2/epoxide carbonate units. When the CO_2 copolymerized with epoxides containing long alkyl groups, the resulting polymer chain had a "crowded" side alkyl group,[30,46] and thus it increased the steric hindrance, which hampered the continuous epoxide insertion.[46]

When the number of carbons on the epoxide pendant groups was the same, the branched pendant groups led to a clear improvement in F_{CO_2}. The CO_2/**H** copolymer has a F_{CO_2} of >99% (**H** in Figure 3), which was higher than that of CO_2/**D** copolymer, i.e. 95.6% (**D** in Figure 2). Similar data was observed when comparing F_{CO_2} of CO_2/**E** copolymer (98.6%) with that of CO_2/**I** copolymer (>99%). Clearly, both **H** and **I** with branched alkyl groups presented more significant steric repulsion effects than **D** and **E** with linear alkyl groups. Species **G** with two substituted methyls provided strong steric hindrance on the

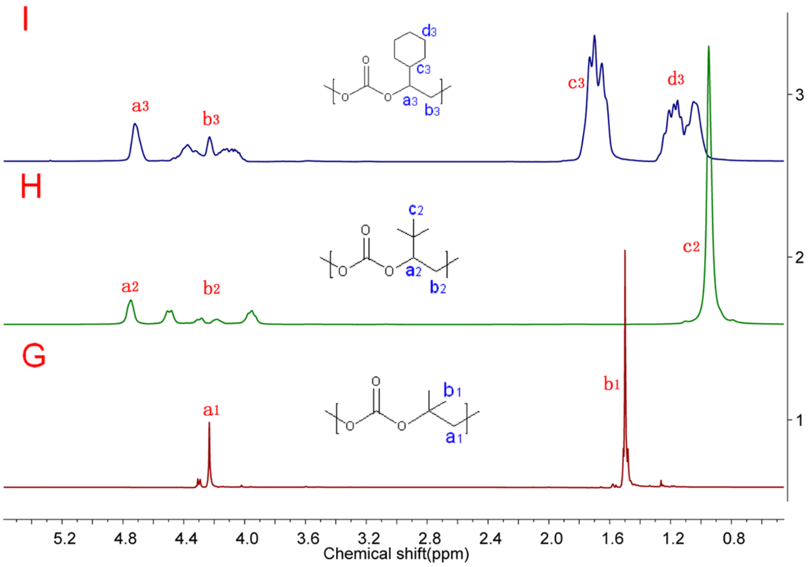


Figure 3. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of the purified copolymers from **G**, **H** and **I** via Zn−Co(III) DMCC catalysis at 60 °C (for **G**, 50 °C), 4.0 MPa CO_2 pressure and 15 h.

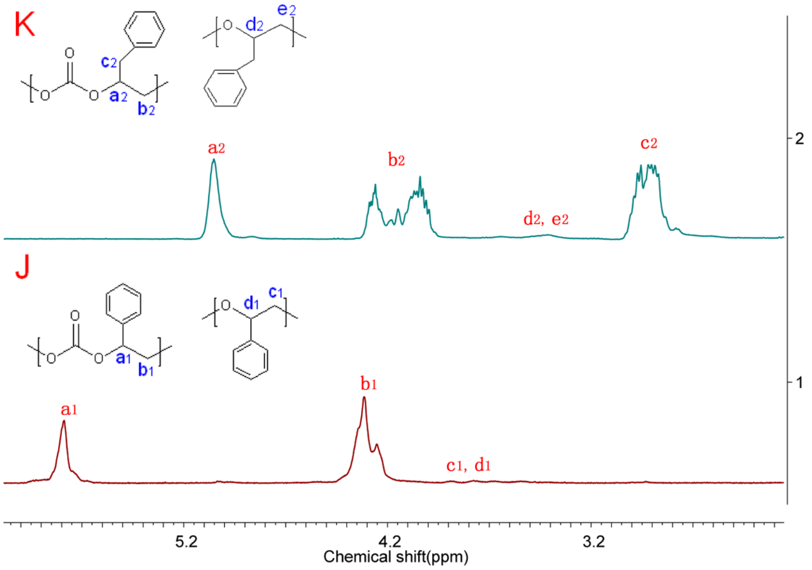


Figure 4. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of the purified copolymers from CO_2 with epoxides **J** and **K** with side electron-withdrawing groups.

