Regioregular Polymerization of Fluorine-Containing Epoxides

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Received February 17, 2007; Revised Manuscript Received May 4, 2007

ABSTRACT: Epoxides bearing fluorine (F)-containing substituents on ethylene oxide were polymerized under mild conditions to give regioregular polyethers. To alleviate the electron-withdrawing effect of fluoroalkyl or fluoroaryl groups, more than one unit of methylene spacer had to be introduced into a side chain for regioregular polymerization with high activity. Optically active isotactic polyethers were obtained from enatiopure monosubstituted ethylene oxides as a result of regioselective ring opening via successive cleavage of the less substituted carbon−oxygen bond. Obtained optically active isotactic polyethers were investigated through circular dichroism (CD) spectra or optical rotatory dispersion (ORD) spectra in solution states. As a result, no evidence for the formation of helical conformation was detected in both the F-substituted and the corresponding hydrogen (H)-substituted optically active isotactic polyethers.

Introduction

Organofluorine compounds have demonstrated countless unique properties derived from specialty of fluorine atom, and their synthetic procedures have been widely studied.[1,2] In materials science, organofluorine polymers have also exhibited many useful qualities which non-fluorine polymers cannot attain.[2] Since physical and chemical properties of polymers depend much on their molecular weight, molecular weight distribution, and tacticities, precise control of these factors (precision polymerization) is one of the most powerful tools to yield novel polymers. Recent rapid development of precision polymerization methods using olefin has triggered many attempts to apply to fluorine-containing olefins, such as coordination polymerization,[3−5] ring-opening metathesis polymerization,[6] living radical polymerization,[7−11] and anionic polymerization.[12,13] On the other hand, precision polymerization of epoxides and their derivatives is also as advancing as that of olefins to yield polyethers and their derivatives.[14−21] However, few reports have been seen about precision polymerization of fluorine-containing epoxides. Only regioregular poly(3,3,3-trifluoropropylene oxide) and its copolymers were reported by using a zinc complex or KOH[22−25] before our study.[26] Atactic or isotactic polyether was obtained from racemic or optically pure 3,3,3-trifluoropropylene oxide, respectively. Generally, the more fluorine atoms the polymer contains, the more special properties the polymer will appear, which results from the peculiar nature of the fluorine atom. Hence, we started our search for polymerization catalysts applicable to highly fluorinated epoxides.

Standard handlings and synthetic procedures of non-fluorine compounds often cannot be applied directly to those of organofluorine compounds due to their unusual propensities.[1,2] In general, the higher content of fluorine atom is in molecules, the more difficult their handling becomes. Particularly, highly fluorine-rich molecules or fragments are often insoluble in general organic and aqueous solvents, and they tend to display moderate affinity for fluorous solvents.[2] Thus, highly fluorinated polymers could be obtained from catalysts containing perfluoroalkyl substituents under some fluorophilic fluid or solvent.[27−30]

Previously, in our short communication,[26] we reported novel initiator/catalyst system for regioregular polymerization of fluorine-rich epoxides **1**−**3** except for **4** by modification of Deffieux's system[19] which utilizes ^{i}PrONa as an initiator and Al^{i}Bu$_3$ as a Lewis acid catalyst in cyclohexane. In our system, C_6F_6 and MePPh$_3$Br were used as a solvent and an initiator, respectively (Scheme 1). It was essential to use C_6F_6 as a solvent because the produced polymers were soluble only in fluorous solvents. For better activity of the initiator, MePPh$_3$Br was the best choice. The system is advantageous because it regioregularly polymerized more fluorine-rich epoxides than previously reported 3,3,3-trifluoropropylene oxide[22−25] and required no fluorine-containing ligands or catalysts. Additionally, this system enabled us to obtain optically active isotactic polymers from enantiopure epoxides as monomers.

However, the following three problems and questions were left intact in the previous report: (i) The scope and generality of the fluorine-containing epoxides were ambiguous. Concretely speaking, epoxides bearing fluoroaryl groups were not examined as substrates. (ii) Absolute configurations of synthesized enantiopure epoxides were not determined. (iii) Detailed structures of obtained polymers were unexplored. Optically active isotactic polymers have often showed some special conformations which the corresponding atactic polymers cannot possess such as helical structures[31−34] in solution states and/or bulk states. In addition, fluorinated molecules have often shown different conformations from the corresponding H-substituted molecules.[35−43] Thus, F-substituted optically active isotactic polyethers would be expected to possess some special structures which the corresponding atactic and optically active isotactic H-substituted polyethers do not possess. Considering that structural information on polyethers was investigated in solution states through CD and ORD,[44−52] it would be proper to measure CD or ORD spectra of both F-substituted and the corresponding H-substituted optically active isotactic polyethers in order to detect structural differences between F-substituted and the corresponding H-substituted polyethers in solution states.

