

Metal-Free Alternating Copolymerization of CO₂ with Epoxides: Fulfilling “Green” Synthesis and Activity

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S Supporting Information

ABSTRACT: Polycarbonates were successfully synthesized for the first time through the anionic copolymerization of epoxides with CO₂, under metal-free conditions. Using an approach based on the activation of epoxides by Lewis acids and of CO₂ by appropriate cations, well-defined alternating copolymers made of CO₂ and propylene oxide (PO) or cyclohexene oxide (CHO) were indeed obtained. Triethyl borane was the Lewis acid chosen to activate the epoxides, and onium halides or onium alkoxides involving either ammonium, phosphonium, or phosphazanium cations were selected to initiate the copolymerization. In the case of PO, the carbonate content of the poly(propylene carbonate) formed was in the range of 92–99% and turnover numbers (TON) were close to 500; in the case of CHO perfectly alternating poly(cyclohexene carbonate) were obtained and TON values were close to 4000. The advantages of such a copolymerization system are manifold: (i) no need for multistep catalyst/ligand synthesis as in previous works; (ii) no transition metal involved in the copolymer synthesis and therefore no coloration of the samples isolated; and (iii) no necessity for postsynthesis purification.

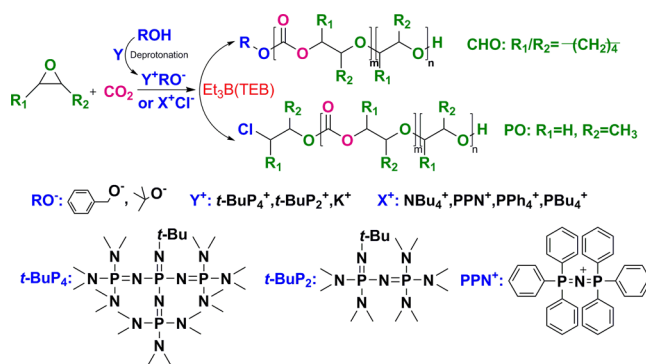
Since the earlier attempts by Inoue et al. to copolymerize carbon dioxide (CO₂) and epoxides,¹ significant advances have been made resulting in the development of catalysts that nowadays serve to industrially produce aliphatic polycarbonates.² Thanks to a precise design of the ligands bound to transition metals, these catalysts exhibit simultaneously high activity and high selectivity toward the alternating insertion of CO₂ and epoxides.^{2,3} Examples indeed abound of homogeneous catalysts based on transition metals such as Zn(II),⁴ Cr(III),⁵ Co(III)⁶ and featuring precisely designed ligands that efficiently catalyze the copolymerization of aliphatic or alicyclic epoxides with CO₂.

In all these organo-metallic complexes involving transition metals or earth-abundant main group metals such as aluminum,^{3a,7} magnesium⁸ and iron,⁹ the chain growth occurs by prior coordination of epoxides to the growing metal complex before their insertion at the chain ends.^{4a,9a,10} Another common feature of these very active catalysts is the complexity of their ligands that are generally synthesized through multistep synthesis. In addition, transition-metal-based complexes are colored and often toxic, and even if the latter are very active and

used in a minute amount, a postpolymerization metal/removal step is always necessary.^{6b,11}

Using an approach that totally departs from the coordination–insertion mechanism and thus from all the work done so far, we demonstrate in this study how CO₂ and epoxides can be efficiently copolymerized using a metal-free process as shown in Scheme 1. From an initiator that can be an onium salt or an

