

Alternating Copolymerization of Propylene Oxide with Biorenewable Terpene-Based Cyclic Anhydrides: A Sustainable Route to Aliphatic Polyesters with High Glass Transition Temperatures**

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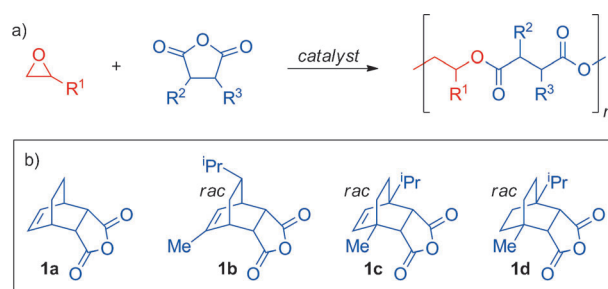
Abstract: The alternating copolymerization of propylene oxide with terpene-based cyclic anhydrides catalyzed by chromium, cobalt, and aluminum salen complexes is reported. The use of the Diels–Alder adduct of α -terpinene and maleic anhydride as the cyclic anhydride comonomer results in amorphous polyesters that exhibit glass transition temperatures (T_g) of up to 109°C. The polymerization conditions and choice of catalyst have a dramatic impact on the molecular weight distribution, the relative stereochemistry of the diester units along the polymer chain, and ultimately the T_g of the resulting polymer. The aluminum salen complex exhibits exceptional selectivity for copolymerization without transesterification or epimerization side reactions. The resulting polyesters are highly alternating and have high molecular weights and narrow polydispersities.

Concern regarding the long-term supply of petroleum has motivated the development of biorenewable plastics.^[1] Aliphatic polyesters (specifically, polymers that do not contain aromatic groups in the main chain or pendant substituents) are a compelling alternative to petroleum-based polymers because in many cases they are biorenewable^[2] and biodegradable.^[2,3] The most commercially successful aliphatic polyester today, polylactide (PLA), is derived from carbohydrates and has found use in biomedical devices^[4] and a variety of consumer products.^[5] Unfortunately, amorphous PLA is a poor alternative to glassy petroleum-based polymers such as polystyrene, which has a glass transition temperature (T_g) of 100°C,^[6] because it deforms at moderate temperature as a result of its modest T_g (50–60°C).^[4] Given the ubiquity of glassy polymers with high T_g values, there is substantial demand for an aliphatic polyester that could serve as a sustainable alternative.

Previous studies of polymer structure–property relationships predict that an amorphous, high- T_g aliphatic polyester will be stereo- and regiorregular and have a rigid backbone.^[6] Stereo- and regiorregularity inhibit the formation of polymer

crystallites, and bulky or cyclic groups rigidify polymer chains by restricting segmental motion.^[6] Early examples derived from bicyclic carbohydrate-based monomers exhibit T_g values up to 75°C; however, these polymers are synthesized by energy-intensive processes.^[7] Recent work has focused on the ring-opening polymerization of bulky glycolide-based monomers.^[8] In 2007, Baker and co-workers^[9] synthesized 3,6-dicyclohexylglycolide, which was polymerized to produce a polyester with T_g values as high as 104°C. Hillmyer and co-workers^[10] reported a series of spiro bicyclic lactide derivatives that can be polymerized to give aliphatic polyesters with T_g values of up to 119°C.^[10b] Although these poly(glycolide) derivatives exhibit higher T_g values than that of amorphous PLA, the monomers require multistep syntheses and stoichiometric reagents.

An alternative method to synthesize aliphatic polyesters is the alternating copolymerization of epoxides with cyclic anhydrides (Scheme 1 a). Our group and others have utilized a variety of zinc(II),^[11] aluminum(III),^[12] chromium(III),^[12,13]



Scheme 1. a) Alternating copolymerization of epoxides with cyclic anhydrides. b) Cyclic anhydride comonomers investigated in this work.

and cobalt(III)^[12,14] complexes to catalyze this copolymerization. To date, none of the aliphatic polyesters synthesized by this process have exhibited T_g values greater than 100°C. We hypothesized that Diels–Alder adducts of cyclic monoterpene dienes and maleic anhydride could serve as inexpensive and sustainable comonomers for this application. Terpenes are an abundant, biorenewable source of chemical building blocks primarily obtained from tree resin and citrus,^[15] and few reports exist regarding their use as a feedstock for the production of aliphatic polyesters.^[15d,e] Propylene oxide (PO) is an appealing comonomer owing to its low cost, ease of handling, high reactivity, and recently improved industrial synthesis.^[16] Herein we report the metal-catalyzed copolymerization of propylene oxide with terpene-based cyclic anhydrides to produce high- T_g aliphatic polyesters.