In this paper, we report the scope and generality of the fluorine-containing epoxides. Additionally, the corresponding H-substituted polyethers were also synthesized and characterized to detect some structural differences from F-substituted polyethers. Structural information on optically active isotactic

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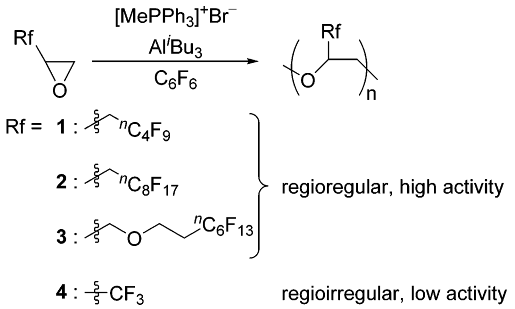
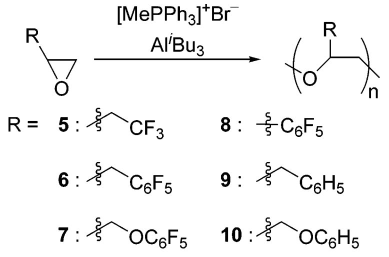
10.1021/ma070428j CCC: $37.00

Scheme 1. Polymerization System for Fluorine-Rich Epoxides[26]



Scheme 2. Fluorine-Containing Epoxides for Polymerization



polyethers in solution states was investigated through CD and ORD spectra.

Results and Discussion

Polymerization of Epoxides. Polymerizations of monomers **5**−**10** shown in Scheme 2 were examined. Synthetic procedures of racemic and optically pure epoxides as well as determinations of absolute configurations of the optically active epoxides are shown in the Supporting Information. Epoxides **4**−**10** were polymerized by our previously reported method,[26] and the results are listed in Table 1. The datum of epoxide **4** was cited from the previous literature (Table 1, run 1).[26] Polymerization of epoxide **5** was investigated to compare activity and structure of the polymer with epoxide **4** (Table 1, run 2). Polymerizations of epoxides **6**−**8** were attempted to scrutinize the scope and generality of the fluorine-containing epoxides. In order to detect structural differences between F-substituted optically active isotactic polyethers and the corresponding H-substituted polyethers, polymers from epoxides **9** and **10** were synthesized.

Epoxides **5**−**7** and **9** were polymerized efficiently to obtain polyethers (Table 1, runs 2−6 and 8−10). Polymerization of *rac*-**8** resulted in lower yield (Table 1, run 7). In addition, polymerization of epoxide (*S*)-**10** resulted in a low yield because of low solubility of the product, isotactic poly**(**glycidyl phenyl ether), precipitated before full consumption of substrate (Table 1, run 11). This assumption was supported by previously reported isotactic poly**(**glycidyl phenyl ether) which was not fully characterized.[53] Difference of activity between *rac*-**4** and *rac*-**5** would result from the existence of the side-chain methylene between CF_3 and ethylene oxide (Table 1, runs 1 and 2). Similarly, the difference of activity between *rac*-**6** and *rac*-**8** may also be due to the existence of the side-chain methylene between C_6F_5 and ethylene oxide (Table 1, runs 3 and 7). The effect of side-chain methylene on activity is discussed in a later section.

Polyethers made from epoxides **5**−**7**, **9**, and **10** clearly evidenced regioregular polymerization (Table 1, runs 2−6 and 8−11) unlike regioirregular polymerizations of epoxides **4** and **8** (Table 1, runs 1 and 7). Polyethers made from racemic epoxides disclosed atactic polymers (Table 1, runs 2, 3, 5, 8, and 10), while polyethers from enantiopure epoxides gave isotactic polymers (Table 1, runs 4, 6, 9, and 11). Assignments of these structures by ^{13}C NMR will be discussed in the next section.