Scheme 1. Anionic Copolymerization of Epoxides and CO₂ with TEB as Activator

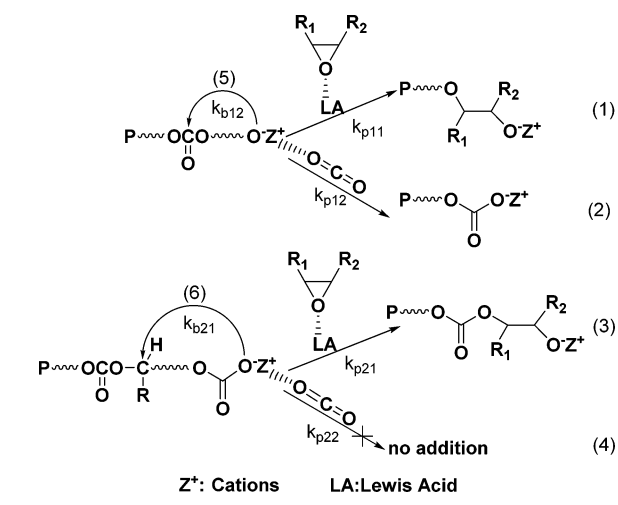


alkoxide associated with an organic cation, the strategy used here is to bring about the alternating copolymerization of CO₂ with epoxides by manipulating the reactivity of the two monomers through their activation by nonmetal external activators. The activator selected for epoxides was triethyl borane (TEB) and for CO₂ organic cations associated with the growing chains.

An example of such noncoordinating species involving lithium salts associated with triisobutyl aluminum (TiBA) and eliciting the alternating copolymerization of CO₂ with cyclohexene oxide (CHO) was recently described.¹² As illustrated in Scheme 2, the following conditions were fulfilled, allowing the alternating copolymerization to occur: (i) the rate constant of CO₂ addition to the growing alkoxide chain-end ($k_{p,1,2}$) was much higher than the rate constant of homopolymerization of epoxide due to the activation of CO₂ by Li⁺, thus preventing the formation of ether units; (ii) because of the activation of CHO by TiBA, lithium-bound carbonate chain ends could ring-open it. The respective activation of CHO and CO₂ also averted backbiting reactions ($k_{b,1,2}$ and $k_{b,2,1}$), affording perfectly

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Scheme 2. Reactions Involved in the Anionic Copolymerization of CO₂ with Epoxides

linear vs cyclic selectivity. Although very simple to implement, the system comprising lithium alkoxides or lithium salts as initiator and TiBA as CHO activator suffered from its sluggishness and its overall low activity. To address this issue of low activity of the previously investigated system, we substituted cations of larger size for lithium in association with alkoxides. We purposely selected cations capable of interacting with CO₂ and activating it and at the same time bulky enough to bring about its fast copolymerization with epoxides. We reasoned that oniums and phosphazanium cations, all organic species, should fulfill the above requirements; as for the epoxide activator, we opted for TEB, a Lewis acid strong enough to allow the addition of epoxides by growing carbonate anions and mild enough not to foster the homopolymerization of epoxides

and the subsequent formation of ether units (see Figure S1 for its mild activation of PO).

In the copolymerization of CO₂ with PO, the best performing system of all tried in this study was the one composed of tetrabutyl ammonium chloride (NBu₄⁺Cl⁻) and TEB. The latter system indeed exhibited the highest activity and excellent selectivity and at the same time afforded samples with the highest carbonate content (higher than 90% for entries 9, 15, 16 in Table 1). This NBu₄Cl/TEB-based system thus stands out with respect to the other systems studied, exhibiting respectable TON values in the range of 500 (entry 14) and TOF values close to 50 (entry 14). Phosphonium salts also produced samples with a high content in carbonate units (>90%) but were slightly less active (TON = 350). It should be noted that both onium salts and TEB were indispensable for the formation of polycarbonates because in the absence of either TEB or onium salts, no copolymerization between CO₂ and PO occurred (entries 10 and 11, Table 1).