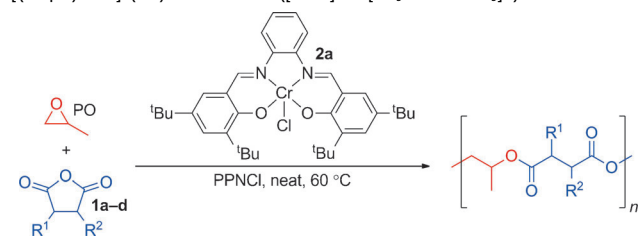
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The cyclic anhydrides **1a**, **1b**, and **1c** (Scheme 1b) were synthesized by reacting 1,3-cyclohexadiene, α -phellandrene, and α -terpinene, respectively, with maleic anhydride. Although **1a** is not biosourced, it was included as an unsubstituted comparison to **1b** and **1c**. The saturated cyclic anhydride **1d** was prepared by catalytic hydrogenation of **1c**. The copolymerization of **1a–c** with an excess of neat racemic PO in the presence of [(salph)CrCl] (**2a**, salph = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene) as a catalyst and PPNCl ([PPN]⁺ = [Ph₃P=N=PPh₃]⁺) as a cocatalyst was investigated (Table 1). Complex **2a** has previously been found

Table 1: Polymerization of PO with cyclic anhydrides **1a–1d** using [(salph)CrCl] (**2a**) and PPNCl ([PPN]⁺ = [Ph₃P=N=PPh₃]⁺).^[a]



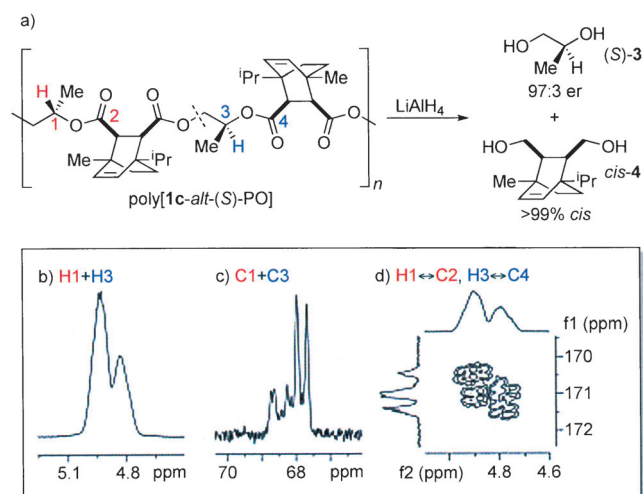
Entry	1	Time [h]	Conv. [%] ^[b]	<i>M_n</i> [kDa] ^[c]	<i>M_w</i> / <i>M_n</i> ^[c]	<i>T_g</i> [°C] ^[d]	<i>T_d</i> [°C] ^[e]
1	1a	2.0	85	17.5	1.32	83	286
2	1b	1.0	77	21.9	1.26	86	313
3	1c	2.0	91	21.2	1.24	106	314
4	1d	0.5	74	19.9	1.21	86	331

[a] Reactions were performed in neat PO (6.4 mmol), [PO]/[**1**]/[**2a**]/[PPNCl] = 1000:200:1:1. [b] Conversion of **1**, determined by ¹H NMR spectroscopy. [c] Determined by GPC in THF at 30 °C, calibrated with polystyrene standards. [d] Determined by DSC. [e] Decomposition temperature, determined by TGA.

to be an active catalyst for the copolymerization of epoxides with cyclic anhydrides.^[12c,13a,17] Polymerizations were performed at 60 °C and reached high conversion in 2 h or less. The resulting polyesters are amorphous with molecular weights up to 21.9 kDa, *M_w*/*M_n* values of 1.21–1.32, and *T_d* values of 286–331 °C. ¹H and ¹³C NMR spectroscopic analyses revealed that the copolymers have highly alternating structures.^[18]