Except for poly-(*S*)-**10** (Table 1, run 11), all polyethers were soluble in general organic solvents such as THF, $CHCl_3$, and CH_2Cl_2 (Table 1, runs 1−10). Poly-(*S*)-**10** was well dissolved in hot *o*-$C_6H_4Cl_2$ (120 °C) and slightly soluble in hot DMSO (120 °C). It was notable that little difference of molecular weight determined by size exclusion chromatography between F-substituted polyethers and the corresponding H-substituted polyethers (Table 1, runs 3 and 8, runs 4 and 9, runs 5 and 10) was seen, while the molecular weight of each monomer varied. This phenomenon may be due to the small volume of fluorine-containing polymer compared with its weight. In spite of heavy atomic weight (F 19), van der Waals radius of fluorine atom was close on that of hydrogen atom,[2] which would result in displaying lower molecular weight through size exclusion chromatography (SEC) than the absolute value.[54]

Polymer Characterization by ^{13}C NMR Spectra. Obtained polymers were characterized by the peak of either main-chain or side-chain methylene carbon of ^{13}C NMR spectra as shown in Figure 1. (All ^{13}C NMR spectra ranging from main-chain carbons to neighboring side-chain carbons and their assignments are shown in the Supporting Information.) While poly-*rac*-**4** (Table 1, run 1) was regioirregular according to previous literature,[26] the production of regioregular poly-*rac*-**5** (Table 1, run 2) exhibited sharp peaks in the ^{13}C NMR spectrum of the obtained polymer in C_6F_6 (Figure 1a). The four peaks of the methylene carbon in the main chain reflect the tacticity. For poly-*rac*-**5**, the area ratio was 21:25:25:29 from lower magnetic field to higher. Considering that ^{13}C NMR specrum of poly-*rac*-**5** was almost the same as that of poly-*rac*-**1**, it was assumed that assignment of the ^{13}C NMR spectrum of poly-*rac*-**1** should be applied to that of poly-*rac*-**5**.[26] Hence, four peaks are assigned as triad [*mm*, *mr* (or *rm*), *rm* (or *mr*), *rr* from lower magnetic field to higher] corresponding that poly-*rac*-**5** is atactic.

The production of regioregular poly-*rac*-**6** was also revealed by ^{13}C NMR spectrum of the obtained polymer in $CDCl_3$ (Figure 1b). Poly-*rac*-**6** (Table 1, run 3) showed seven broad peaks of the methylene in the main-chain carbon reflecting on the tacticity. In contrast, the ^{13}C NMR spectrum of poly-(*R*)-**6** gave only one methylene carbon peak in the second lowest magnetic field of the seven peaks (Figure 1c). Generally, regioregular ring-opening polymerization of propylene oxide proceeds through successive nucleophilic attacks on the less hindered methylene carbon than the methine carbon.[19] Accordingly, it is reasonable to assume that the methine carbon retains its configuration and that isotactic polyether was obtained by using enatiopure epoxide. Given that only one sharp peak of poly-(*R*)-**6** reflected on isotactic polymer, seven peaks can be regarded as a reflection of the atactic polymer.

A polymer obtained from *rac*-**7** also had regioregular structure supported by the sharp ^{13}C NMR spectrum (Figure 1d). The peak split at 75.11 and 74.99 ppm with area ratio of 1:1 was assigned to a methylene carbon although it is not clear whether it is in the main chain or in the side chain. Polyether from (*S*)-**7** brought only one peak at 75.13 ppm (Figure 1e), which is a proof of isotactic polymer as previously discussed. The two peaks correspond to diad (*m* and *r* from the lower to the higher) and $m{:}r = 50{:}50$ ($mm{:}mr + rm{:}rr = 25{:}50{:}25$).

In contrast, poly-*rac*-**8** had regioirregular structure, which was supported by the complex ^{13}C NMR of main-chain methylene