If the size of the cations associated with the growing anions and thus their interionic distance were the sole factor controlling the overall activity of the different systems investigated, one would have ranked the latter in the following order: P₄ + BnOH > PPnCl > P₂ + BnOH ~ PBu₄Cl > NBu₄Cl.¹³ The fact that the supposedly least active NBu₄Cl/TEB system actually exhibits the highest activity (TON) indicates that besides the size of the cation both the activation of PO by TEB in (3) and that of CO₂ by the cation in (2) come also into play and determine the overall activity. In the context of this investigation NBu⁺ cations thus appeared to simultaneously afford the highest activity (highest TONs, Table 1) and yet a high polycarbonate content. In an attempt to shed light on the interaction between these organic cations (N⁺, P⁺) and CO₂, we characterized by ¹H NMR the two following mixtures: PBu₄Cl/CO₂ and NBu₄Cl/CO₂. A slight upfield chemical shift is observed in the two cases for the protons in α -

Table 1. Results of PO and CO₂ Copolymerization by Different Initiators in the Presence of TEB (2 equiv to the Initiator)^a

entry	initiator	solvent	DP targeted	yield ^b (%)	TON ^c	PPC ^d (mol %)	selectivity (%) ^e	M _{n(theo)} ^f (10 ³)	M _{n(GPC)} ^g (10 ³ /PDI)
1	<i>t</i> BuOLi	THF	50	8	—	—	— ^h	—	—
2	<i>t</i> BuONa	THF	50	10	—	76	95	0.5	1.6/1.3
3	<i>t</i> BuOK	THF	50	87	43	94	97	4.5	5.1/1.1
4 ⁱ	<i>t</i> BuOK	THF	50	5	—	—	97	—	—
5	BnOH+P ₂	THF	50	82	41	85	96	4.2	5.8/1.1
6	BnOH+P ₂	THF	100	82	82	88	97	8.4	11.0/1.1
7	BnOH+P ₄	THF	50	81	40	85	95	4.1	5.7/1.1
8	BnOH+P ₄	THF	100	78	78	85	96	8.0	9.5/1.1
9	NBu ₄ Cl	THF	50	85	42	95	97	4.3	4.8/1.1
10 ^j	NBu ₄ Cl	THF	50	11	—	—	— ^h	—	—
11 ^k	—	THF/PO	—	—	—	—	—	—	—
12	NBu ₄ Cl	bulk	50	79	39	82	95	4.0	4.7/1.1
13	NBu ₄ Cl	bulk	500	71	355	73	94	36.2	43.0/1.1
14	NBu ₄ Cl	bulk	1000	49	490	83	87	50.0	40.0/1.1
15	NBu ₄ Cl	THF	500	66	330	94	95	34.0	25.0/1.1
16	NBu ₄ Cl	THF	1000	46	460	92	94	45.0	50.0/1.2
17	PPnCl	THF	500	52	260	94	82	26.0	27.0/1.1
18	PPnCl	THF	1000	35	350	98	85	36.0	37.0/1.2
19	PBu ₄ Cl	THF	1000	19	190	99	88	20.0	15.0/1.1

^aAll polymerizations were carried out in 50 mL autoclaves under 10 atm of CO₂ at 60 °C for 10 h with equal volume of THF and PO or under conditions otherwise mentioned. ^bCalculated by gravimetry. ^cTON = mol_(PO consumed)/mol_(initiator). ^dCalculated by ¹H NMR. ^eCalculated from IR spectra. ^fCalculated based on the formula: M_{n(theo)} = 102(DP_{target}) × (yield%). ^gDetermined by GPC in chloroform with polystyrene standard. ^hOnly cyclic carbonate(propylene carbonate) was obtained. ⁱTiBA was used instead of TEB. ^jNo TEB was added. ^kOnly TEB was added with same composition of TEB and PO as in entry 9.

