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Enantioselective Epoxide Polymerization Using a Bimetallic Cobalt Catalyst

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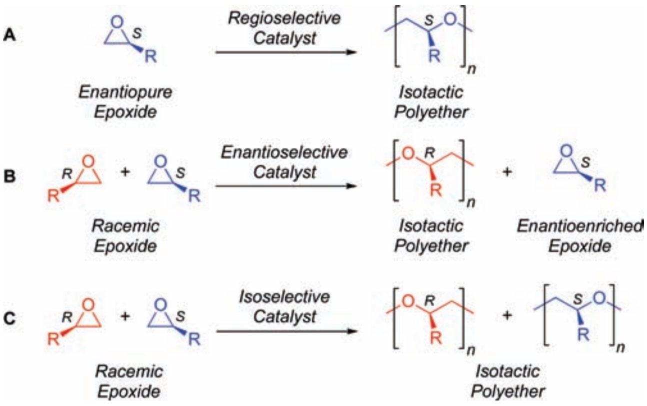
Abstract: A highly active enantiopure bimetallic cobalt complex was explored for the enantioselective polymerization of a variety of monosubstituted epoxides. The polymerizations were optimized for high rates and stereoselectivity, with *s*-factors ($k_{\text{fast}}/k_{\text{slow}}$) for most epoxides exceeding 50 and some exceeding 300, well above the threshold for preparative utility of enantiopure epoxides and isotactic polyethers. Values for *mm* triads of the resulting polymers are typically greater than 95%, with some even surpassing 98%. In addition, the use of a racemic catalyst allowed the preparation of isotactic polyethers in quantitative yields. The thermal properties of these isotactic polyethers are presented, with many polymers exhibiting high T_m values. This is the first report of the rapid synthesis of a broad range of highly isotactic polyethers via the enantioselective polymerization of racemic epoxides.

Introduction

Polyethers are an important class of materials with great commercial value, commonly used to manufacture products such as foams, sealants, surfactants, elastomers, and biomedical components.[1] Traditionally, polyethers have been synthesized using cationic, anionic,[2] and metal-mediated polymerizations[3] with little to no stereocontrol. Despite the importance of these polymers, synthetic methods to produce their stereoregular analogues with improved thermal and mechanical properties have been relatively unsuccessful.[4]

Several methods for the synthesis of isotactic polyethers are shown in Scheme 1. In route A, enantiopure epoxides are polymerized using a regioselective catalyst to produce isotactic polyethers.[5] Enantioselective polymerizations (also known as stereoelective or kinetic resolution polymerizations), shown in route B, are attractive methods that selectively enchain one enantiomer of racemic epoxides to produce isotactic polyethers and enantiopure epoxides.[6] An aluminum salen complex was shown by Spassky et al. to display an *s*-factor ($k_{\text{fast}}/k_{\text{slow}}$) of 1.3 with a turnover frequency (TOF) of 0.2 h^{-1} for the oligomerization of propylene oxide (PO).[7] Finally, route C shows the formation of isotactic polyethers from racemic epoxides using an isoselective catalyst. Heterogeneous catalysts have been reported but suffer from low stereoselectivities, and they produce product mixtures containing atactic polymer.[6a] Regarding homogeneous catalysts, aluminum porphyrin catalysts have been reported to produce partially isotactic polypropylene oxide (PPO) with an *m*-dyad content of 69%.[8] A zinc cluster used by Tsuruta enabled the isoselective polymerization of *rac*-PO with

Scheme 1. Synthetic Routes to Isotactic Polyethers



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[1] (a) *Encyclopedia of Chemical Technology*; Kroschwitz, J. I.,; Howe-Grant, M., Eds.; Wiley: Chichester, 1993; Vol. 8, pp 1079−1093. (b) Stevens, M. P. *Polymer Chemistry*; Oxford University Press: New York, 1999; Chapter 11. (c) Wilms, D.; Stiriba, S.; Frey, H. *Acc. Chem. Res.* **2010**, *43*, 129–141.

