

Selective Polymerization Catalysis: Controlling the Metal Chain End Group to Prepare Block Copolyesters

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S Supporting Information

ABSTRACT: Selective catalysis is used to prepare block copolyesters by combining ring-opening polymerization of lactones and ring-opening copolymerization of epoxides/anhydrides. By using a dizinc complex with mixtures of up to three different monomers and controlling the chemistry of the Zn–O(polymer chain) it is possible to select for a particular polymerization route and thereby control the composition of block copolyesters.

A central challenge in polymer synthesis is to develop methods that enable complex architectures to be prepared from mixtures of monomers.¹ Generally, using two or more monomers, the copolymer composition or sequence is determined by empirical monomer “reactivity ratios”.² Recently, controlled radical polymerization methods have enabled pioneering sequence control.³ Using catalysis to control monomer enchainment from mixtures would be highly attractive, but there are not yet many such options for oxygenated copolymers.

Some of the best routes to such oxygenated polymers are by catalyzed ring-opening polymerization (ROP) of lactones or the ring-opening copolymerizations of (ROCOP) of epoxides and heterocumulenes (Figure 1).⁴ Previously, Coates pioneered

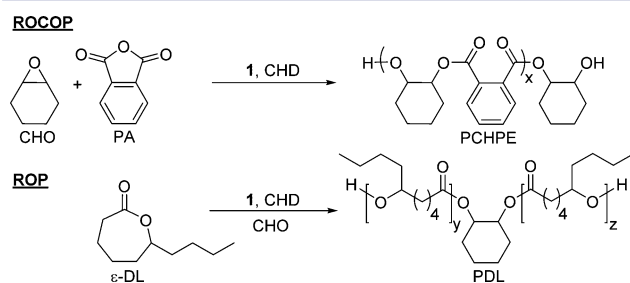


Figure 1. ROCOP and ROP reactions catalyzed by **1**, where CHD is 1,2-cyclohexanediol.

selective ROCOP catalysts for mixtures of epoxide, anhydride, and CO₂, to yield AB block copoly(ester carbonates).⁵ Subsequently others have shown the same selectivity applies to various catalysts/monomers.⁶ Darenbourg and Lu used tandem catalysis with epoxides, CO₂, and *rac*-lactide to prepare block copoly(ester carbonates).⁷ Last year, we reported a dizinc catalyst (Figure S1) able to switch between the two different polymerization cycles: ROP and ROCOP and to control block sequences from mixtures of epoxide, CO₂, and ϵ -caprolactone.⁸

Multiblock copolymers have the potential for significantly enhanced properties and functionality.⁹ Block regulation provides a means to differentiate macroscopic thermal/mechanical performances and, of particular relevance for oxygenated polymers, degradation rates.¹⁰ Directing the block compositions in conventional polyester synthesis (by polycondensations) would be extremely difficult and more often impossible, due to step-growth synthetic methods. In contrast, the ROP of lactones¹¹ or ROCOP of epoxides/anhydrides^{5,6,12} allow the controlled syntheses.¹³ Currently, the catalysts used for these polyester syntheses have been reported separately and are almost totally incompatible: there is just one report, from 1985, of a homogeneous aluminum porphyrin complex active for both routes to polyesters.¹⁴ Here, a new catalyst is reported for both controlled ROP and ROCOP, as well as for selective catalysis using monomer mixtures, leading to the clean formation of ABA and multiblock copolyesters.

