Coordination Copolymerization

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A One-Pot Synthesis of a Triblock Copolymer from Propylene Oxide/Carbon Dioxide and Lactide: Intermediacy of Polyol Initiators**

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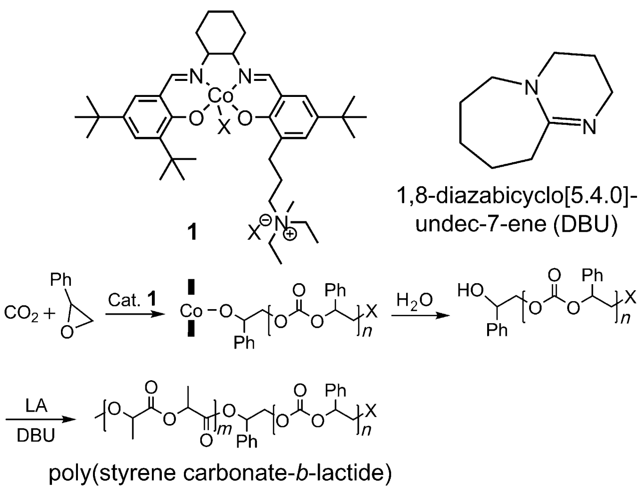
The energy and environmental concerns of petroleum-based plastics have stimulated the development of new polymeric materials that incorporate renewable resources.[1] Synthesis of polymers by copolymerization of CO_2 and epoxides offers the possibility of providing a wide variety of degradable polycarbonates. In contrast to the alternative route of condensation polymerization, which involves the use of toxic phosgene or its derivatives, this process represents an environmentally benign approach.[2] Since the seminal discovery by Inoue et al. in 1969,[3] numerous well-defined catalyst systems developed for the CO_2/epoxide copolymerization have resulted in greatly suppressing ether linkages, increasing polymer selectivity, and controlling molecular-weight distributions.[4] Although these reported studies are very significant and impressive, current attempts at the industrialization of this green technology are limited to ethylene oxide and propylene oxide to produce poly(ethylene carbonate) and poly(propylene carbonate).[5] Moreover, the relatively low T_g value ($< 35\,°C$) of these kind of polymers further thwart their use as commercial thermoplastics. Therefore, the synthesis of more diverse CO_2-based copolymers to improve material performances as well as categories of this greener polymer is an important and challenging topic for research and development.

Modifications of the thermal and mechanical properties of manufactured plastics can be achieved by incorporating two or more distinct homopolymers through covalent bonds, thereby providing di- and multiblock polymers.[6] Based on this methodology, two main strategies have been explored for the synthesis of block copolymers incorporating CO_2/epoxides and other monomers.[7] One synthetic method involves a polymer with a terminal initiating site that can be used as a chain-transfer agent during the copolymerization of CO_2/epoxides to prepare block copolymers. Based on this methodology, Lee and co-workers reported the preparation of di- and triblock copolymers by introducing polymers during the copolymerization of CO_2/epoxides.[8] Similarly, Williams and co-workers reported the preparation of poly(cyclohexene carbonate)-*b*-polylactide copolymers in a two-step process. The first step involves synthesis of a poly(cyclohexene carbonate) macroinitiator, which can be used subsequently to initiate the third monomer polymerization.[9] Alternatively, the synthesis of polyester-*b*-polycarbonate polymers have been carried out in a one-pot terpolymerization reaction of cyclohexene oxide, cyclic acid anhydrides, and carbon dioxide using various metal catalysts.[10–12] This process is based on the fact that the cyclic anhydride monomer copolymerizes with epoxides at a much faster rate than the copolymerization of epoxides with CO_2. Unfortunately, this strategy is not applicable in general, that is, when lactone,[13] lactide (LA),[14] or maleic anhydride[15] are introduced as the third monomer with epoxides and CO_2, polymers with random structures are produced.