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[6] (a) For a review, see: Ajiro, H.; Allen, S. D.; Coates, G. W. Discrete Catalysts for Stereoselective Epoxide Polymerization. In *Stereoselective Polymerization with Single Site Catalysts*; Baugh, L. S., Canich, J. M., Eds.; CRC Press: Boca Raton, 2008; Chapter 24, pp 627−644. (b) Haubenstock, H.; Panchalingam, V.; Odian, G. *Makromol. Chem.* **1987**, *188*, 2789–2799. (c) Takeda, N.; Inoue, S. *Makromol. Chem.* **1978**, *179*, 1377–1381. (d) Le Borgne, A.; Spassky, N.; Jun, C. L.; Momtaz, A. *Makromol. Chem.* **1988**, *189*, 637–650. (e) Wu, B.; Harlan, C. J.; Lenz, R. W.; Barron, A. R. *Macromolecules* **1997**, *30*, 316–118. (f) Zhang, Z.; Xu, J.; Yu, Y. *J. Appl. Polym. Sci.* **2002**, *84*, 1223–1232.

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[8] (a) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1162–1166. (b) Le Borgne, A.; Spassky, N.; Jun, C. L.; Momtaz, A. *Makromol. Chem.* **1988**, *189*, 637–650.

10.1021/ja1058422

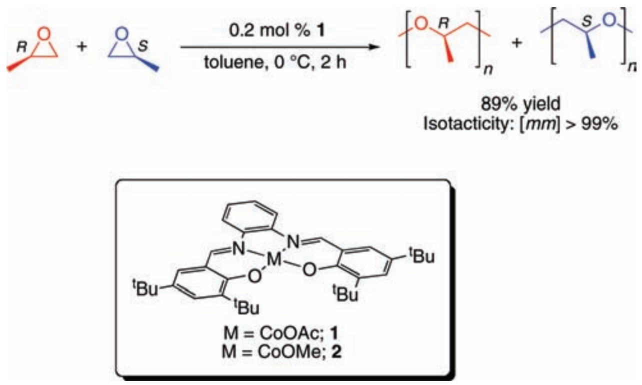

Figure 1. Isospecific polymerization of propylene oxide using **1**.

a moderate *m*-dyad content of 79% and TOF of 0.9 h^{-1}.[9] Until recently, these were the most successful catalysts for synthesizing isotactic PPO from *rac*-PO. The low stereoselectivities, low activities, formation of atactic impurities, and limited substrate scope has highlighted the need for developing active catalysts that are both enantio- and isoselective for a wide range of epoxides.

In 2005, we reported a highly active and isoselective (*mm*-triad content, [*mm*] > 99%) cobalt catalyst (**1**; Figure 1) for the polymerization of *rac*-PO.[10] Complex **1** displayed only modest activity for butene oxide and hexene oxide, despite being structurally similar to PO, while all other epoxides showed no activity. Although suitable single crystals of **1** could not be obtained, a crystal structure of its methoxide analogue (**2**) was obtained and revealed the formation of chiral clefts that are proposed to facilitate the catalysts' isoselective nature. Adjacent cobalt atoms are separated by 7.13 Å, with the planes defined by the chelating atoms of the salen ligands oriented approximately 52° relative to each other.[11] Since it is currently impossible to predetermine the solid-state packing arrangement of a metal complex, the improvement of **1** through rational ligand modification is also impossible. We therefore sought to design a covalently tethered bimetallic complex as a mimic of the putative active species in **1** and **2** capable of synthesizing isotactic polyethers. Since many epoxide ring-opening reactions have been proposed to proceed via a bimetallic mechanism,[12] we targeted tethered bimetallic cobalt salen complexes that would maintain the structural features of **1**, specifically a Co−Co distance between 5 and 7 Å and an almost perpendicular orientation of the salen ligand planes relative to one another. This led to the design of **3** (Figure 2), where a binaphthol linker oriented the salen planes in the appropriate geometry and maintained the ideal distance between metal centers for epoxide polymerization.[13] The catalytic system consisting of **3** with cocatalyst bis(triphenylphosphine)iminium (PPN) acetate was found to enantioselectively polymerize terminal aliphatic racemic epoxides to form highly isotactic polyethers, and resolve valuable enantiopure epoxides.