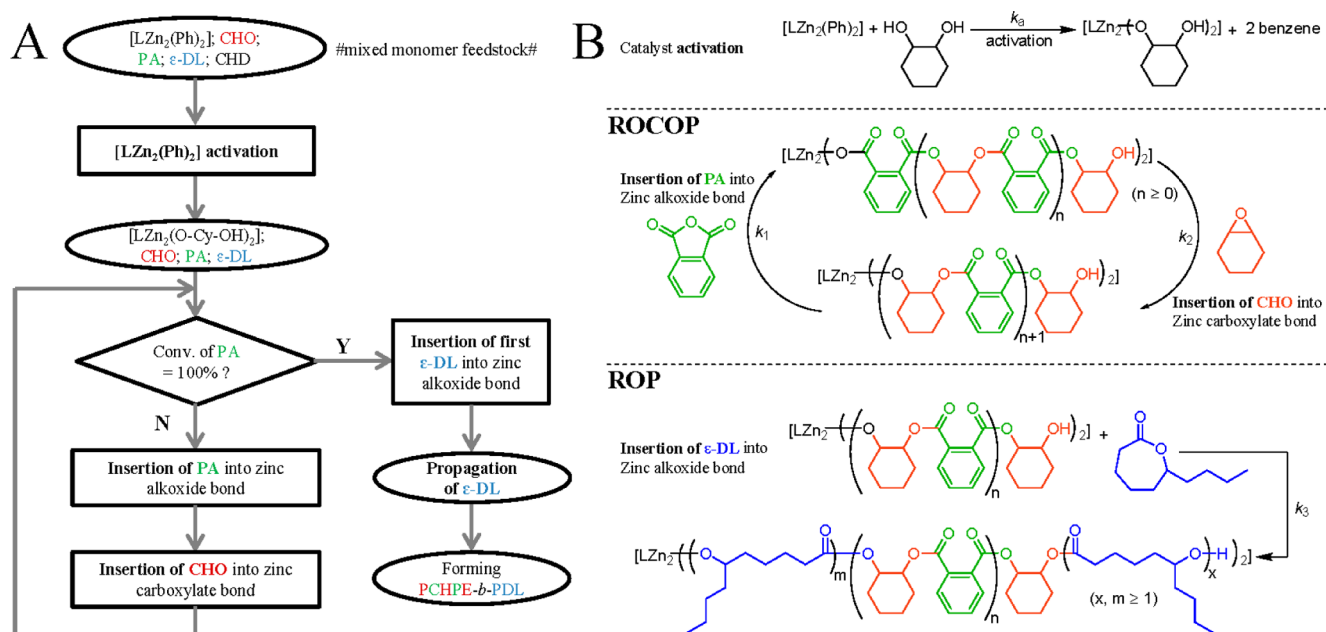
Using the dizinc acetate catalyst, previously reported for epoxide/CO₂/lactone copolymerization,⁸ the terpolymerization of ϵ -decalactone (ϵ -DL), phthalic anhydride (PA), and cyclohexene oxide (CHO) afforded a mixture of polymers featuring different end-groups (Table S1). Despite the high degree of control exerted, both α -acetyl- ω -hydroxyl and α,ω -dihydroxyl polymer end-groups were observed.^{6e,15} Although an encouraging result, the limitation is that both AB and ABA type copolymers formed concurrently, causing bimodal molecular weight distributions.

In order to solve this problem, a new dizinc complex was prepared: [L₁Zn₂(Ph)₂] **1** (Figure S1–S4). Complex **1** is activated by reaction with a diol to form, *in situ*, the catalyst system (Scheme 1B and Figure S5) and thus is expected to yield only α,ω -dihydroxyl polymer end-groups. It showed a good performance in epoxide/anhydride ROCOP (Table 1, Figure 1).

It showed good activity, with TOF values of 25 h⁻¹ and an excellent selectivity for polyester (>99%, Figure S6). It also showed high degrees of polymerization control, with predictable molecular weights (MW) and narrow dispersities (≤ 1.30). The MWs of the polymers are determined using SEC, calibrated with polystyrene standards, and using multiple-angle-laser light scattering (SEC-MALLS) (Table 1, Figure S7). Previously, the MW of poly(cyclohexylene phthalate) (PCHPE) was only determined by PS calibrated SEC; there was a poor correlation between theoretical and experimental MW.^{6a,e} In contrast, using SEC-MALLS, excellent agreement between MW values is observed, confirming that the ROCOP is very well-controlled.

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Scheme 1. (A) Diagram Illustrating the Chemoselective Sequence Controlled Polymerization; (B) Reactions Corresponding to the Steps Illustrated in Part (A)^a

^aThe typical reaction conditions are in the footnotes to Table 3.