Recently, we have demonstrated a tandem catalytic approach for the synthesis of model AB CO_2 diblock copolymers containing poly(styrene carbonate) and polylactide (PLA; Scheme 1).[16] The key to this strategy is the choice of water as a chain-terminating reagent, which was added at the end of [(salen)CoX] (**1**; X = 2,4-dinitrophenoxide; salen = *N*′-ethylenebis(salicylimine)) catalyzed styrene oxide/CO_2 copolymerization to generate an hydroxy end group in situ. These monohydroxy end-capped polymers serve as macroinitiators that allow direct chain extension by organocatalytic lactide ring-opening polymerization to obtain well-defined diblock copolymers.[17] In an effort to develop and expand CO_2-based polymers, we have further optimized the application of this tandem strategy to prepare model ABA triblock copolymers.



Scheme 1. Tandem strategy for the synthesis of CO_2-based model AB diblock copolymer and the related catalyst system. X = 2,4-dinitrophenoxide.

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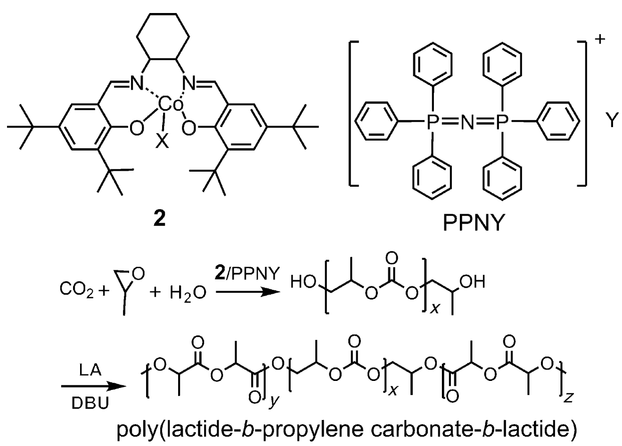


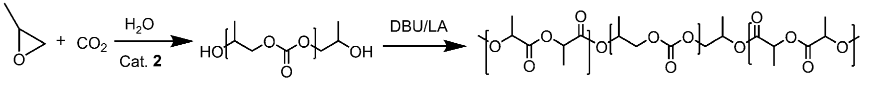
Scheme 2. Tandem strategy for synthesis of CO_2-based model ABA triblock copolymer and the related catalyst system, [(salen)Co^{III}X] (**2**)/PPNY = 1:1, (molar ratio), X = Y = CF_3COO^-.

Scheme 2 shows our tandem strategy for the preparation of model ABA triblock copolymers comprising propylene carbonate (PC) and lactide. Different from the previously tandem strategy for preparation of model AB diblock copolymers wherein the water was added to terminate the reaction at the end of the styrene oxide/CO_2 copolymerization, in this strategy water was added along with the propylene oxide(PO)/CO_2 copolymerization process as a chain-transfer reagent. In this case, one of the key roles of water is protonation of the anion of the growing polymer chain end to afford an −OH group. Another role of water is hydrolysis of the initiating group at the other end of poly(propylene carbonate) (PPC) chain to ensure the presence of −OH groups at both ends of the polymer chain; these groups can be directly used as macroinitiators to subsequently initiate organocatalytic ring-opening polymerization of lactide to prepare the triblock copolymers. Based on this idea, the binary [(salen)Co^{III}X] (**2**)/PPNY catalyst system containing trifluoroacetate axial groups were synthesized (Scheme 2), in which the trifluoroacetate has proven to undergo hydrolysis more rapidly and easily than other end-groups.[9]

Although water is an ideal substitute for traditional chain-transfer agents (e.g., diols or diacids) for the preparation of low-molecular-weight polyols in CO_2/epoxide copolymerization processes, metal-catalyzed CO_2/epoxide copolymerization reactions are often adversely affected by the presence of water.[18] For example, the introduction of water can deactivate the metal catalyst, lead to poor control of molecular weight, and increase the reaction's induction period.[19] Furthermore, the generated low-molecular-weight polyols in some instances are readily degraded to cyclic carbonates as the result of a facile back-biting reaction.[20] Hence, in order to achieve the tandem strategy outlined in Scheme 2, we first needed to assess the tolerance of the propylene oxide/CO_2 copolymerization process to added water in the presence of the binary catalyst system.