copolymerization and led to the production of a CO_2/**G** copolymer with an F_{CO_2} of >99% (**G** in Figure 3). This was higher than that of the CO_2/**C** copolymer with a side ethyl group (91.5%).

The steric hindrance of the electron-withdrawing substituents of the epoxides also favored to improve of the alternating degrees of the resulting copolymers. As shown in Figure 4, the F_{CO_2} of the resulting copolymers from the copolymerization of CO_2 with epoxides **J** and **K** followed the sequence order of the steric hindrance of **J** (94.2%, 50 °C) < **K** (99.0%, 60 °C), which was consistent with our previous report at different reaction temperatures.[14]

The above results indicated that Zn−Co(III) DMCC was an effective catalyst for the copolymerization of CO_2 with various epoxides containing long pendent linear and branched alkyl groups. It afforded alternating CO_2/epoxide copolymers. The alternating degree of the CO_2/epoxide copolymer via Zn−Co(III) DMCC catalysis was determined by the steric hindrance of the pendant groups of the monosubstituted epoxides regardless of whether such pendant groups had electron-donating or withdrawing properties.

Production of Cyclic Carbonate (W_{CC}). The formation of the cyclic carbonate during CO_2/epoxide copolymerization mainly resulted from the backbiting reaction of the end carbonate anions.[47] Therefore, the production of cyclic carbonate was closely correlated to the properties of the pendent group of the epoxides under Zn−Co(III) DMCC catalysis.

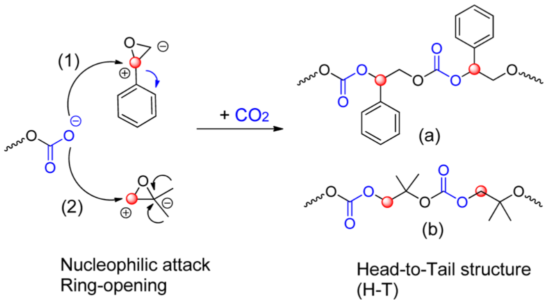
For the epoxides with linear alkyl groups shown in Table 1 (Figure S3, ^{1}H NMR spectra of the crude products), the content of the cyclic carbonate W_{CC} decreased from 14.2 to 1.1 wt % with increasing carbon numbers from 0 to 10 for epoxides **A**, **B**, **C**, **D**, **E**, and **F** (entries 1−6, Table 1). That is, increasing the length of the pendant alkyl group inhibited the production of cyclic carbonates. This result could be attributed to the intramolecular steric repulsion effects of the long side alkyl group of the copolymer,[30,46] which hampered the backbiting reaction.

Surprisingly, the copolymerization of epoxides **G** and **H** with CO_2 resulted in the production of considerable amounts of cyclic carbonates of 20 and 13 wt % (Figure S4, ^1H NMR spectra of the crude products), respectively. These values were clearly higher than those achieved with epoxides **C** and **D** that contain side groups with the same number of carbons. This result indicated that the stronger steric hindrance and electron-donating ability of the dimethyl and tertiary butyl groups favored the backbiting reaction and formed cyclic carbonate.