The structure of the cyclic anhydride comonomers dramatically influences the *T_g* values of the resulting polyesters. The α -phellandrene-based poly(**1b-alt**-PO) exhibits a *T_g* of 86 °C (entry 2), which is only slightly higher than that of the comparatively unsubstituted poly(**1a-alt**-PO) (83 °C, entry 1). The α -terpinene-based poly(**1c-alt**-PO) exhibits a much higher *T_g* (106 °C, entry 3) than that of either the 1,3-cyclohexadiene- or α -phellandrene-based polymers, which is consistent with the prediction that the spatial orientation of the methyl and isopropyl groups along the polymer chains would have a strong influence on *T_g*. Surprisingly, the saturated version of this polymer, poly(**1d-alt**-PO), has a *T_g* of only 86 °C (entry 4), further demonstrating that minor structural changes have a major effect on the *T_g* values for these types of polymers.

Given the high *T_g* and thermal stability of poly(**1c-alt**-PO), the microstructure was further investigated using post-polymerization degradation studies and NMR spectroscopy. (*S*)-PO was copolymerized with **1c** under the conditions described for entry 3 of Table 1 to produce poly(**1c-alt**-(*S*)-PO).^[19] Reductive degradation of the polymer yielded a mixture of (*S*)-propylene glycol [(*S*)-**3**, 97:3 e.r.] and racemic *cis*-**4** (Scheme 2a). The high enantiopurity of (*S*)-**3** indicates



Scheme 2. Investigation of the structure of poly(**1c-alt**-(*S*)-PO).

a) Reductive degradation of poly(**1c-alt**-(*S*)-PO). b) ¹H NMR signal of the methine protons of the propylene glycol units. c) ¹³C NMR signal of the methine carbons of the propylene glycol units. d) HMBC NMR correlation between the methine protons of the propylene glycol units and the carbonyl carbons of the diester units.

that **2a** is highly regioselective for ring-opening (*S*)-PO at the methylene carbon and that the polymer is thus highly regioregular with respect to the propylene glycol units. The stereochemistry of *cis*-**4** confirms that the relative stereochemistry of **1c** is retained under these conditions.

The regio- and stereoregularity of the diester units was qualitatively characterized using 1D- and 2D-NMR spectroscopy experiments. For the diester groups directly adjacent to the methine groups of the (*S*)-propylene glycol units, there are four regio- and stereochemical possibilities for the incorporation of **1c**, which are outlined in the Supporting Information, Scheme S2. Although high regio- and stereoregularity is observed for the (*S*)-propylene glycol units, the complex fine features observed in the ¹H and ¹³C NMR spectra suggest that the diester units are regio- and stereo-irregular. In particular, the methine proton of the (*S*)-propylene glycol unit exhibits two broad overlapping signals at 4.7–5.0 ppm in the ¹H NMR spectrum (Scheme 2b), and the carbon atom of this methine group exhibits a complex ¹³C NMR signal at 67.5–68.9 ppm (Scheme 2c). The HMBC NMR spectrum further supports this hypothesis, as four major sets of correlations between the methine protons of the propylene glycol units and the carbonyl carbons of the diester units are observed (Scheme 2d).

In an attempt to further increase the *T_g* and *M_n* of poly(**1c-alt**-PO), the copolymerization of **1c** with PO was optimized

Table 2: Optimization of conditions for the copolymerization of **1c** with PO using [(salph)MCl] (M = Cr, Co, and Al).^[a]

Entry	Cat.	[PO]/[2] ^[b]	[1c]/[2] ^[b]	Time [h]	Conv. [%] ^[c]	M_n [kDa] ^[d]	M_w/M_n ^[d]	% <i>cis</i> ^[e]	T_g [°C] ^[f]
1	2a	500	100	0.75	86	11.4	1.25	> 99	105
2	2a	500	100	2.0	> 99	18.8	1.66	52	91
3 ^[g]	2a	100	150	3.0	> 99 ^[h]	12.2	1.22	> 99	102
4	2b	500	100	2.0	76	9.0	1.18	> 99	101
5	2b	500	100	3.0	> 99	14.6	1.72	10	78
6	2c	500	100	1.0	63	7.4	1.11	> 99	97
7	2c	500	100	2.5	> 99	10.2	1.16	97	103
8	2c	500	100	5.0	> 99	9.8	1.16	95	102
9	2c	1000	200	4.0	> 99	22.5	1.28	88	104
10	2c	2000	400	9.0	> 99	36.7	1.30	94	107
11	2c	4000	800	20.5	> 99	55.4	1.29	98	109