Initially, we examined the copolymerization of PO and CO_2 by employing the binary catalyst system of complex **2** and PPNY (Y = trifluoroacetate) without any water added intentionally. The copolymerization of propylene oxide/CO_2 in the presence of catalyst system (0.2 mol% loading) was carried out at 1.5 MPa CO_2 pressure and ambient temperature in toluene and dichloromethane (Table 1, entry 1). The polymerization reaction was performed for 48 h to ensure the quantitative conversion of propylene oxide. The GPC analysis revealed a bimodal weight distribution with a PDI of 1.22 and an M_n value of 16800 $g\,mol^{-1}$, which is significantly lower than the theoretical value based on both trifluoroacetate anions (Table 1, entry 1 and Figure S1 in the Supporting Information). This value is very similar to those reported by us and others.[19,21] As pointed out previously, although every effort is made to keep the copolymerization reactions anhydrous, trace quantities of water are present in the system and result in chain-transfer phenomena.[19f,21] When a quantity of water was intentionally added, that is, from 5 to 20 times more than that of the catalyst **2**/PPNY system (entries 2–4, and Figure S1), copolymers with gradually decreased molecular weights with monomodal distributions were generated, thus indicating successful chain-transfer reactions had occurred. Notably, when 20 equivalents of water were added, the isolated polymer showed an extremely narrow PDI (< 1.05) and only one series of signals assigned to two hydroxy end groups was observed by MALDI-TOF mass spectrometry

Table 1: Results from tandem strategy to prepare model ABA poly(lactide-*b*-propylene carbonate-*b*-lactide).[a]



Entry	Cat./[H_2O]/[PO] (molar ratio)	$M_{n\ (PPC)}$ [$g\,mol^{-1}$] theoretical	$M_{n\ (PPC)}$[b] [$g\,mol^{-1}$] measured	PDI[b]	Lactide [mmol]/ stereochem.	T [h]	Conv.[c] [%]	PPC/ PLA[c]	T_g/T_m[d] [°C]	M_n[b] [$g\,mol^{-1}$]	PDI[b]
1	1:0:500	25500	16800	1.28	–	–	–	1:0	35	16800	1.22
2	1:5:500	4200	11000	1.12	–	–	–	1:0	35	11000	1.12
3	1:10:500	2300	7800	1.06	–	–	–	1:0	30	7800	1.06
4	1:20:500	1200	4300	1.03	5/*rac*-LA	1.0	96	1:1.56	43	8800	1.04
5	1:20:500	1200	4800	1.04	10/*rac*-LA	4.0	99	1:0.75	44	19300	1.02
6	1:20:500	1200	4600	1.03	5/D-LA	1.0	93	1:1.61	45/110	9200	1.04
7	1:20:500	1200	4400	1.02	10/D-LA	4.0	95	1:0.79	46/128	20100	1.03

[a] See the Experimental Section for the exact procedure. [b] PDI = M_w/M_n. Determined by GPC. [c] Molar ratio. Determined by ^{1}H NMR spectroscopy. [d] Determined by DSC.

(Figure 1). It should be noted that, by comparing the theoretical and actual molecular weights of the resulting polyols, a certain amount of water remains in the reaction system (Table 1). In addition, the trifluoroacetate end-group signal was absent in the ^{19}F NMR spectrum of the copolymer. It is also gratifying to find that even in the presence of such an excess of water, the coupled product of propylene oxide and CO_2 is exclusively poly(propylene carbonate) (> 99% polymer selectivity and carbonate linkages).

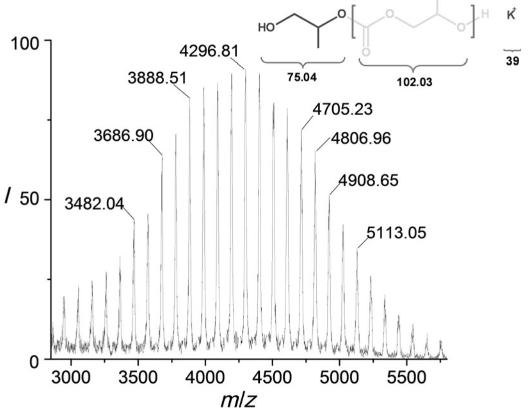


Figure 1. MALDI-TOF mass spectrum of poly(propylene carbonate) end-capped with −OH groups. The polymer was obtained from propylene oxide/CO_2 copolymerization with 20 equiv water under catalyst **2**/PPNY (Y = trifluoroacetate), 48 h, 1.5 MPa CO_2.