Interestingly, for epoxides **I** and **J** in which cyclohexyl and phenyl had the same carbon numbers, the CO_2/**J** copolymerization gave relatively higher amounts of the cyclic carbonate in the product (4.9 wt %), which indicates that the substituents with more electron-withdrawing groups favored the production of the cyclic carbonate. The copolymerization of CO_2 with **K**, which has a less electron-withdrawing benzyl group, also gave a lower W_{CC} (1.8 wt %, 60 °C) than that of CO_2/**J** copolymer (4.9 wt %, 60 °C, Figure S5) containing a phenyl group. These results indicated that Zn−Co(III) DMCC was excellent for the CO_2/epoxide copolymerization because relatively small amounts of cyclic carbonates were produced at 50−60 °C for the most of epoxides in Table 1. In contrast, most of the reported catalysts required low reaction temperatures to avoid production of cyclic carbonates.

Regioselectivity. It is of great interest to investigate the regiochemistry of the CO_2/epoxide copolymerization because regioregular CO_2/epoxide copolymers should expand the range of the thermal and mechanical properties of the resulting copolymers versus their regioirregular counterparts.[10,13,15,45,48] Here, CO_2/epoxide copolymers with highly alternating degrees (94.2% - >99%, entries 4−11 in Table 1) were selected for further analysis of regiochemistry because the carbonate anion ($-OOCO^-$) was the main nucleophilic species attacking the methylene (CH_2) or methine (CH) sites to open the epoxide ring (Scheme 2).

Scheme 2. Proposed Mechanism for Regioselective CO_2/J and CO_2/G Copolymerization via Zn−Co (III) DMCC Catalysis[a]



[a] The red dot in the backbone represents the site proposed for attack by the carbonate anion.

CO_2/**J** copolymerization was highly regioselective under Zn−Co(III) DMCC catalysis[14] and afforded a CO_2/**J** copolymer with 90% HT connectivity (50 °C). In this instance, the electron-withdrawing phenyl group made the CH site more positive than the CH_2 site, and thus the carbonate anion predominantly attacked the CH site of **J** (route 1 in Scheme 2) although the CH site had significant steric hindrance due to the phenyl group. This result highlights that the counteracting effect of steric hindrance on regioselectivity could be minimized. When the phenyl group was substituted by a benzyl group (**K**) with less electron-withdrawing ability, the resulting CO_2/**K** copolymer only had a 77% HT connectivity (60 °C).

Because the electron-withdrawing phenyl group of **J** predominantly induced nucleophilic attack on the carbonate anion to CH site, we wondered whether the strong electron-donating ability and steric hindrance of the branched alkyl group linked to the epoxide (**G**, **H** and **I**) would lead a ring-opening event at the less substituted CH_2 site (e.g., route 2 in Scheme 2). Indeed, the CH_2 sites of **G**, **H** and **I** had more positive charges than the substituted carbon, and thus favored nucleophilic attack of the carbonate anion.

The epoxide **G** is special in structure because it has two substituted methyls at the quaternary carbon making it achiral. Therefore, the microstructure of the resulting poly(isobutene carbonate) would be simpler than those with chiral carbons. The ^{13}C NMR spectrum of poly(isobutene carbonate) in the carbonyl region exhibits one sharp peak at δ_C 153.0 ppm and two small peaks at δ_C 154.9 and 151.3 ppm (Figure 5). The three peaks at δ_C 154.9, 153.0, and 151.3 ppm could be ascribed to HH, HT and TT connectivity of the poly(isobutene carbonate), respectively. The proposed HH, HT and TT connectivity of poly(isobutene carbonate) could also be qualified by a random copolymer model using ethylene oxide (EO), cyclohexene oxide (CHO) and CO_2. In this model, the three carbonyl regions of EO−CO_2-EO (154.9 ppm), EO-$\underline{C}O_2$−CHO (154.2 ppm) and CHO−CO_2−CHO (153.2−153.7 ppm) caused by random terpolyemrization were similar to the chemical environments with TT, HT and HH connectivity of the poly(isobutene carbonate), respectively.[49,50]