Table 1. ROCOP of Phthalic Anhydride and Cyclohexane Diol Oxide, Using 1 and Cyclohexane Diol

#	1/diol ^a	$M_{n,theo}$ ^b	$M_{n,SEC-PS}$ ^c (Đ)	$M_{n,SEC-MALLS}$ ^d (Đ)
1	1:2	12.3	5.3 (1.33)	9.3 (1.03)
2	1:4	6.2	2.9 (1.29)	5.2 (1.02)
3	1:6	4.1	2.3 (1.33)	3.6 (1.10)
4	1:8	3.1	1.8 (1.27)	2.9 (1.06)
5	1:10	2.5	1.6 (1.32)	2.5 (1.07)

^a[1]/[PA]/[CHO] = 1:100:800, 100 °C, 3–4 h, PA conversion >99%. Diol refers to 1,2-cyclohexane diol (CHD). ^bDetermined on the basis of $\{(MW_{PA} + MW_{CHO}) \times (\text{conversion of PA})\} / [CHD]$, with units of $\text{kg}\cdot\text{mol}^{-1}$. ^cDetermined by SEC calibrated using narrow MW polystyrene (PS) standards, with units of $\text{kg}\cdot\text{mol}^{-1}$. ^dDetermined by SEC-MALLS in THF ($dn/dc = 0.133 \pm 0.001 \text{ mL}\cdot\text{g}^{-1}$), with units of $\text{kg}\cdot\text{mol}^{-1}$.

The polymerization control is further demonstrated by the linear fits of M_n vs [CHD] (Figure S8). The MALDI spectrum shows a single series of perfectly alternating polyester chains, end-capped by α,ω -dihydroxyl groups (Figure S9).

Complex 1, with 1,2-cyclohexanediol (CHD), was also tested, as a catalyst for the ROP of ϵ -DL, using cyclohexene oxide as the solvent (Table 2, Figure 1). It showed very good activity, with TOF values of 160 h^{-1} and no evidence for any epoxide homopolymerization or insertion into the PDL chain (Figures S10–S11). The polymers' MWs are in close agreement with the theoretical values and show narrow dispersities. Immortal polymerization is also feasible and the amount of CHD used controls the molecular weights while maintaining narrow dispersities (Figures S12–S13).

Given that both ROP and ROCOP are catalyzed independently, it was of high interest to establish whether concurrent reactions could be achieved using 1. Thus, mixtures of lactone (ϵ -DL), epoxide (CHO), and anhydride (PA) monomers were reacted with the catalyst system comprising 1 and diol (Table 3, Scheme 1). The terpolymerizations were all successful and an

Table 2. ROP of ϵ -Decalactone, Using 1 and Cyclohexane Diol

#	1/diol ^a	$M_{n,theo}$ ^b	$M_{n,SEC-PS}$ ^c (Đ)	$M_{n,SEC-MALLS}$ ^d (Đ)
1	1:2	17.0	14.0 (1.16)	13.4 (1.07)
2	1:4	8.5	7.8 (1.10)	6.8 (1.06)
3	1:6	5.7	6.7 (1.12)	4.7 (1.05)
4	1:8	4.3	5.3 (1.11)	3.5 (1.11)
5	1:10	3.4	4.3 (1.12)	3.0 (1.05)

^a[1]/[ϵ -DL]/[CHO] = 1:200:800, 100 °C, 1.25 h, ϵ -DL conversion >95%. Diol refers to 1,2-cyclohexane diol (CHD). ^bDetermined on the basis of $\{MW_{\epsilon\text{-DL}} \times (\text{conversion of } \epsilon\text{-DL})\} / [CHD]$, with units of $\text{kg}\cdot\text{mol}^{-1}$. ^cDetermined by SEC calibrated using narrow MW polystyrene (PS) standards, with units of $\text{kg}\cdot\text{mol}^{-1}$. ^dDetermined by SEC-MALLS, in THF, ($dn/dc = 0.054 \pm 0.001 \text{ mL}\cdot\text{g}^{-1}$ for entry 1, $0.067 \pm 0.001 \text{ mL}\cdot\text{g}^{-1}$ for entry 2, and $0.072 \pm 0.002 \text{ mL}\cdot\text{g}^{-1}$ for entries 3–5), with units of $\text{kg}\cdot\text{mol}^{-1}$.