As mentioned previously, Williams and co-workers recently reported the copolymerization of cyclohexene oxide and CO_2 in the presence of excess water using a dizinc catalyst with a trifluoroacetate initiating group to afford the corresponding hydroxy-end-capped poly(cyclohexene carbonate).[9] In the discussion of the mechanism, they speculated that the trifluoroacetate ion is transformed into trifluoroacetic acid in the presence of excess water during the cyclohexene oxide/CO_2 polymerization process. The relatively low boiling point of the liberated acid (78 °C) compared with the reaction temperature (80 °C) should also be beneficial to the chain-transfer reactions.

Herein, we have endeavored to more definitively identify the resting state of the trifluoroacetate ion from the catalyst system complex **2**/PPNO$_2$CCF$_3$ following the copolymerization of propylene oxide/CO_2 in the presence of 20 equivalents of water. Figure S2 (see the Supporting Information) shows the positive- and negative-mode ESI mass spectra of the polymerization reaction solution after complete conversion of propylene oxide. As shown in Figure S2, in the positive ionization mode, only two species at m/z 538.1 and 603.3. assigned to $[\mathbf{2}-CF_3COO^-]^+$ and $[PPN]^+$, were detected. In the corresponding negative mode, one species at m/z 112.9, assigned to $[CF_3COO]^-$, was clearly observed, thus indicating that the trifluoroacetate ion was still in the binary catalyst system to balance the cobalt(III) and ammonium salt ions in the catalyst system. Based on previous observations, we tentatively propose a possible reaction mechanism for the preparation of the resulting HO−PPC−OH in the presence of excess water under the binary catalyst system. The first process involves the copolymerization of propylene oxide/CO_2 under complex **2**/PPNY (Y = trifluoroacetate), where the trifluoroacetate ion initiates the polymerization at the cobalt center. In the presence of water, the trifluoroacetate end-capped nucleophilic anion bound to the cobalt center deprotonates water to afford a neutral polymer chain end-capped with a hydroxy group. During the polymerization, hydroxy ion substitutes the trifluoroacetate end-group to produce the poly(propylene carbonate) with hydroxy groups at two ends of the main chain. Furthermore, the catalyst system is reformed after the trifluoroacetate end groups are replaced by −OH.

In subsequent experiments, after the careful release of excess CO_2, various quantities of *rac*-lactide and DBU were added in situ into the reaction to prepare predesigned model poly(lactide-*b*-propylene carbonate-*b*-lactide) triblock copolymers (Scheme 2, Table 1, entries 4–5). The GPC traces of the resultant copolymers are shown in Figure 2, where it is apparent that an increase in reaction time and lactide loading leads to an increase in the copolymer's molecular weight. The very narrow PDI values (< 1.05) of the resulting copolymer and the identical environments of the initiating hydroxy groups demonstrate the successful chain extension from the two chain ends of poly(propylene carbonate) to afford the predesigned poly(lactide-*b*-propylene carbonate-*b*-lactide) triblock copolymers. In addition, when using D-lactide (D-LA) as the substrate (Table 1, entries 6–7) PDLA-*b*-PPC-*b*-PDLA copolymers were produced of varying molecular weight and composition. Importantly, a much higher thermal deformation resistance (T_g ≈ 45 °C and $T_m > 110$ °C) could be found when D-lactide units are introduced into the two ends of poly(propylene carbonate) (Table 1). Meanwhile, the very narrow PDI values after chain extension and the carbonyl region of ^{13}C NMR spectra of the obtained copolymer both showed that little transesterification had occurred in the chain propagation (Figure S4 and S5).