Moreover, the ^{13}C NMR spectrum for the other quaternary carbons of poly(isobutene carbonate) only showed a single sharp peak at δ_C 81.5 ppm (Figure 5), which is also indicative of the oversimplified chemical environment around this quaternary carbon. Therefore, poly(isobutene oxide) is proposed to be a regioregular copolymer with high HT connectivity, which was calculated to be 83% based on the integral area ratio of these peaks. The strong and direct electron-donating ability of the two methyls toward the quaternary carbon of **G** induced the carbonate anion to attack the CH_2 site with a more positive charge (Scheme 2). Moreover, the steric hindrance of the two methyls could hinder and repel attack of the carbonate anion to the quaternary carbon of **G**.

The CO_2/**H** copolymer with a side tertiary butyl group was also expected to have a regioregular structure to some extent because the tertiary butyl group has strong electron-donating ability and steric hindrance. However, it was difficult to determine the regioregular structure of CO_2/**H** copolymer based only on the peak splitting data for the carbonyl region in the ^{13}C NMR spectrum (Figure S7). We did observe two asymmetric neighboring peaks at δ_C 155.0 ppm. Because **H** has a chiral CH site, we attempted to probe the regioregular structure of the CO_2/**H** copolymer by determining the optical properties of the hydrolyzed CO_2/(*S*)-**H** copolymer via Zn−Co(III) DMCC from an optically active epoxide (*S*)-**H**. This was because the (*S*)-configuration of the carbonate unit of the CO_2/(*S*)-**H** copolymer would be retained after hydrolysis if the (*S*)-**H** copolymerized with CO_2 through a regioselective attack on the CH_2 site of (*S*)-**H**. However, we failed to resolve the racemic mixture of **H** needed to obtain pure (*S*)-**H** via an (*R*)-(Salen)Co complex (see Supporting Information part). Indeed, the bulky tertiary butyl group of **H** hampered the resolution.[51] Similarly, the microstructure of the CO_2/**I** copolymer (Figure S8) was also difficult to determine.

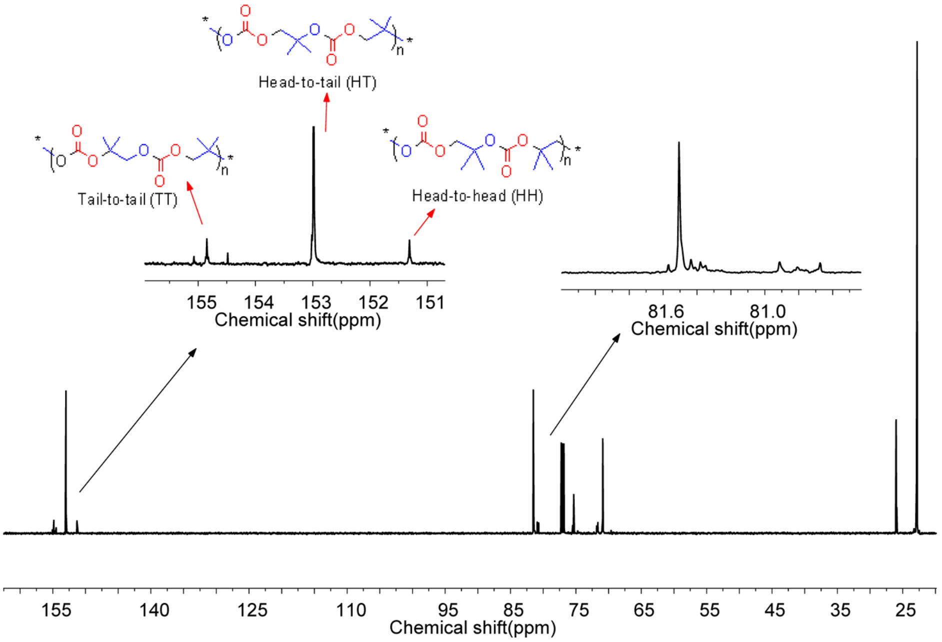


Figure 5. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of poly(isobutene oxide) from CO_2/**G** copolymerization with Zn−Co(III) DMCC. Key: TT = tail-to-tail; HT = head-to-head; HH = head-to-head.