Table 2. Results of CHO and CO₂ Copolymerization by Different Initiators in the Presence of TEB (2 equiv to the Initiator)^a

entry	initiator	DP targeted	yield ^b (%)	TON ^c	PCHC ^d (mol %)	selectivity (%) ^e	M _{n(theo)} ^f (10 ³)	M _{n(GPC)} ^g (10 ³ /PDI)
1	tBuOK	75	96	72	>99	>99	10.2	12.0/1.1
2	tBuOK	500	22	110	>99	>99	15.6	22.2/1.1
3	BnOH/DiP-NHC ^h	100	75	75	>99	85	10.7	7.60/1.1
4 ⁱ	BnOH+P ₄	250	88	220	>99	93	31.2	14.7/1.2
5	NBu ₄ Cl	500	95	480	>99	>99	67.4	34.1/1.2
6	PPh ₄ Cl	500	88	440	>99	>99	62.5	11.8/1.2
7	PPh ₄ Cl	1000	92	920	>99	>99	131	19.3/1.4
8	PPh ₄ Cl	3000	76	2280	>99	>99	324	32.4/2.1
9	PPNCl	1000	89	890	>99	>99	126	76.4/1.2
10	PPNCl	2000	74	1480	>99	94	239	29.6/1.7
11	PPNCl	4000	90	3600	>99	95	511	28.3/1.9

^aAll the polymerizations were carried out in 50 mL autoclaves under 10 atm of CO₂ at 80 °C for 6 h with THF/CHO (1:3, v/v) or otherwise mentioned. ^bCalculated by gravimetry. ^cTON = mol_(CHO consumed)/mol_(initiator). ^dCalculated by ¹H NMR. ^eCalculated from IR spectra. ^fCalculated based on this formula: M_{n(theo)} = 142(DP_{target}) × (yield%). ^gDetermined by GPC in chloroform with polystyrene standard. ^hDiP-NHC is 1,3-diisopropylimidazol-2-ylidene. ⁱ1.0 equiv of TEB vs initiator charged.

positions to the two organic cations, indicative of a small electron density donation from CO₂ to them (Figure S2).

For comparison purpose, alkoxides associated with alkali cations (Li⁺, Na⁺, K⁺) were also investigated: In the case of K⁺, samples with high carbonate content were obtained, but the overall activity was significantly lower than that of the nonmetallic systems tried. One can also see (entry 4, Table 1) that stronger Lewis acids, e.g., TiBA instead of TEB as an activator of PO, afforded only oligomers with very low yield. Using less TEB (<2.0 equiv) resulted in a lower linear vs cyclic selectivity (entry 4, Table 2, vide infra) and even in absence of any polymerization for a ratio of TEB to initiator equal to 1 in the case of PO/CO₂ (not shown).

As expected the copolymerization solvent and its polarity play an important role in such reactions: A more dissociating medium such as THF boosts the reactivity of the growing anions and favors a higher propagation rate as compared to experiments carried out in toluene where polymerization was very sluggish. No polymerization occurred in chloroform, dichloromethane, and dioxane (not shown). In bulk, slightly higher activities were observed at the expense of a lower linear vs cyclic selectivity.

The analysis by GPC, MALDI-Tof, and NMR also provided useful and compelling information. All the samples characterized by GPC exhibited narrow molar mass distribution ($\bar{D} = M_w/M_n < 1.20$) and expected molar masses which buttresses the livingness of the copolymerization triggered by the systems previously described. The high carbonate content and even alternating structures could be precisely determined by ¹H NMR characterization (Figure S3). MALDI-Tof also provided useful information about the initiation step and the structure of the carbonate units formed (Figure S4); onium chloride first ring-opened the PO before the addition of CO₂ by the alkoxide formed. In contrast, alkoxides associated with phosphazanium or potassium cations, which afforded partly alternating poly(propylene carbonate) (PPC), first reacted either with CO₂ or PO, indicating that both reactions are possible. In agreement with the NMR characterization MALDI-Tof clearly shows the formation of one main population (a) of perfectly alternating polycarbonates with Bu₄NCl as initiator and TEB as activator. A second population (b) of less intensity including one additional ether unit can also be seen from the same initiating system (Figure S4B). For the sample initiated by potassium alkoxide, four populations were formed as indicated

in the MALDI-Tof spectrum (Figure S4A). Besides the perfectly alternating polycarbonate family (c) three other populations containing one (a), two (b), and three (d) additional ether units can be seen. The characterization of the regioselectivity of the samples was carried out by ¹³C NMR (Figure S5) which showed the presence of 82% of head/tail linkages, a value comparable to that measured for samples generated from cobalt-salen catalysts^{6e,f} but much higher than the one exhibited by copolymers obtained from zinc glutarate (~60% HT linkages),¹⁴ and zinc β-diiminato (~54% HT linkages) catalysts.^{4c}