[a] Reactions were performed in neat PO (0.45 mL, 6.4 mmol) unless noted otherwise. [b] [**2**]/[PPNCI] = 1:1. [c] Conversion of **1c** unless noted otherwise, determined by ¹H NMR spectroscopy. [d] Determined by GPC in THF at 30 °C, calibrated with polystyrene standards. [e] Relative stereochemistry of the diester units, determined by ¹³C NMR spectroscopy. [f] Determined by DSC. [g] Reaction performed with 0.09 mL PO (1.3 mmol) in 0.36 mL toluene. [h] Conversion of PO, determined by ¹H NMR spectroscopy.

using a variety of conditions and catalysts (Table 2). At a higher catalyst loading, complex **2a** reaches 86% conversion of **1c** in 45 min to give poly(**1c-alt**-PO) with an M_n of 11.4 kDa, an M_w/M_n of 1.25, and a T_g of 105 °C (entry 1). The α -methine region of the ¹³C NMR spectrum is diagnostic for the relative stereochemistry of the diester units; the two resonances at 52.3–53.2 and 55.3–56.2 ppm correspond to *cis*-diester units (Figure 1a).

When the copolymerization was performed for 2 h (entry 2), **1c** is fully consumed. The resulting polymer has

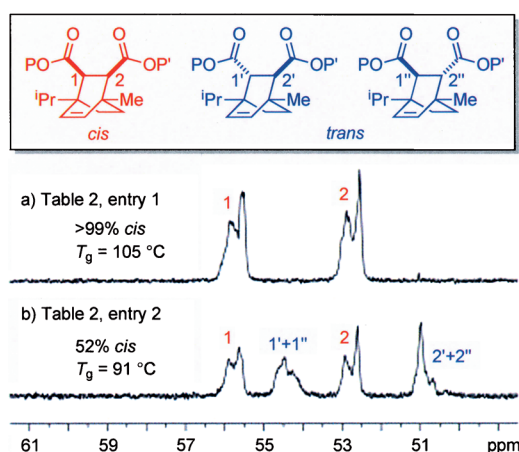


Figure 1. Diagnostic α -methine region of the ¹³C NMR spectra of poly(**1c-alt**-PO) produced using **2a** for a) 45 min and b) 2 h (P and P' = polymer chain).

a broader M_w/M_n (1.66 vs. 1.25), indicating that polymer transesterification occurs after high conversion of **1c** is reached. Unexpectedly, this polymer exhibits new sets of signals in the ¹H and ¹³C NMR spectra that correspond to *trans*-diester units.^[20] In the ¹³C NMR spectrum, two new resonances at 50.5–51.3 and 54.0–54.9 ppm are observed in the α -methine region (Figure 1b). Integration of these signals revealed that only 52% of the diester units are *cis*. Although the polymer has a higher molecular weight, a significantly lower T_g is observed (91 vs. 105 °C). We hypothesize that *trans*-diester units impart less rigidity to the polymer chain than *cis*-diester units and are thus detrimental to the T_g of the polymer.

Because the polymerization was performed in excess PO, the active species at the end of the polymerization is proposed to be a chromium(III) alkoxide, which may cause polymer transesterification and epimerization of diester stereochemistry. We reasoned that

it would be thermodynamically unfavorable for a chromium-(III) carboxylate to undergo these side reactions. Indeed, when the polymerization was conducted in toluene with an excess of **1c** relative to PO, full conversion of PO is achieved without epimerization or transesterification (entry 3). However, it is more convenient to perform the reaction in neat PO because it is easier to remove unreacted PO from the polymer than unreacted **1c**. Excess PO can also be easily recovered by distillation and recycled in future polymerizations.

In an attempt to minimize transesterification and epimerization, the effect of catalyst Lewis acidity was investigated by screening cobalt and aluminum analogues of **2a**. The cobalt complex **2b** is less active than **2a**, reaching only 76% conversion of **1c** in 2 h (entry 4), though it exhibits similar regioselectivity for ring-opening of PO.^[21] When the reaction was performed for 3 h, **1c** is fully consumed. The resulting polymer has an M_w/M_n of 1.72 and a T_g of only 78 °C (entry 5). A substantial amount of epimerization is observed under these conditions, as only 10% of the diester units of this polymer are *cis*. Additionally, polyether linkages are detected by ¹³C NMR spectroscopy, which may also lower the T_g (Supporting Information, Figure S2).