In contrast to the regioregular CO_2/**J** copolymer, the CO_2/**G** copolymer presented a relatively low content for the HT connectivity (90% vs 83%) suggesting that the ability of the bulky electron-donating alkyl groups to induce a regioselective ring-opening reaction at the CH (or C) site of the epoxide was weaker than that of the aryl group for a regioselective ring-opening reaction at the CH_2 site. This was further proved by the fact that the copolymerization of CO_2 and **B**—with one methyl group and thus less electron-donating behavior—leads to a complete regioirregular copolymer. Even increasing the length of the pendant linear alkyl groups (i.e., keeping the electron-donating ability but enhancing the steric hindrance) gave no regioselective copolymerization. The ^{13}C NMR spectra of the CO_2/**D**, CO_2/**E**, and CO_2/**F** copolymers in the carbonate region show several overlapping peaks, which were similar to that of the CO_2/**B** copolymers (Figure S6). The contents of HT connectivity of these copolymers were roughly estimated to be 52%. This implied no stereoselectivity in the epoxide ring-opening step.

As discussed above, the regioselective CO_2/epoxide copolymerization via Zn−Co(III) DMCC catalysis was mainly determined by the electron induction effect of the epoxide rather than the steric hindrance of the substituents. Indeed, it is a meaningful topic in the field of CO_2 copolymerization that the regioselective ring-opening reaction happens at CH_2 site of the epoxides with alkyl group (e.g., **B**) during copolymerization with CO_2. The Lu group has reported an elegant work on regioselective CO_2/**B** copolymerization through subtle design of bifunctional (Salen)Co(III) complexes.[10] In the present work, Zn−Co(III) DMCC is active for many epoxides to copolymerize with CO_2, which provides a chance to look into the substituent effects of the epoxide on the regioselectivity of the CO_2/epoxide copolymerization.

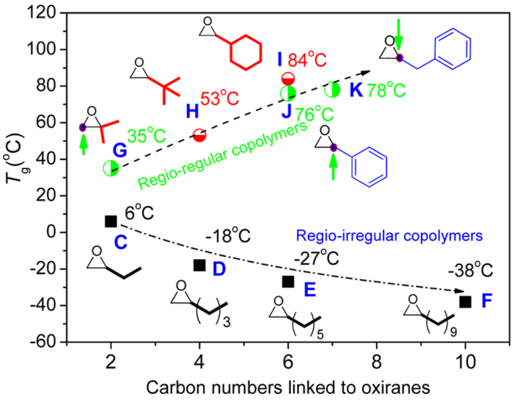


Figure 6. Substituent effect of the epoxides on the glass transition temperatures (T_gs) of the resulting CO_2/epoxide copolymers (F_{CO_2} = 91.5−99%; M_n = 6.6−93.2 kg/mol).

Glass Transition Temperatures (T_gs). The epoxide substituents had a strong impact on the T_gs of the CO_2/epoxide copolymers (Figure 6). The T_gs of the copolymers ranged from −38 to +84 °C, depending on the substituent groups of the epoxide. The T_gs of the copolymers with side linear groups decreased from +6 to −38 °C with increasing lengths of the side chain from C2 to C10 because the longer side linear alkyl group caused stronger plasticizing effects and regioirregular microstructures. Herein, the T_g of the CO_2/**C** copolymer was 6 °C, which was lower than that of fully alternating CO_2/**C** copolymer (i.e., 9 °C).[12] Importantly, it is also possible to regulate T_g of the CO_2/epoxide copolymer via Zn−Co(III) DMCC catalysis by tuning the reaction temperature and CO_2 pressure.[29,52]