The systems described above were also tested in the copolymerization of CO₂ with CHO. As listed in Table 2, in all cases perfectly alternating polycarbonates (Figure S6 for ¹H NMR characterization) were obtained with TON and TOF values up to 3600 and 600, respectively (entry 11, Table 2). From the TON values obtained, the following ranking could be established for the respective activity of the different systems investigated: phosphonium > ammonium > phosphazanium > imidazolium > potassium, which almost follows the same order as the one observed for the copolymerization of PO with CO₂. When targeting high molar masses and thus increasing the feeding ratio of CHO to initiator, the linear vs cyclic selectivity slightly decreased, and the GPC traces of the samples isolated tended to become broad, or even to exhibit a bimodal distribution. A series of control experiments targeting different molar masses with PPNCl as initiator (see Table S1, Figure S7) showed that the molar masses eventually measured by GPC were lower than the expected ones, which is very likely due to the presence of water acting as transfer agent and thus affording a second population of α,ω-dihydroxyl polycarbonates besides the main population created by the initiator. Such bimodal distributions were also observed by other authors, in their attempts to synthesize samples of high molar mass from the copolymerization of CHO with CO₂.^{8a,10b,d,e}

In contrast, samples of low DP_n exhibited narrow and unimodal distribution in close agreement with the expected values (Tables 2 and S1, Figure S7). Such samples of low molar masses initiated respectively by potassium alkoxide and Bu₄NCl were subjected to characterization by MALDI-Tof (Figure S8). In both cases only one main population with a peak to peak mass difference of 142.1 was observed, corresponding to the expected alternating structure and underpinning the incorporation of either chloride or alkoxyl moieties at the chain ends

during the initiating step. The poly(cyclohexene carbonate) (PCHC) produced, on the other hand, showed no stereoselectivity with almost equal intensities of the peak at 153.8 ppm and those at 153.3, 153.2, 153.1 ppm (Figure S9).^{5c}

Here, we have demonstrated that alternating polycarbonates could be synthesized for the first time through the anionic copolymerization of epoxides with CO₂ under metal-free conditions: such a method which relies on the activation of both epoxides and CO₂ by Lewis acids and appropriate organic cations, respectively, is facile, versatile, and applicable to the copolymerization of CO₂ with either PO or CHO; the TON values (around 500 for PPC and 3600 for PCHC) are in the range of those measured for some well-known organometallic systems.^{4c,5a,6g,10d} The polycarbonates synthesized under such metal-free conditions do not exhibit coloration and are thus free of metal residues; they could well be used without further purification in areas such as food package, coating, biological and electronic fields. Their respectable TON values combined with the easy availability of both initiator and activator make polycarbonates produced under these conditions very attractive for various applications. Metal-free syntheses of polycarbonates with other epoxides than PO or CHO and structures are currently investigating in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06679.

Experimental details and data (PDF)