unexpected monomer selectivity was observed, resulting in the controlled formation of only ABA type block copolyesters. Such selectivity is very unusual, yet is potentially useful given the importance of block copolymers. The terpolymerizations were monitored by ATR-IR spectroscopy (Figure 2), which showed that initially epoxide/anhydride ROCOP occurred, as shown by the disappearance of the diagnostic PA resonance at 1790 cm^{-1} and the growth of the characteristic polyester (PCHPE) resonance ($1065\text{--}1068 \text{ cm}^{-1}$). During this time, there was no change to any resonances associated with the lactone (ϵ -DL), a finding confirmed by aliquot analysis using ^1H NMR spectroscopy, which only showed signals for perfectly alternating polyester (PCHPE) and residual ϵ -DL (Figure S14). Once the PA was consumed, in the presence of excess CHO, the reaction entered the second phase whereby ϵ -DL ROP occurred, leading to triblock polyester formation. During this stage, the ATR-IR monitoring showed the decrease of the ϵ -DL resonance, at 1735 cm^{-1} , accompanied by the growth of the block of poly(ϵ -decalactone) as signaled by its resonance at 1190 cm^{-1} . All IR

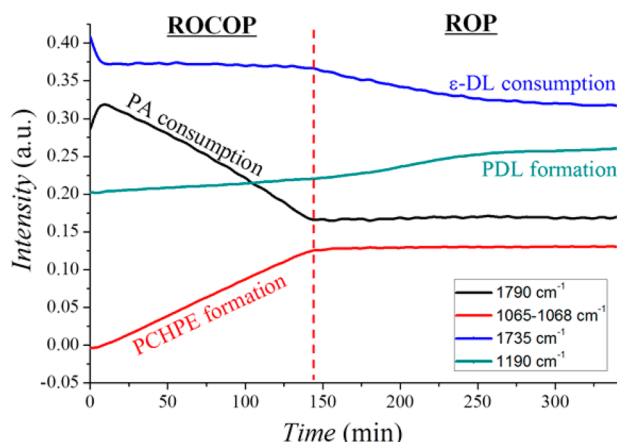
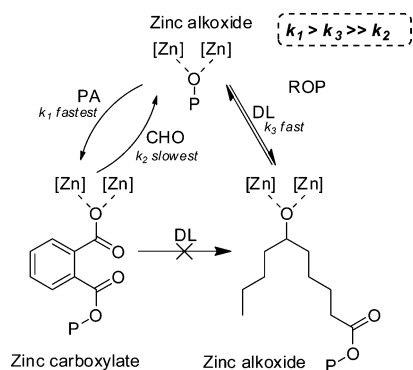


Figure 2. Shows a representative ATR-IR spectrum acquired during (PDL-*b*-PCHPE-*b*-PDL) formation (Table 3, entry 2).

absorptions were independently confirmed in control experiments using pure monomers/polymers (Figure S15).

The selectivity would not be expected on the basis of the activities, where the TOF values are ROP 160 h⁻¹ and ROCOP 25 h⁻¹, respectively. Scheme 2 illustrates the key intermediates

Scheme 2. Reactions Proposed to Occur during Sequence-Selective Polymerizations^a



^a[Zn] [Zn] is the active site of **1**, and P is a propagating polymer chain.

present during polymerization. The different rate of insertion of monomers into the zinc alkoxide intermediate, which is common to both catalytic cycles, is proposed to be responsible for the selectivity. Accordingly, the rate of PA insertion into the Zn-alkoxide bond is significantly faster than the insertion of ϵ -DL (i.e., $k_1 \gg k_3$). It is also relevant that the zinc-carboxylate intermediate, formed by PA insertion, does not react with lactones, a finding supported by the failure of LZn₂(OAc)₂ to catalyze ϵ -DL ROP (Table S2). The further reaction of the zinc-alkoxide intermediate with epoxide (CHO) has been calculated to have a significantly higher barrier, and thus, ether linkages are not observed experimentally.¹⁷