For copolymers with side branched alkyl and aryl groups, the T_gs increased from 35 to 84 °C with increasing steric hindrance (i.e., carbon numbers C2, C4, and C6 to C7) of the substituent groups. This could effectively inhibit the free rotation of the backbone. Moreover, the CO_2/**K** and CO_2/**J** copolymers with regioregular microstructures improved the T_gs.[14] The copolymers with branched side groups had higher T_gs than their linear counterparts. This is seen when comparing the CO_2/**C** copolymer (6 °C) with CO_2/**G** copolymer (35 °C), CO_2/**D** copolymer (−18 °C) with CO_2/**H** copolymer (53 °C) and CO_2/**E** copolymer (−27 °C) with CO_2/**I** (84 °C) copolymer.

Therefore, various CO_2/epoxide copolymers with wide T_g ranges from −38 to 84 °C could be obtained with the Zn−Co(III) DMCC catalyst. These could potentially be used as elastomers or plastics.[29,52,53]

CONCLUSIONS

The substituent effect of the epoxides on CO_2/epoxide copolymerization with nanosized Zn−Co(III) DMCC was systematically investigated. The F_{CO_2} of the resulting CO_2/epoxide copolymers was determined by the steric effect of the substituents of the epoxides, while the regioselective CO_2/epoxide copolymerization was dominated by the electron induction effect of the substituents. The electron-withdrawing group could effectively induce the regioselective copolymerization. A new regioselective reaction at the CH_2 site of CO_2/isobutene oxide copolymerization was observed and attributed to the strong electron-donating ability of the two methyls of isobutene oxide. The correlation of T_g with the substituents of the CO_2/epoxide copolymers was discussed. Various CO_2/epoxide copolymers with a wide range of the T_g values (−38 to +84 °C) were obtained.

ASSOCIATED CONTENT

Supporting Information

Text and figures giving general experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*(X.-H.Z.) Telephone and Fax: +86-571 87953732. E-mail: xhzhang@zju.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for financial support by the National Science Foundation of the People's Republic of China (No. 21474083 and 21274123).

REFERENCES

(1) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci, Part C: Polym. Lett.* **1969**, *7*, 287−292.

(2) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174.

(3) Coates, G. W.; Moore, D. R. *Angew. Chem. Int. Ed* **2004**, *43*, 6618−6639.

(4) Sugimoto, H.; Inoue, S. *J. Polym. Sci, Part A: Polym. Chem.* **2004**, *42*, 5561−5573.

(5) Kember, M. R.; Buchard, A.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 141−163.

(6) (a) Lu, X. B.; Ren, W. M.; Wu, G. P. *Acc. Chem. Res.* **2012**, *45*, 1721−1735. (b) Lu, X. B.; Darensbourg, D. J. *Chem. Soc. Rev.* **2012**, *41*, 1462−1484.

(7) Lee, B. Y.; Cyriac, A. *Nat. Chem.* **2011**, *3*, 505−507.

(8) For production and application of CO_2-based copolymer, see Web sites: (a) . Novomer: Carbon Dioxide, http://www.novomer.com/?action=CO2;. (b) . Bangfeng Technology: http://www.cn-bf.net/en/;. (c) . ZhongkeJinLong: http://www.zhongkejinlong.com.cn/en/index.asp;. (d) . Nanyang Zhongju Tianguan Low Carbon Technology: http://www.tgnbm.com/cpzx/111.htm;. (e) . Empower Materials: www.empowermaterials.com. (f) . Aschenbrenner, N.; Kunze, K. *Green Polymer Made of CO_2 from Exhaust Gases*, http://www.siemens.com/innovation/en/news/2012/e_inno_1213_2.htm;. (h) . Econic Technologies: Polymers from CO_2, http://www.econic-technologies.com/.

(9) Allen, S. D.; Byrne, C. M.; Coates, G. W. Feedstocks for the Future: Renewables for the Production of Chemicals and Materials. *ACS Symp. Ser.* **2006**, *921*, 116−128.