The aluminum complex **2c** has similar activity to that of **2a**, reaching 63% conversion in 1 h (entry 6). Complex **2c** is also highly regioselective for the ring-opening of PO at its methylene carbon.^[22] When the reaction was quenched after 2.5 h, full conversion of **1c** is observed, and the resulting polyester has an M_w/M_n of 1.16 and a T_g of 103 °C (entry 7). No polyether linkages are detectable by ¹³C NMR spectroscopy.

copy and 97% *cis*-diester units remain, indicating that **2c** is highly selective for copolymerization without significant transesterification, epoxide homopolymerization, or epimerization. When the reaction time was further increased to 5 h, the resulting polymer has essentially the same M_w/M_n (1.16) and slightly decreased *cis*-diester content (95%), demonstrating that **2c** remains highly selective for copolymerization with extended reaction times (entry 8). By decreasing the catalyst loading of **2c** and employing long reaction times to ensure that **1c** was fully consumed, polyesters with M_n values up to 55.4 kDa and T_g values up to 109°C are obtained while maintaining low M_w/M_n values and high *cis*-diester contents (entries 8–11). We propose that the higher Lewis acidity of aluminum salens relative to that of chromium and cobalt salens results in a less nucleophilic and less basic alkoxide species at the end of the polymerization, which minimizes transesterification and epimerization.^[23]

In conclusion, we report the copolymerization of terpene-based cyclic anhydrides with propylene oxide using metal salen catalysts. The copolymer of propylene oxide and the Diels–Alder adduct of maleic anhydride and α -terpinene exhibits T_g values up to 109°C. Given the low cost of the monomers, exceptional T_g , and high content of renewable material (47% w/w), this polyester could potentially serve as a sustainable alternative to petroleum-based high- T_g polymers. The polymerization conditions and choice of catalyst have a dramatic effect on the structure of the resulting polymer. By tuning the Lewis acidity of the catalyst, undesirable side reactions were minimized. We are currently investigating the physical properties of these polymers and exploring the effect of catalyst structure on this class of polymerization.