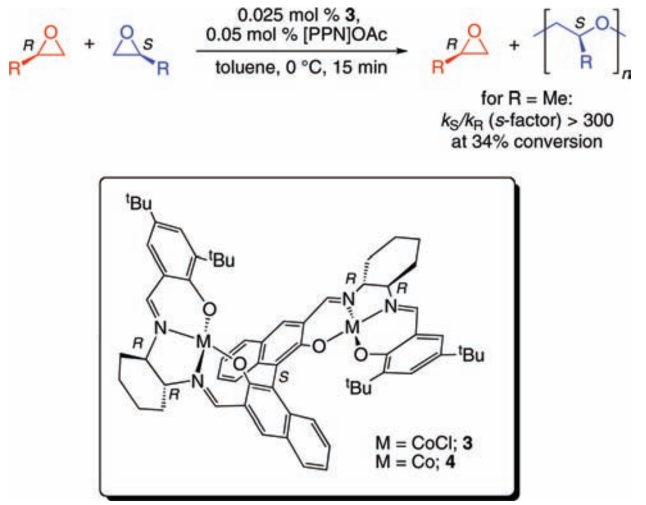

Figure 2. Enantioselective polymerization of epoxides with **3**.

The use of **3** as a catalyst achieves two major objectives of asymmetric catalysis: preparing enantiopure building blocks[14] and synthesizing stereoregular macromolecules.[4] The synthesis[15] and resolution[16] of enantiopure epoxides has received significant attention because epoxides are attractive chiral building blocks.[17] In comparison, the synthesis of enantiopure polymers has received significantly less attention despite their potential applications, primarily the result of a lack of active stereoselective catalysts.[18] Prior to the discovery of **3**, a catalyst capable of forming highly isotactic polyethers from a variety of racemic epoxides was not known. In the presence of cocatalyst, **3** selectively enchains the *S* enantiomer of aliphatic epoxides via an enantiomorphic site control mechanism to form polyethers, leaving the *R* enantiomer enriched in the starting material with *s*-factors typically above 50, and as high as 300. Subsequent work on catalyst variations showed that the enantioselectivity of **3** is determined by the stereochemistry of the binaphthol linker.[19]

In this manuscript, we present the characterization of complex **3** and the enantioselective polymerization of a broad range of racemic, monosubstituted epoxides using this complex. Additionally, a racemic mixture of **3** is used to synthesize isotactic polyethers in quantitative yields from racemic epoxides. The thermal properties of these isotactic polyethers are also presented.

Experimental Section

General Considerations.[20] All manipulations of air- or water-sensitive compounds were carried out under dry nitrogen using a

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(20) See Supporting Information.

Braun Labmaster drybox or standard Schlenk line techniques. NMR spectra were recorded on Varian Mercury (^{1}H, 300 MHz), Varian INOVA 400 (^{1}H, 400 MHz), Varian INOVA 500 (^{1}H, 500 MHz), or Varian INOVA 600 (^{1}H, 600 MHz) spectrometers. ^{1}H NMR spectra were referenced with residual solvent shifts ($CHCl_3 = 7.26$ ppm, benzene-d_5 = 7.16 ppm, acetone-d_5 = 2.05 ppm, DMSO-d_5 = 2.54 ppm, 1,1,2,2-tetrachloroethane-d_1 = 6.0 ppm, pyridine-d_4 = 8.74 ppm). ^{13}C NMR spectra were referenced by solvent shifts ($CDCl_3 = 77.23$ ppm, benzene-d_6 = 128.32 ppm, acetone-d_6 = 29.92 ppm, 1,1,2,2-tetrachloroethane-d_2 = 73.78 ppm, pyridine-d_5 = 150.35 ppm).