(10) Lu, X. B.; Shi, L.; Wang, Y. M.; Zhang, R.; Zhang, Y. J.; Peng, X. J.; Zhang, Z. C.; Li, B. *J. Am. Chem. Soc.* **2006**, *128*, 1664−1674.

(11) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem. Int. Ed* **2006**, *118*, 7432−7435.

(12) Darensbourg, D. J.; Chung, W.-C. *Macromolecules* **2014**, *47*, 4943−4948.

(13) Wu, G. P.; Wei, S. H.; Lu, X. B.; Ren, W. M.; Darensbourg, D. J. *Macromolecules* **2010**, *43*, 9202−9204.

(14) Wei, R. J.; Zhang, X. H.; Du, B. Y.; Sun, X. K.; Fan, Z. Q.; Qi, G. R. *Macromolecules* **2013**, *46*, 3693−3697.

(15) Wu, G. P.; Wei, S. H.; Ren, W. M.; Lu, X. B.; Xu, T. Q.; Darensbourg, D. J. *J. Am. Chem. Soc.* **2011**, *133*, 15191−15199.

(16) Wei, R. J.; Zhang, X. H.; Du, B. Y.; Fan, Z. Q.; Qi, G. R. *Polymer* **2013**, *54*, 6357−6362.

(17) Hu, Y.; Qiao, L.; Qin, Y.; Zhao, X.; Chen, X.; Wang, X.; Wang, F. *Macromolecules* **2009**, *42*, 9251−9254.

(18) Luinstra, G. A.; Haas, G. R.; Molnar, F.; Bernhart, V.; Eberhardt, R.; Rieger, B. *Chem.—Eur. J.* **2005**, *11*, 6298−6314.

(19) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem. Int. Ed* **2006**, *45*, 7274−7277.

(20) Noh, E. K.; Na, S. J.; S, S.; Kim, S. W.; Lee, B. Y. *J. Am. Chem. Soc.* **2007**, *129*, 8082−8083.

(21) Ren, W. M.; Liu, Z. W.; Wen, Y. Q.; Zhang, R.; Lu, X.-B. *J. Am. Chem. Soc.* **2009**, *131*, 11509−11518.

(22) (a) Lu, X.-B.; Wang, Y. *Angew. Chem. Int. Ed* **2004**, *43*, 3574−3577. (b) Zhang, J. F.; Ren, W. M.; Sun, X. K.; Meng, Y.; Du, B. Y.; Zhang, X. H. *Macromolecules* **2011**, *44*, 9882−9886.

(23) Darensbourg, D. J.; Moncada, A. I. *Macromolecules* **2009**, *42*, 4063−4070.

(24) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869−10878.

(25) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans* **2006**, 237−249.

(26) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251−6253.

(27) Sun, X. K.; Zhang, X. H.; Liu, F.; Chen, S.; Du, B. Y.; Wang, Q.; Fan, Z. Q.; Qi, G. R. *J. Polym. Sci, Part A: Polym. Chem.* **2008**, *46*, 3128−3139.

(28) Sun, X. K.; Zhang, X. H.; Wei, R. J.; Du, B. Y.; Wang, Q.; Fan, Z. Q.; Qi, G. R. *J. Polym. Sci, Part A: Polym. Chem.* **2012**, *50*, 2924−2934.

(29) Zhang, X. H.; Wei, R. J.; Sun, X. K.; Zhang, J. F.; Du, B. Y.; Fan, Z. Q.; Qi, G. R. *Polymer* **2011**, *52*, 5494−5502.

(30) (a) Zhang, Y. Y.; Zhang, X. H.; Wei, R. J.; Du, B. Y.; Fan, Z. Q.; Qi, G. R. *RSC Adv.* **2014**, *4*, 36183−36188. (b) Zhang, Y. Y.; Wei, R. J.; Zhang, X. H.; Du, B. Y.; Fan, Z. Q. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, DOI: 10.1002/pola.27497.