To confirm the ABA polymer structure, aliquots were analyzed by SEC just before the complete conversion of PA (ca. 95%) and after the propagation of PDL block (ca. 96% conv. of ϵ -DL) (Figure 3). It is quite clear that after ϵ -DL ROP the polymer has a higher MW and that in both cases distributions are monomodal, with narrow dispersities. Since the block formed by ROCOP (PCHPE) has an aromatic repeat unit, analysis using SEC with a UV-detector can be used to confirm block attachment. ³¹P{¹H}

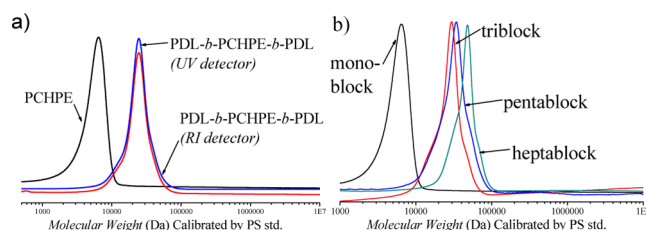


Figure 3. (a) SEC traces of the polymer aliquots before and after propagation of the PDL block (Table 3, # 3). (b) SEC traces during formation of the heptablock copolyester (Table S3).

NMR spectroscopy was also used to distinguish the two different hydroxyl end-groups (from PCHPE and PDL, respectively), on the basis of their chemical shifts after reaction with excess 2-chloro-4,4,5,5-tetramethyl dioxaphospholane. There was a shift from a peak at 147.1 ppm, due to PCHPE end groups, after the first phase, to a single peak at 149.2 ppm, due to PDL end groups for the ABA triblock (Figure S16). The ¹H DOSY NMR spectrum showed that all NMR signals belong to a single copolymer with the same diffusion coefficient (Figure S17); in contrast to a blend of PCHPE/PDL, of near equivalent MW, which showed two different diffusion coefficients.

If transesterification reactions occur these would scramble the block structure. The ¹³C{¹H} NMR spectrum of the copolymer shows only two carbonyl resonances, at 172.4 and 166.5 ppm, assigned to the carbonyl groups of the PDL and PCHPE blocks, respectively (Figure S18). In contrast, the ¹³C{¹H} NMR spectrum of the copolymer after reaction with a well-known transesterification catalyst (1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), at 60 °C for 48 h) shows new signals at 168.1 and 164.2 ppm (Figure S19). The signals are assigned to scrambled [CHO-DL] and [PA-DL] diads.^{7b} Thus, there is no significant inter- or intrachain transesterification, a finding previously observed for other lactone ROP catalysts.¹⁸

The selective catalysis was extended, by addition of further monomers, to prepare a multiblock copolymer (Table S3). Thus, a PDL-*b*-PCHPE-*b*-PDL triblock was synthesized, and after complete consumption of the ϵ -DL, the addition of more PA and ϵ -DL led to the formation of a heptablock copolymer. The block selectivity followed the same “rules” already established (Figures 3b and S20–S21).

Triblock copolyesters with different MW values and compositions were prepared (Table 3). The copolymers showed *T_g* values tunable over the range -59 to 61 °C. The

Table 3. Sequence Controlled Block Copolyester Syntheses

#	[PA]/[ϵ -DL] ^a	% PCHPE ^b	<i>M</i> _{theo} ^c	<i>M</i> _{nexp} ^d	<i>D</i> ^d	<i>T_g</i> (°C) ^e
1	0:100	0	8.5	6.9	1.20	-58
2	50:100	33	18.9	12.3	1.25	-49
3	100:200	42	28.0	15.9	1.21	-49;57
4	100:100	59	22.4	12.0	1.15	-47; 61
5	150:50	81	22.7	11.9	1.29	55
6	100:0	100	12.3	5.3	1.33	97

^a[**1**]/[CHD]/[CHO] = 1:2:800, 100 °C, PA and ϵ -DL conversion >95%. ^bWeight content of PCHPE block in the polyester (PDL-*b*-PCHPE-*b*-PDL). ^cDetermined by {(MW_{PA} + MW_{CHO}) × (conversion of PA) + MW _{ϵ -DL} × (conversion of ϵ -DL)}/[CHD] with units of kg·mol⁻¹. ^dDetermined by SEC using polystyrene calibration, with units of kg·mol⁻¹. MALLS is not suitable for such block copolymer analysis.¹⁶ ^eDetermined after three heating-cooling cycles, on the third cycle.

homopolymers are both amorphous, with T_g values of -58 °C (PDL) and 97 °C (PCHPE), respectively. A blend of them showed identical T_g values to the homopolymers. Copolyesters with low (33 wt %) or high (81 wt %) PCHPE compositions showed only a single T_g close to that of the dominant block material (PDL or PCHPE). Where the block composition was more evenly balanced (42–59 wt % PCHPE), two T_g values were observed, suggesting microphase separation of the soft/hard blocks (Figure S22).