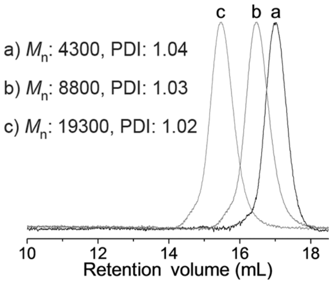


Figure 2. GPC analysis of hydroxy-functionalized poly(propylene carbonate) macroinitiator prepared by PO/CO_2 copolymerization in the presence of 20 equiv water (a: Table 1, entry 4) and poly(lactide-*b*-propylene carbonate-*b*-lactide) triblock copolymers (b: Table 1, entry 4; c: Table 1, entry 5).

We also monitored the synthesis of the LA block from the end hydroxyl groups of poly(propylene carbonate) by using in situ infrared spectroscopy. Figure 3 shows the three-dimen-

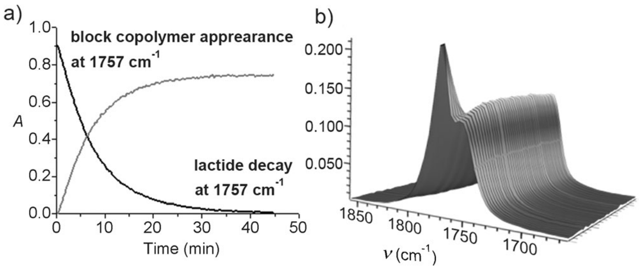


Figure 3. a) Reaction profile and b) resulting three-dimensional stack plot of IR spectra (y-axis values are given in arbitrary units) collected during the ring-opening polymerization in the presence of DBU. Deconvolution was performed by ReactIR ic10 software; the absorption at 1772 cm^{-1} is the carbonyl group from lactide, and 1757 cm^{-1} is the absorption of the carbonyl groups from the resulting triblock copolymer.

sional plot of the ring-opening polymerization of lactide initiated by PPC end-capped with hydroxy groups in the presence of DBU. From the infrared spectra, it is apparent that the carbonyl absorption at 1772 cm^{-1} for lactide gradually decrease with a concomitant increase in the carbonyl absorption at 1757 cm^{-1} because of the triblock copolymer. Meanwhile, the absence of a cyclic propylene carbonate absorption around 1800 cm^{-1} also indicated that the two ends of the poly(propylene carbonate) were protected by the polylactide segments.

In summary, we have demonstrated an in situ tandem catalytic strategy for the one-pot synthesis of a novel poly(lactide-*b*-propylene carbonate-*b*-lactide) triblock copolymers. The combination of [(salen)CoX]-catalyzed propylene oxide/CO_2 copolymerization and DBU-initiated ring-opening polymerization of lactide provides an efficient and straightforward route to the synthesis of model ABA triblock copolymers. This approach is enabled by the judicious choice of water as a chain-transfer reagent, which, when added at the beginning of the metal-catalyzed propylene oxide/CO_2 copolymerization process, generates in situ hydroxy end groups on the polymer chain. In the presence of an organocatalyst, DBU, this −OH-terminated poly(propylene carbonate) serves as a macroinitiator for subsequent ring-opening polymerization of lactide. The well-defined structure of the block copolymers and the mild reaction conditions for the polymerization process provides an excellent opportunity to expand the scope of applications of these green copolymers. For example, it has been shown that a blend of PCC and PLA possesses attractive new properties.[22] These efforts, as well as detailed studies of the thermal and physical properties of these triblock polymers, are currently being carried out in our laboratory.

Experimental Section

The poly(lactide-*b*-propylene carbonate-*b*-lactide) copolymer was synthesized following the procedure. In a dry-box, complex **2** (0.015 mmol, 10.7 mg) and PPNY (Y = trifluoroacetate; 9.7 mg, 0.015 mmol) were dissolved in propylene oxide (0.44 g, 500 equiv) and toluene/CH_2Cl_2 (1:1 *v*/*v*; 1 mL) with 0.3 mmol water under an argon atmosphere. The solution was charged into a predried 15 mL autoclave equipped with a magnetic stirrer, and pressurized to the appropriate pressure with CO_2. After the allotted reaction time, the CO_2 pressure was slowly released and a small amount of the resultant polymerization mixture was removed from the autoclave for ^1H NMR analysis to determine the conversion of propylene oxide, the selectivity of polycarbonates to cyclic carbonate, carbonate linkages, and also used for GPC analysis. Subsequently, CH_2Cl_2 (3 mL) containing a certain amount of lactide were added into the reaction solution, and after 5 min, DBU (0.3 mmol) in CH_2Cl_2 (1 mL) was added in situ to prepare the triblock polymer. Stirring was continued for 2 h, and benzoic acid was added to quench the reaction, and the solvent was evaporated to yield the crude polymer. The crude polymer was dissolved in a cold 5 mL CH_2Cl_2/MeOH (1:5 *v*/*v*) mixture and precipitated from methanol. This process was repeated 3–5 times to completely remove the catalyst, and the white polymer was obtained by vacuum drying.