Materials. HPLC grade methylene chloride and toluene were purchased from Fisher Scientific and purified over solvent columns. Styrene oxide was synthesized according to a literature procedure[21] and fractionally distilled at reduced pressure. All other epoxides were purchased from commercial sources and dried over calcium hydride, degassed through several freeze−pump−thaw cycles, and then vacuum transferred and stored under nitrogen in a glovebox. Catalysts **3** and *rac*-**3** were synthesized as previously reported.[13] (1*R*,2*R*)-Diaminocyclohexane (99% ee) and (1*S*,2*S*)-diaminocyclohexane (99% ee) were purchased from Aldrich, and (*S*)- and (*R*)-1,1′-bi-2-naphthol were purchased from TCI. (*S*)- and (*R*)-3,3′-diformyl-1,1′-bi-2-naphthol[22] and bis(triphenylphosphine)iminium acetate ([PPN]OAc)[23] were prepared according to literature procedures. All other reagents were purchased from commercial sources and used as received.

Representative Procedure for the Enantioselective Polymerization of Epoxides. Polymerization of Racemic Propylene Oxide (Table 1, entry 1). In a drybox under nitrogen atmosphere, **3** (8.2 mg, 7.1 μmol) and [PPN]OAc (8.5 mg, 14 μmol) were added to a Schlenk tube containing a stir bar. A vacuum adaptor was attached to the tube, which was sealed before the apparatus was removed from the drybox. The Schlenk tube was placed under nitrogen and subsequently cooled in an ice bath. Anhydrous toluene (12 mL) was added via syringe, and the resulting mixture was stirred for 10 min at 0 °C. PO (1.7 g, 28 mmol) was added via syringe. The polymerization was kept at 0 °C during the course of the reaction. After 15 min, an aliquot was taken for NMR analysis, and the unreacted PO was vacuum-transferred to another Schlenk tube cooled in liquid nitrogen. To quench the catalyst, 1 mL of methanol containing a trace amount of HCl was added to the reaction mixture. The remaining polymer solution was quantitatively transferred to a tared round-bottom flask and dried overnight under vacuum. Conversion was determined by polymer mass (0.556 g) to be 34%.

The ee of recovered PO was measured by chiral GC to be 51% (*R*)-PO, with t_R (major, *R*) = 14.7 min and t_R (minor, *S*) = 15.4 min. The absolute stereoconfiguration was confirmed by chiral GC using commercially available (*R*)-PO. The conditions for separation were as follows: flow, 1.4 mL/min; velocity, 34 cm/s; pressure, 7 psi; isothermal at 40 °C. The optical rotation of the polymer was measured $[[\alpha]^{23}_{D} = -26.7°$, (1.5 g/100 mL, $CHCl_3$)] and compared to that reported by Price et al.[5] The negative rotation shows that the polymer synthesized with **3** is (*S*)-PPO, giving evidence for epoxide ring-opening at the methylene carbon with retention of the configuration at the methine carbon. A concentrated sample of polymer (50 mg in 0.5 mL of $CDCl_3$) was analyzed using ^{13}C NMR spectroscopy to determine polymer tacticity.[5,20,24] ^{13}C NMR ($CDCl_3$, 125 MHz): δ 75.70, 73.61, 17.64. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.52 (m, 2H), 3.39 (m, 1H), 1.11 (m, 3H). M_n = 26 400 g/mol, $M_w/M_n = 1.8$, M_n^{theo} = 79 000 g/mol. Details regarding the synthesis and characterization of other polymers can be found in the Supporting Information.

Results and Discussion

Characterization of Complex 3. Complex **3** is isolated as a black solid, and all attempts at crystallization from nondonating solvents have been unsuccessful thus far. We propose that this is due to **3** being a mixture of diastereomers in the form of exo-exo, exo-endo, and endo-endo chlorides. Crystals of the tetrapyridine adduct of *rac*-**3** (*rac*-**5**) were obtained from pyridine and toluene as shown in Figure 3. The presence of two chlorides confirms that the complex is Co(III)−Co(III). Two pyridines are bound to each cobalt atom, and the complex has a pseudo-C_2 symmetry. The complex displays a Co−Co distance of 6.45 Å and an endo naphthyl−naphthyl dihedral angle of 79°. In comparison to the reduced complex **4**,[13] *rac*-**5** has a wider Co−Co separation, consistent with the flexible nature of the binaphthol linker. Complex **3** was also studied by NMR spectroscopy. In the strongly donating solvent pyridine-d_5, **3** displays sharper resonances than described in our previous report using DMSO-d_6,[13] allowing for characterization by a combination of ^{1}H, ^{13}C, COSY, and HMBC spectroscopy.[20] The spectra were consistent with **3** forming a single C_2 symmetric tetrapyridine adduct in solution.