As part of a preliminary evaluation of the generality of the selective synthesis, it was successfully applied using other epoxides and cyclic esters (Table 4). In all cases, the

Table 4. Block Copolyesters Prepared Using Other Epoxides and Cyclic Esters: 4-Vinyl-1-cyclohexene 1,2-Epoxyde (v-CHO), *rac*-Lactide (*rac*-LA), and δ -Valerolactone (δ -VL)^a

#	monomers ^b	M_{nexp} ^c (Đ) of the first aliquot	M_{nexp} ^d (Đ) of the final polymer
1	PA/v-CHO/ ϵ -DL	4.2 (1.32)	12.8 (1.34)
2	PA/CHO/ <i>rac</i> -LA	2.5 (1.16)	6.0 (1.53)
3	PA/CHO/ δ -VL	5.5 (1.34)	11.6 (1.59)
4	PA/vCHO/ δ -VL	3.9 (1.33)	12.0 (1.60)

^aSee Scheme S1 for monomer structure and Figures S24–S27. ^b[1]/[CHD]/[anhydride]/[epoxide]/[cyclic ester] = 1:2:100:800:200, 100 °C. ^cDetermined by SEC using polystyrene calibration, with units of $\text{kg}\cdot\text{mol}^{-1}$ (PA conversion >90%); ^dDetermined by SEC using polystyrene calibration, with units of $\text{kg}\cdot\text{mol}^{-1}$ (cyclic ester conversion >80%).

polymerizations showed the same sequence selectivity with ROCOP of the epoxide/anhydride occurring prior to ROP of the lactone (Figure S23). The block structures were confirmed, in all cases, using ¹H DOSY NMR and ¹³C NMR spectroscopy (Figures S24–S27).

In summary, a single homogeneous catalyst for both lactone ROP and epoxide/anhydride ROCOP is reported. ABA triblock copolyesters are prepared, in one-pot from monomer mixtures, using the selective catalysis that bridges between the two polymerization cycles. The ground rules for implementing the selective process are uncovered, and the ability to apply it to other monomers is demonstrated; it is clear that other classes of catalysts and monomers warrant investigation. The method also simplifies the preparation of block copolyesters and is expected to be of value for the preparation of materials with tailored properties, such as new types of thermoplastic elastomer.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04541.

Experimental section and supporting figures (PDF)

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Notes

The authors declare the following competing financial interest(s): C.K.W. is a director and CSO of Eonic Technologies.