(31) Huang, Y. Jun.; Zhang, X. H.; Hua, Z. J. *Macromol. Chem. Phys.* **2010**, *211* (11), 1229−1237.

(32) Kim, I.; Ahn, J.-T.; Ha, C. S.; Yang, C. S.; Park, I. *Polymer* **2003**, *44*, 3417−3428.

(33) Kruper Jr, W. J.; Swart, D. J. Carbon dioxide oxirane copolymers prepared using double metal cyanide complexes. US Patent 4,500,704, 1985.

(34) Chen, S.; Hua, Z.; Fang, Z.; Qi, G. *Polymer* **2004**, *45*, 6519−6524.

(35) Darensbourg, D. J.; Adams, M. J.; Yarbrough, J. C.; Phelps, A. L. *Inorg. Chem.* **2003**, *42*, 7809−7818.

(36) Yi, M. J.; Byun, S. H.; Ha, C. S.; Park, D. W.; Kim, I. *Solid State Ionics* **2004**, *172*, 139−144.

(37) Wu, L. C.; Yu, A. F.; Zhang, M.; Liu, B. H.; Chen, L. B. *J. Appl. Polym. Sci.* **2004**, *92*, 1302−1309.

(38) Gao, Y. G.; Qin, Y. S.; Zhao, X. J.; Wang, F. S.; Wang, X. H. *J. Polym. Res.* **2012**, *19*, 1−9.

(39) Zhang, X. H.; Hua, Z. J.; Chen, S.; Liu, F.; Sun, X. K.; Qi, G. R. *Appl. Catal., A* **2007**, *325*, 91−98.

(40) Zhang, X. H.; Chen, S.; Wu, X. M.; Sun, X. K.; Liu, F.; Qi, G. R. *Chin. Chem. Lett.* **2007**, *18*, 887−890.

(41) Robertson, N. J.; Qin, Z. Q.; Dallinger, G. C.; Lobkovsky, E. B.; Lee, S.; Coates, G. W. *Dalton Trans* **2006**, 5390−5395.

(42) Sun, X. K.; Chen, S.; Zhang, X. H.; Qi, G. R. *Prog. Chem.* **2012**, *24*, 1776−1784.

(43) Kyper, J.; Boxhoorn, G. *J. Catal.* **1987**, *105*, 163−174.

(44) Kim, I.; Yi, M. J.; Byun, S. H.; Park, D. W.; Kim, B. U.; Ha, C. S. *Macromol. Symp.* **2005**, *224*, 181−192.

(45) Li, B.; Zhang, R.; Lu, X. B. *Macromolecules* **2007**, *40*, 2303−2307.

(46) Okada, A.; Kikuchi, S.; Yamada, T. *Chem. Lett.* **2011**, *40*, 209−211.

(47) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388−2410.

(48) Lu, X. B.; Ren, W. M.; Wu, G. P. *Acc. Chem. Res.* **2012**, *45*, 1721−1735.

(49) Min, J. D.; Zhang, Y. M.; Chen, Y. Y.; Wang, X. H.; Zhao, X. J.; Wang, F. S. *Acta Polym. Sin.* **2008**, *1*, 1076−1081.

(50) Zou, Y. N.; Xiao, M.; Li, X. H.; Wang, S. J.; Meng, Y. Z. *Polym. Compos.* **2007**, *15*, 53−58.

(51) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936−938.

(52) Liu, S.; Qin, Y.; Chen, X.; Wang, X.; Wang, F. *Polym. Chem.* **2014**, *5*, 6171−6179.

(53) Lim, J. W.; Oh, H. J.; Kim, Y.; Jeong, K. E.; Yim, J. H.; Ko, Y. S. *Polymer (Korea)* **2010**, *34*, 507−510.

DOI: 10.1021/ma5023742