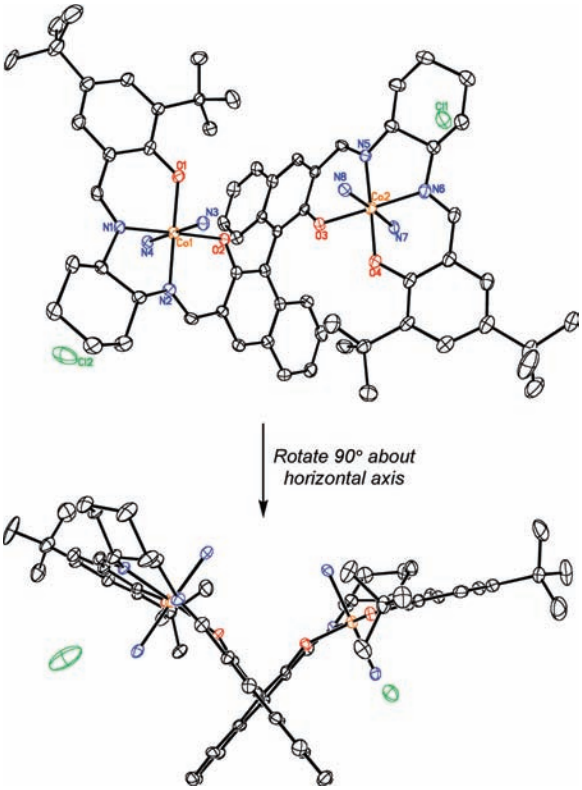

Figure 3. Molecular structure of *rac*-**5** (hydrogen atoms omitted and pyridine ligands truncated for clarity; carbon atoms are unlabeled). Thermal ellipsoids are at the 30% probability level.

The Enantioselective Polymerization of Monosubstituted Epoxides by 3. After completion of our initial reactivity studies of **3**,[13] we focused our efforts on studying the scope of its reactivity toward other epoxides. To prevent chain transfer and catalyst deactivation, we targeted a wide range of epoxides that

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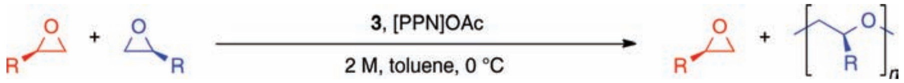
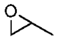
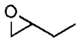
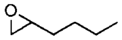
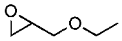
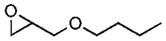
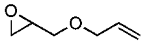
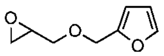
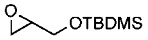
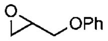
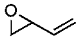
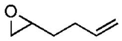
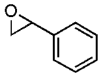
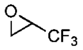
Table 1. Enantioselective Polymerization of Racemic Monosubstituted Epoxides Using Complex **3**[a]



entry	epoxide	time (min)	**3** (mol %)	conv.[b] (%)	$ee_{(SM)}$[c] (%)	[*mm*][d] (%)	$ee_{(P)}$[e] (%)	M_n[f] (kg/mol)	M_w/M_n[f]	*s*-factor[g]
1		15	0.025	34	51	98.3	98.9	26.4	1.8	>300
2		14	0.10	22	29	98.8	99.2	61.4	2.0	>300
3		20	0.15	19	24	96.6	97.7	76.8	2.1	>100
4		50	0.050	24	31	91.8	94.4	7.6	1.5	>50
5		64	0.050	46	77	86.4	90.5	32.7	2.0	>50
6		11	0.025	36	57	95.8	97.2	106	1.5	>100
7		7	0.025	41	80	92.9	95.6	68.9	1.2	>80
8		2	0.025	38	66	92.2	94.6	144	2.1	>70
9		1	0.025	24	15	94.4	96.2	127	2.0	>70
10		32	0.10	45	73	74.5	81.2	79.3	1.8	>20
11		11	0.15	35	53	98.6	99.0	45.7	1.9	>300
12		30	0.10	34	70	93.6	95.6	50.0	2.4	>70
13[h]		2	0.10	37	53	98.8	99.2	19.5[i]	1.7[i]	>300