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[1] a) C. K. Williams, M. A. Hillmyer, *Polym. Rev.* **2008**, *48*, 1–10; b) G. W. Coates, M. A. Hillmyer, *Macromolecules* **2009**, *42*, 7987–7989.

[2] L. Bottenbruck in *Engineering Thermoplastics: Polycarbonates, Polyacetals, Polyesters, Cellulose Esters* (Ed.: L. Bottenbruck), Hanser, New York, **1996**, pp. 112–287.

[3] a) S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. Part B* **1969**, *7*, 287–292; b) S. Inoue, H. Koinuma, T. Tsuruta, *Makromol. Chem.* **1969**, *130*, 210–220.

[4] For comprehensive reviews on CO_2/epoxide copolymerization, see: a) D. J. Darensbourg, M. W. Holtcamp, *Coord. Chem. Rev.* **1996**, *153*, 155–174; b) G. W. Coates, D. R. Moore, *Angew. Chem.* **2004**, *116*, 6784–6806; *Angew. Chem. Int. Ed.* **2004**, *43*, 6618–6639; c) D. J. Darensbourg, R. M. Mackiewicz, A. L. Phelps, D. R. Billodeaux, *Acc. Chem. Res.* **2004**, *37*, 836–844; d) H. Sugimoto, S. Inoue, *J. Polym. Sci. Part A* **2004**, *42*, 5561–5573; e) M. H. Chisholm, Z. Zhou, *J. Mater. Chem.* **2004**, *14*, 3081–3092; f) D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388–2410; g) M. R. Kember, A. Buchard, C. K. Williams, *Chem. Commun.* **2011**, *47*, 141–163; h) S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* **2011**, *255*, 1460–1479; i) X.-B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, *41*, 1462–1484; j) D. J. Darensbourg, S. J. Wilson, *Green Chem.* **2012**, *14*, 2665–2671; k) X.-B. Lu, W.-M. Ren, G.-P. Wu, *Acc. Chem. Res.* **2012**, *45*, 172–1735.

[5] Presently, attempts at industrialization of CO_2/epoxide derived copolymer are mainly concentrated on ethylene oxide and propylene oxide to produce poly(ethylene carbonate) and poly(propylene carbonate) by Novomer and Empower Materials in the United States, SK in Korea, China Blue Chemical, Henan Tianguan, and Tai-zhou Bangfeng in China.

[6] N. Hadjichristidis, S. Pispas, G. A. Floudas, *Block Copolymers, Synthetic Strategies, Physical Properties, and Applications*, Wiley-VCH, Weinheim, **2003**.

[7] For other types of CO_2-based block polymers synthesized by sequentially added different epoxides or by gradient-enantiomer selective polymerization see: a) J. G. Kim, C. D. Cowman, A. M. LaPointe, U. Wiesner, G. W. Coates, *Macromolecules* **2011**, *44*, 1110–1113; b) D. J. Darensbourg, M. Ulusoy, O. Karroonnirum, R. R. Poland, J. H. Reibenspies, B. Cetinkaya, *Macromolecules* **2009**, *42*, 6992–6998; c) K. Nakano, S. Hashimoto, M. Naka-

mura, T. Kamada, K. Nozaki, *Angew. Chem.* **2011**, *123*, 4970–4973; *Angew. Chem. Int. Ed.* **2011**, *50*, 4868–4871.