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■ REFERENCES

- (1) Lutz, J. F.; Ouchi, M.; Liu, D. R.; Sawamoto, M. *Science* **2013**, *341*, 628–636.
- (2) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259–262.
- (3) (a) Badi, N.; Lutz, J. F. *Chem. Soc. Rev.* **2009**, *38*, 3383–3390. (b) Lutz, J. F. *Nat. Chem.* **2010**, *2*, 84–85. (c) Anastasaki, A.; Nikolaou, V.; Pappas, G. S.; Zhang, Q.; Wan, C.; Wilson, P.; Davis, T. P.; Whittaker, M. R.; Haddleton, D. M. *Chem. Sci.* **2014**, *5*, 3536–3542. (d) Gody, G.; Maschmeyer, T.; Zetterlund, P. B.; Perrier, S. *Nat. Commun.* **2013**, *4*, 2505.
- (4) (a) Ajellal, N.; Carpentier, J. F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. *Dalton Trans.* **2010**, *39*, 8363–8376. (b) Childers, M. I.; Longo, J. M.; Van Zee, N. J.; LaPointe, A. M.; Coates, G. W. *Chem. Rev.* **2014**, *114*, 8129–8152. (c) Lu, X.-B.; Darensbourg, D. J. *Chem. Soc. Rev.* **2012**, *41*, 1462–1484. (d) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. *Chem. Commun.* **2015**, *51*, 6459–6479.
- (5) Jeske, R. C.; Rowley, J. M.; Coates, G. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 6041–6044.
- (6) (a) Hosseini Nejad, E.; van Melis, C. G. W.; Vermeer, T. J.; Koning, C. E.; Duchateau, R. *Macromolecules* **2012**, *45*, 1770–1776. (b) Hosseini Nejad, E.; Paoniasari, A.; Koning, C. E.; Duchateau, R. *Polym. Chem.* **2012**, *3*, 1308–1313. (c) Harrold, N. D.; Li, Y.; Chisholm, M. H. *Macromolecules* **2013**, *46*, 692–698. (d) Darensbourg, D. J.; Poland, R. R.; Escobedo, C. *Macromolecules* **2012**, *45*, 2242–2248. (e) Saini, P. K.; Romain, C.; Zhu, Y.; Williams, C. K. *Polym. Chem.* **2014**, *5*, 6068–6075. (f) Winkler, M.; Romain, C.; Meier, M. A. R.; Williams, C. K. *Green Chem.* **2015**, *17*, 300–306.
- (7) (a) Darensbourg, D. J.; Wu, G.-P. *Angew. Chem., Int. Ed.* **2013**, *52*, 10602–10606. (b) Wu, G.-P.; Darensbourg, D. J.; Lu, X.-B. *J. Am. Chem. Soc.* **2012**, *134*, 17739–17745.
- (8) Romain, C.; Williams, C. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 1607–1610.
- (9) Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. *Science* **2012**, *336*, 434–440.
- (10) (a) Takizawa, K.; Tang, C.; Hawker, C. J. *J. Am. Chem. Soc.* **2008**, *130*, 1718–1726. (b) Lee, H. S.; Roy, A.; Lane, O.; Lee, M.; McGrath, J. E. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 214–222. (c) Lendlein, A.; Neunschwander, P.; Suter, U. W. *Macromol. Chem. Phys.* **1998**, *199*, 2785–2796.
- (11) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11–63.
- (12) (a) Jeske, R. C.; DiCiccio, A. M.; Coates, G. W. *J. Am. Chem. Soc.* **2007**, *129*, 11330–11331. (b) Longo, J. M.; DiCiccio, A. M.; Coates, G. W. *J. Am. Chem. Soc.* **2014**, *136*, 15897–15900.
- (13) Brule, E.; Guo, J.; Coates, G. W.; Thomas, C. M. *Macromol. Rapid Commun.* **2011**, *32*, 169–185.
- (14) Aida, T.; Sanuki, K.; Inoue, S. *Macromolecules* **1985**, *18*, 1049–1055.
- (15) Zhu, Y.; Romain, C.; Poirier, V.; Williams, C. K. *Macromolecules* **2015**, *48*, 2407–2416.
- (16) Gores, F.; Kilz, P. *Chromatography of Polymers*; American Chemical Society: Washington, DC, 1993; Vol. 521, pp 122–148.
- (17) Buchard, A.; Jutz, F.; Kember, M. R.; White, A. J. P.; Rzepa, H. S.; Williams, C. K. *Macromolecules* **2012**, *45*, 6781–6795.
- (18) (a) Bouyahyi, M.; Duchateau, R. *Macromolecules* **2014**, *47*, 517–524. (b) Zhang, D.; Hillmyer, M. A.; Tolman, W. B. *Biomacromolecules* **2005**, *6*, 2091–2095. (c) Jasinska-Walc, L.; Bouyahyi, M.; Rozanski, A.; Graf, R.; Hansen, M. R.; Duchateau, R. *Macromolecules* **2015**, *48*, 502–510. (d) Jasinska-Walc, L.; Hansen, M. R.; Dudenko, D.; Rozanski, A.; Bouyahyi, M.; Wagner, M.; Graf, R.; Duchateau, R. *Polym. Chem.* **2014**, *5*, 3306–3310.