[a] Polymerization conditions: [epoxide] = 2 M in toluene; [**3**]:[(PPN)OAc] = 1:2; $T_{rxn} = 0$ °C.[20] [b] Conversion determined by ^{1}H NMR spectroscopy of the crude reaction mixture, or gravimetrically. [c] Determined by chiral gas chromatography or ^{1}H NMR using a chiral shift reagent. [d] Determined by ^{13}C NMR. [e] Calculated using: $ee_{(P)} = (2[mm] + [mr] + [rm] - 1)^{1/2}$. [f] Determined by gel permeation chromatography (GPC) calibrated with polystyrene samples in 1,2,4-trichlorobenzene at 140 °C. [g] Calculated using $s = \ln[1 - c(1 + ee_{(P)})]/\ln[1 - c(1 - ee_{(P)})]$, where *c* is the conversion of epoxide. [h] Polymerization run neat. [i] Determined by GPC at 35 °C in *N*,*N*-dimethylformamide containing 0.01 M lithium nitrate and calibrated with poly(methyl methacrylate).

did not possess protic functional groups or strong Lewis basic functionality. All polymerizations were conducted at 0 °C in toluene to maximize selectivity and control the reaction exotherm. Our initial screening conditions were optimized by varying catalyst loadings and reaction times to achieve conversions between 20 and 40%, allowing us to calculate accurate *s*-factors to assess the enantioselectivity of **3**. It has been observed in previous studies that a more accurate calculation of *s*-factors can be attained by measuring the enantiomeric excess of the product, as opposed to the starting material as a function of conversion (*c*).[25] Thus, we examined the enantiomeric purity of monomer units in the resulting polymer ($ee_{(P)}$) as a function of *c*. The $ee_{(P)}$ was calculated using ^{13}C NMR spectroscopy (vide supra). The *s*-factors for the polymerizations were calculated using eq 1,[26] applicable only when monomer conversions are less than 50%.

$$s\text{-factor} = \ln[1 - c(1 + ee_{(P)})]/\ln[1 - c(1 - ee_{(P)})] \qquad (1)$$

Complex **3** was found to display very high enantioselectivity with *s*-factors exceeding 50 for many epoxides, well above the threshold for preparative utility of enantiopure epoxides (Table 1). However, it is important to note that small errors in measuring percent conversion and *mm* contents from the NMR spectra are propagated when calculating *s*-factors. Therefore, the *s*-factors calculated are lower limits and are likely much higher than reported.[25] Considering the signal-to-noise ratios in the ^{13}C NMR spectra, an *s*-factor of 300 was chosen as the maximum

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s-factor that could be measured experimentally.[20] The optimized results are shown in Table 1 and are discussed below.

Polymerization of Aliphatic Epoxides. As reported previously, the *s*-factors for PO and butene oxide are both very high, indicating that these polyethers are highly isotactic (Table 1, entries 1 and 2).[13] Hexene oxide is also polymerized with an *s*-factor above 100 (entry 3). These are the highest selectivities reported for the enantioselective polymerizations of these monomers.

Polymerization of Glycidyl Ethers. Glycidyl ethers are of particular interest due to the range of pendant functional groups available in this class of epoxides. We found that **3** is an active catalyst for the polymerization of a number of glycidyl epoxides. Ethyl glycidyl ether and *n*-butyl glycidyl ether both polymerize in the presence of **3** at moderate rates with *s*-factors above 50 (Table 1, entries 4 and 5). Allyl glycidyl ether polymerizes rapidly to form highly isotactic polymer with an *s*-factor over 100 (entry 6). Poly(allyl glycidyl ether) is of interest because it possesses pendant olefins that can allow further functionalization.[27] Furfuryl glycidyl ether is made from two biorenewable feedstocks,[28] and it polymerizes rapidly with an *s*-factor higher than 80 (entry 7). The monomer *tert*-butyldimethylsilyl glycidyl ether polymerizes rapidly with an *s*-factor greater than 70 (entry 8). This polyether is attractive because it can be deprotected to yield linear enantiopure poly(glycidol), a hydrophilic biocompatible polymer.[29] Linear poly(glycidol) can be used for efficient cytoplasmic delivery of bioactive molecules after esterification with cyclic anhydrides.[30] Phenyl glycidyl ether displays the highest rate of polymerization with a TOF of 1000 min^{-1} and an *s*-factor of at least 70 (entry 9). Isotactic poly(phenyl glycidyl ether) is a toughening agent in epoxy resins.[31] It has previously been synthesized using coordination polymerization[19,32] and anionic polymerization of enantiopure monomer.[33]