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Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7*, 287–292.
- (2) Trott, G.; Saini, P.; Williams, C. *Philos. Trans. R. Soc., A* **2016**, *374*, 20150085.
- (3) (a) Ikpo, N.; Flogeras, J. C.; Kerton, F. M. *Dalton Trans.* **2013**, *42*, 8998–9006. (b) Darensbourg, D. J.; Wilson, S. J. *Green Chem.* **2012**, *14*, 2665. (c) Kember, M. R.; Buchard, A.; Williams, C. K. *Chem. Commun. (Cambridge, U. K.)* **2011**, *47*, 141–163. (d) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388–2410. (e) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618–6639. (f) Sugimoto, H.; Inoue, S. J. *Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5561–5573. (g) Lu, X.-B.; Ren, W.-M.; Wu, G.-P. *Acc. Chem. Res.* **2012**, *45*, 1721–1735.
- (4) (a) Kissling, S.; Lehenmeier, M. W.; Altenbuchner, P. T.; Kronast, A.; Reiter, M.; Deglmann, P.; Seemann, U. B.; Rieger, B. *Chem. Commun.* **2015**, *51*, 4579–4582. (b) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S. I.; Yun, H.; Lee, H.; Park, Y. W. *J. Am. Chem. Soc.* **2005**, *127*, 3031–3037. (c) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284–14285. (d) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749. (e) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018–11019.
- (5) (a) Darensbourg, D. J.; Ulusoy, M.; Karroonnirum, O.; Poland, R. R.; Reibenspies, J. H.; Çetinkaya, B. *Macromolecules* **2009**, *42*, 6992–6998. (b) Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C.; Fang, C. C. J.

Am. Chem. Soc. **2003**, *125*, 7586–7591. (c) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335–6342.

(6) (a) Ren, W. M.; Liu, Z. W.; Wen, Y. Q.; Zhang, R.; Lu, X. B. *J. Am. Chem. Soc.* **2009**, *131*, 11509–11518. (b) S, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 7306–7309. (c) Noh, E. K.; Na, S. J.; S, S.; Kim, S. W.; Lee, B. Y. *J. Am. Chem. Soc.* **2007**, *129*, 8082–8083. (d) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7274–7277. (e) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869–10878. (f) Lu, X. B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574–3577. (g) Qin, Z.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484–5487.

(7) (a) Sheng, X.; Wu, W.; Qin, Y.; Wang, X.; Wang, F. *Polym. Chem.* **2015**, *6*, 4719–4724. (b) Wu, W.; Sheng, X.; Qin, Y.; Qiao, L.; Miao, Y.; Wang, X.; Wang, F. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 2346–2355.

(8) (a) Kember, M. R.; Williams, C. K. *J. Am. Chem. Soc.* **2012**, *134*, 15676–15679. (b) Xiao, Y.; Wang, Z.; Ding, K. *Macromolecules* **2006**, *39*, 128–137.

(9) (a) Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 212–214. (b) Nakano, K.; Kobayashi, K.; Ohkawara, T.; Imoto, H.; Nozaki, K. *J. Am. Chem. Soc.* **2013**, *135*, 8456–8459.

(10) (a) Ohkawara, T.; Suzuki, K.; Nakano, K.; Mori, S.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136*, 10728–10735. (b) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911–11924. (c) Saini, P. K.; Romain, C.; Williams, C. K. *Chem. Commun. (Cambridge, U. K.)* **2014**, *50*, 4164–4167. (d) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 931–933. (e) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.-i.; Yun, H.; Lee, H.; Park, Y.-W. *J. Am. Chem. Soc.* **2005**, *127*, 3031–3037. (f) Garden, J. A.; Saini, P. K.; Williams, C. K. *J. Am. Chem. Soc.* **2015**, *137*, 15078–15081.

(11) (a) Hongfa, C.; Tian, J.; Andreatta, J.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun.* **2008**, 975–977. (b) Hauenstein, O.; Reiter, M.; Agarwal, S.; Rieger, B.; Greiner, A. *Green Chem.* **2016**, *18*, 760–770. (c) Bahramian, B.; Ma, Y.; Rohanizadeh, R.; Chrzanowski, W.; Dehghani, F. *Green Chem.* **2016**, *18*, 3740.

(12) Zhang, D.; Zhang, H.; Hadjichristidis, N.; Gnanou, Y.; Feng, X. *Macromolecules* **2016**, *49*, 2484–2492.

(13) Labbé, A.; Carlotti, S.; Billouard, C.; Desbois, P.; Deffieux, A. *Macromolecules* **2007**, *40*, 7842–7847.

(14) Chisholm, M. H.; Navarro-Llobet, D.; Zhou, Z. *Macromolecules* **2002**, *35*, 6494–6504.