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- [1] a) A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484–489; b) A. Gandini, *Green Chem.* **2011**, *13*, 1061–1083; c) C. Vilela, A. F. Sousa, A. C. Fonseca, A. C. Serra, J. F. J. Coelho, C. S. R. Freire, A. J. D. Silvestre, *Polym. Chem.* **2014**, *5*, 3119–3141.
- [2] a) W. Amass, A. Amass, B. Tighe, *Polym. Int.* **1998**, *47*, 89–144; b) R. A. Gross, B. Kalra, *Science* **2002**, *297*, 803–807; c) S. Mecking, *Angew. Chem. Int. Ed.* **2004**, *43*, 1078–1085; *Angew. Chem.* **2004**, *116*, 1096–1104; d) M. Vert, *Biomacromolecules* **2005**, *6*, 538–546; e) O. Coulembier, P. Degée, J. L. Hedrick, P. Dubois, *Prog. Polym. Sci.* **2006**, *31*, 723–747; f) C. K. Williams, *Chem. Soc. Rev.* **2007**, *36*, 1573–1580.
- [3] R.-J. Müller, I. Kleeberg, W.-D. Deckwer, *J. Biotechnol.* **2001**, *86*, 87–95.
- [4] Y. Ikada, T. Hideto, *Macromol. Rapid Commun.* **2000**, *21*, 117–132.
- [5] a) E. T. H. Vink, K. R. Rábago, D. A. Glassner, P. R. Gruber, *Polym. Degrad. Stab.* **2003**, *80*, 403–419; b) R. Auras, B. Harte, S. Selke, *Macromol. Biosci.* **2004**, *4*, 835–864; c) R. Datta, M. Henry, *J. Chem. Technol. Biotechnol.* **2006**, *81*, 1119–1129; d) A. P. Gupta, V. Kumar, *Eur. Polym. J.* **2007**, *43*, 4053–4074.
- [6] G. Odian, *Principles of Polymerization*, 4th ed., Wiley, Hoboken, **2004**.
- [7] a) F. Fenouillot, A. Rousseau, G. Colomines, R. Saint-Loup, J. P. Pascault, *Prog. Polym. Sci.* **2010**, *35*, 578–622; b) D. S. van Es, *J. Renewable Mater.* **2013**, *1*, 61–72; c) C. Lavilla, A. Alla, A. Martinez de Ilarduya, S. Munoz-Guerra, *Biomacromolecules* **2013**, *14*, 781–793.
- [8] J. M. Becker, R. J. Pounder, A. P. Dove, *Macromol. Rapid Commun.* **2010**, *31*, 1923–1937.
- [9] F. Jing, M. R. Smith, G. L. Baker, *Macromolecules* **2007**, *40*, 9304–9312.
- [10] a) F. Jing, M. A. Hillmyer, *J. Am. Chem. Soc.* **2008**, *130*, 13826–13827; b) G. L. Fiore, F. Jing, J. V. G. Young, C. J. Cramer, M. A. Hillmyer, *Polym. Chem.* **2010**, *1*, 870–877.
- [11] a) R. C. Jeske, A. M. DiCiccio, G. W. Coates, *J. Am. Chem. Soc.* **2007**, *129*, 11330–11331; b) R. C. Jeske, J. M. Rowley, G. W. Coates, *Angew. Chem. Int. Ed.* **2008**, *47*, 6041–6044; *Angew. Chem.* **2008**, *120*, 6130–6133.
- [12] a) A. M. DiCiccio, G. W. Coates, *J. Am. Chem. Soc.* **2011**, *133*, 10724–10727; b) C. Robert, F. de Montigny, C. M. Thomas, *Nat. Commun.* **2011**, *2*, 586; c) E. Hosseini Nejad, C. G. W. van Melis, T. J. Vermeer, C. E. Koning, R. Duchateau, *Macromolecules* **2012**, *45*, 1770–1776; d) A. Bernard, C. Chatterjee, M. H. Chisholm, *Polymer* **2013**, *54*, 2639–2646.
- [13] a) S. Huijser, E. Hosseini Nejad, R. Sablong, C. de Jong, C. E. Koning, R. Duchateau, *Macromolecules* **2011**, *44*, 1132–1139; b) D. J. Daresbourg, R. R. Poland, C. Escobedo, *Macromolecules* **2012**, *45*, 2242–2248; c) J. Liu, Y.-Y. Bao, Y. Liu, W.-M. Ren, X.-B. Lu, *Polym. Chem.* **2013**, *4*, 1439–1444.
- [14] Z. Duan, X. Wang, Q. Gao, L. Zhang, B. Liu, I. Kim, *J. Polym. Sci. Part A* **2014**, *52*, 789–795.
- [15] a) K. A. D. Swift, *Top. Catal.* **2004**, *27*, 143–155; b) C. S. Sell, *Terpenoids, Kirk-Othmer Encycl. Chem. Tech.*, Vol. 24, 5th ed., Wiley, Hoboken, **2006**, pp. 468–591; c) A. Behr, L. Johnen, *ChemSusChem* **2009**, *2*, 1072–1095; d) P. A. Wilbon, F. Chu, C. Tang, *Macromol. Rapid Commun.* **2013**, *34*, 8–37; e) D. Dakshinamoorthy, A. K. Weinstock, K. Damodaran, D. F. Iwig, R. T. Mathers, *ChemSusChem* **2014**, *7*, 2923–2929.
- [16] A. H. Tullo, P. L. Short, *Chem. Eng. News* **2006**, *84*, 22–23.
- [17] a) E. Hosseini Nejad, A. Paoniasari, C. E. Koning, R. Duchateau, *Polym. Chem.* **2012**, *3*, 1308–1313; b) E. H. Nejad, A. Paoniasari, C. G. W. van Melis, C. E. Koning, R. Duchateau, *Macromolecules* **2013**, *46*, 631–637.
- [18] A detailed discussion regarding the alternating microstructure of these polyesters can be found in the Supporting Information.
- [19] Poly(**1c-alt**-(S)-PO) has an M_n of 21.4 kDa, a M_w/M_n of 1.20, and a T_g of 105°C.
- [20] A detailed discussion regarding the epimerization of diester stereochemistry can be found in the Supporting Information.
- [21] (S)-PO was copolymerized with **1c** using **2b** under the conditions described for Table 2, entry 4. The polymer was degraded to yield (S)-**3** with an e.r. of 97:3.
- [22] (S)-PO was copolymerized with **1c** using **2c** under the conditions described in Table 2, entry 6. The polymer was degraded to yield (S)-**3** with an e.r. of 96:4.
- [23] Sequential monomer addition experiments excluded the possibility of irreversible catalyst deactivation after reaching high conversion of **1c**; please see the Supporting Information for details.