Polymerization of Unsaturated, Aryl, and Fluorinated Epoxides. The polymerizations of 3,4-epoxy-1-butene[19] and 5,6-epoxy-1-hexene, two functionally similar monomers, exhibited very different *s*-factors, above 20 and 300, respectively (Table 1, entries 10 and 11). We hypothesize that the increased distance between the olefin and the oxirane of 5,6-epoxy-1-hexene results in similar reactivity to an aliphatic epoxide consistent with the observation of a higher *s*-factor. The pendant olefins present in these polyethers enable postpolymerization modification. Another polymer of interest, poly(styrene oxide), has been reported.[19,34,35] Complex **3** exhibits good activity for the polymerization of styrene oxide with an *s*-factor exceeding 70 (Table 1, entry 12).

There are limited reports on the polymerization of 1,1,1-trifluoro-2,3-epoxypropane.[19,36] Fluorinated polyethers have unique properties and often require fluorinated solvents for their synthesis.[36c] Complex **3** has high activity and selectivity for the polymerization of 1,1,1-trifluoro-2,3-epoxypropane without the use of solvent and displays an *s*-factor over 300 (Table 1, entry 13).

Screening of Sterically Encumbered Epoxides. Complex **3** was also screened for the polymerization of bulky aliphatic epoxides. Epoxides with 1,1- and 1,2-disubstitution are of particular interest since the resulting isotactic polymers would possess novel architectures. Unfortunately, **3** is inactive for the polymerization of the members of these classes of epoxides that were examined. Similarly, the bulky terminal epoxides 1,2-epoxy-3-methylbutane and 1,2-epoxy-3,3-dimethylbutane are not polymerized by **3**. We propose that polymerization occurs inside the catalyst cleft, which may be less accessible to these monomers due to steric hindrance.

Isoselective Polymerization of Racemic Epoxides Using *rac*-3. We have briefly shown that the racemic form of **3** (*rac*-**3**) can give near quantitative yields of highly isotactic polymers from their respective epoxides.[13] In order to achieve such high conversions, the reaction times were lengthened and epoxide concentrations were reduced to circumvent viscosity issues. Complex *rac*-**3** polymerizes racemic epoxides to form highly isotactic polyethers in quantitative yields, with >99% *mm* content observed for most. These racemic polyethers were chosen to study their material thermal properties; many possess high T_m values, as shown in Table 2. Enantiopure polyethers displayed slightly lower T_m values[20] consistent with their reduced tacticity; no evidence for stereocomplex formation was found.[37]

Near quantitative conversion and high isotacticity are obtained for all substrates tested. Poly(3,4-epoxy-1-butene) (Table 2, entry 4) has the lowest isotacticity with *mm* content of 85%. This was expected based on the low *s*-factor for the enantioselective polymerization of this epoxide. Despite the moderate isotacticity displayed by this polymer, it still has a T_m of 66 °C. Notable examples of polyethers with high melting points include poly(phenyl glycidyl ether) with a T_m of 193 °C (entry 7), which is higher than that observed by Nozaki and co-workers (T_m of 172 °C for a polymer with a M_n value of 7.9 kg/mol).[33] Poly(1,1,1-trifluoro-2,3-epoxypropane) has a T_m value of 119 °C (entry 9).