[8] A. Cyriac, S. H. Lee, J. K. Varghese, E. S. Park, J. H. Park, B. Y. Lee, *Macromolecules* **2010**, *43*, 7398–7401.

[9] M. R. Kember, J. Copley, A. Buchard, C. K. Williams, *Polym. Chem.* **2012**, *3*, 1196–1201.

[10] R. C. Jeske, J. M. Rowley, G. W. Coates, *Angew. Chem.* **2008**, *120*, 6130–6133; *Angew. Chem. Int. Ed.* **2008**, *47*, 6041–6044.

[11] S. Huijser, E. Hosseini Nejad, R. Sablong, C. de Jong, C. E. Koning, R. Duchateau, *Macromolecules* **2011**, *44*, 1132–1139.

[12] D. J. Darensbourg, R. R. Poland, C. Escobedo, *Macromolecules* **2012**, *45*, 2242–2248.

[13] Y. Hwang, J. Jung, M. Ree, H. Kim, *Macromolecules* **2003**, *36*, 8210–8212.

[14] M. Kröger, C. Folli, O. Walter, M. Döring, *Adv. Synth. Catal.* **2006**, *348*, 1908–1918.

[15] Y. Liu, K. Huang, D. Peng, H. Wu, *Polymer* **2006**, *47*, 8453–8461.

[16] G.-P. Wu, D. J. Darensbourg, X.-B. Lu, *J. Am. Chem. Soc.* **2012**, *134*, 17739–17745.

[17] For organocatalytic ring-opening polymerization see: a) B. G. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth, J. L. Hedrick, *Macromolecules* **2006**, *39*, 8574–8583; b) R. C. Pratt, B. G. Lohmeijer, D. A. Long, R. M. Waymouth, J. L. Hedrick, *J. Am. Chem. Soc.* **2006**, *128*, 4556–4557; c) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, J. L. Hedrick, *Chem. Rev.* **2007**, *107*, 5813–5840.

[18] M. R. Kember, C. K. Williams, *J. Am. Chem. Soc.* **2012**, *134*, 15676–15679.

[19] a) K. Nakano, T. Kamada, K. Nozaki, *Angew. Chem.* **2006**, *118*, 7432–7435; *Angew. Chem. Int. Ed.* **2006**, *45*, 7274–7277; b) M. R. Kember, A. J. P. White, C. K. Williams, *Macromolecules* **2010**, *43*, 2291–2298; c) H. Sugimoto, H. Ohtsuka, S. Inoue, *J. Polym. Sci. Part A* **2005**, *43*, 4172–4186; d) X. B. Lu, L. Shi, Y. M. Wang, R. Zhang, Y. J. Zhang, X. J. Peng, Z. C. Zhang, B. Li, *J. Am. Chem. Soc.* **2006**, *128*, 1664–1674; e) S. J. Na, S. Sujith, A. Cyriac, B. E. Kim, J. Yoo, Y. K. Kang, S. J. Han, C. Lee, B. Y. Lee, *Inorg. Chem.* **2009**, *48*, 10455–10465; f) C. T. Cohen, T. Chu, G. W. Coates, *J. Am. Chem. Soc.* **2005**, *127*, 10869–10878; g) C. Chatterjee, M. H. Chisholm, *Inorg. Chem.* **2011**, *50*, 4481–4492.

[20] a) D. J. Darensbourg, J. C. Yarbrough, C. Ortiz, C. C. Fang, *J. Am. Chem. Soc.* **2003**, *125*, 7586–7591; b) D. J. Darensbourg, S.-H. Wei, *Macromolecules* **2012**, *45*, 5916–5922.

[21] a) D. J. Darensbourg, R. M. Mackiewicz, *J. Am. Chem. Soc.* **2005**, *127*, 14026–14038; b) W.-M. Ren, Z. W. Liu, Y. Q. Wen, R. Zhang, X.-B. Lu, *J. Am. Chem. Soc.* **2009**, *131*, 11509–11518.

[22] a) G. A. Luinstra, F. Molnar, *Macromol. Symp.* **2007**, *259*, 203–209; b) G. A. Luinstra, *Polym. Rev.* **2008**, *48*, 192–219.