This method provides excellent yields of some previously unreported isotactic polyethers with the potential for new commercial applications. We are currently exploring the polymerization of other monosubstituted epoxides, with the goal of discovering new highly crystalline polyethers. The polymerization conditions reported herein are quite mild and employ very low catalyst loading, while maintaining rapid rates. An induction period was evident for many of these polymerizations.[20] Similar induction periods have been reported for a related cobalt−salen system used for CO_2/epoxide copolymerization, and we are currently studying this interesting phenomenon.[38] The reported M_n values of the polymers are quite high

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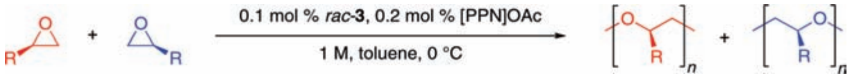
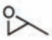
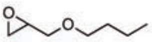
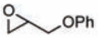
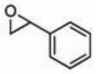
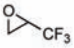
Table 2. Synthesis of Highly Isotactic Polyethers from Racemic Monosubstituted Epoxides Using *rac*-**3**[a]



entry	epoxide	time (h)	conv.[b] (%)	[*mm*][c] (%)	M_n[d] (kg/mol)	M_w/M_n[d]	T_g[e] (°C)	T_m[e] (°C)
1		3.5	>99	>99	86.8	1.6	nd[f]	67
2		38	>99	>99	183	1.6	-70	22
3		15	>99	>99	282	1.5	nd[f]	57
4[g]		21	>99	85	200	1.6	-46	66
5		84	>99	91	105	1.9	-77	21
6		13	>99	91	406	1.5	-36	30
7		0.50	>99	>99	105	1.5	112	193
8		1.7	>99	93	326	1.7	51	nd[f]
9		15	>99	98	23.8[h]	2.1[h]	nd[f]	119

[a] Polymerization conditions: [epoxide] = 1 M in toluene; [*rac*-**3**]:[(PPN)OAc]:[epoxide] = 1:2:1000; T_{rxn} = 0 °C.[20] [b] Conversion determined by ^{1}H NMR spectroscopy of the crude reaction mixture, or gravimetrically. [c] Determined by ^{13}C NMR. [d] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C calibrated with polystyrene standards. [e] Determined by differential scanning calorimetry. [f] Not detected. [g] [*rac*-**3**]:[(PPN)OAc]:[epoxide] = 1:2:2000. [h] Determined by GPC at 35 °C in *N*,*N*-dimethylformamide containing 0.01 M lithium nitrate, calibrated with poly(methyl methacrylate).

with all but one being above 10 kg/mol and many above 100 kg/mol. The experimental M_n values in the case of many polymerizations are higher than calculated theoretical values[39] (e.g., Table 1, entry 2); these results are consistent with both **3** being a mixture of chloride diastereomers of which only a fraction are catalytically active, and the rate of propagation being higher than the rate of initiation. In certain cases where experimental M_n values are lower than the theoretical (e.g., Table 1, entry 1), we believe traces of protic impurities are acting as chain transfer agents. M_n values can also be lowered by oxidative degradations of the uninhibited polymers.[40] The polydispersities (M_w/M_n) were generally two or below, consistent with a single active species.

Conclusions

We have developed and further characterized a highly active and enantioselective bimetallic cobalt(III) catalyst for the polymerization of monosubstituted epoxides. It polymerizes a range of monosubstituted epoxides possessing alkyl, aryl, and ether substituents, yielding highly isotactic polyethers, and also displays great enantioselectivity as reflected by the calculated *s*-factors which exceed 50 for most monomers. The racemic form of the catalyst can also be used to synthesize highly isotactic polyethers in quantitative yields, with many displaying high T_m values.

Acknowledgment. We thank the NSF (CHE-0809778), King Abdullah University of Science and Technology (KAUST; Award No. KUS-C1-018-02), and Sumitomo Chemicals for support. This research made use of the Cornell Center for Materials Research Shared Experimental Facilities supported through the NSF MRSEC program (DMR-0502404). R.M.T. acknowledges a Hunter Rawlings Cornell Presidential Research Scholarship. We thank Mr. Tom Mourey and Ms. Lisa Slater for GPC analysis of poly(1,1,1-trifluoro-2,3-epoxypropane) and Dr. Ivan Keresztes for assistance with the NMR analysis of **3**.

Supporting Information Available: Calculation of ee values and *s*-factors, single crystal X-ray diffraction data, and synthesis and characterization of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

JA1058422

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