Table 1. Polymerization of Epoxides[a]

run	monomer	yield (%)	M_n (g/mol)	M_w/M_n	tacticity mm:mr + rm:rr	appearance	T_g and T_m (°C)
1[b]	*rac*-**4**	45	2 200	1.2	–[d]	viscous liquid	T_g −47
2	*rac*-**5**	99	16 000	1.7	21:50:29	viscous liquid	T_g −34
3	*rac*-**6**	97	20 000	1.2	atactic[c]	viscous liquid	T_g 12
4	(*R*)-**6**	97	21 000	1.6	100:0:0	viscous liquid	T_g 10
5	*rac*-**7**	88	24 000	2.4	25:50:25	viscous liquid	T_g −23
6	(*S*)-**7**	95	26 000	1.6	100:0:0	white solid	T_m 105
7	*rac*-**8**	52	6 000	1.3	–[d]	white solid	T_g 26, T_m 135
8	*rac*-**9**	95	19 000	1.7	25:50:25	viscous liquid	T_g 1.9
9	(*R*)-**9**	98	21 000	1.5	100:0:0	white solid	T_m 115[e]
10	*rac*-**10**	98	24 000	1.8	25:50:25	viscous liquid	T_g 10
11	(*S*)-**10**	38	7 900	1.4	100:0:0	white solid	T_m 175

[a] Epoxide (2.8 mmol), solvent (2.0 mL), $MePPh_3Br$ (0.025 mmol), Al^iBu_3 (0.25 mmol in 1 M toluene solution), 0 °C, 1 h (runs 2−11). In run 1, room temperature, 40 h. In runs 1−2, C_6F_6 was used as a solvent. In runs 3−11, toluene was used as a solvent. [b] Datum was cited from previous report.[26] [c] Ratio could not be determined by the ^{13}C NMR spectrum. [d] Obtained polymer was regioirregular, and the ratio of head-to-tail:tail-to-tail:head-to-head could not be determined. [e] The value was determined from the first heating scan, while the others were determined from the second scans.

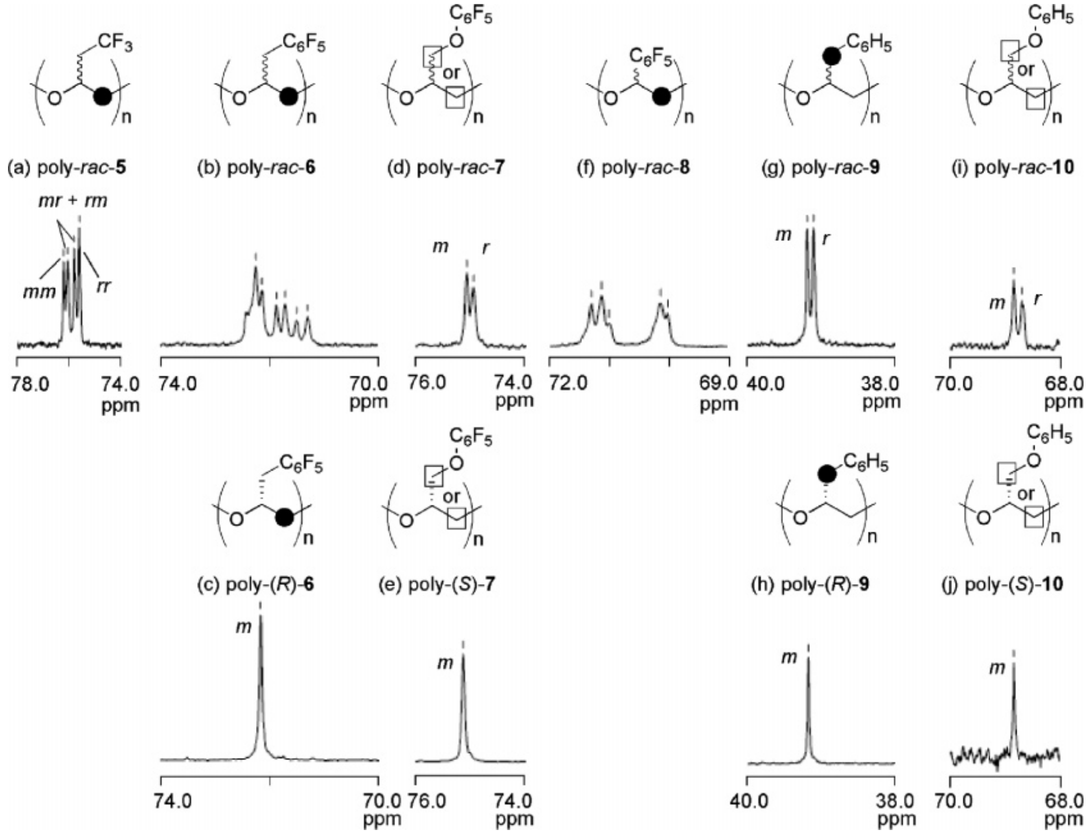


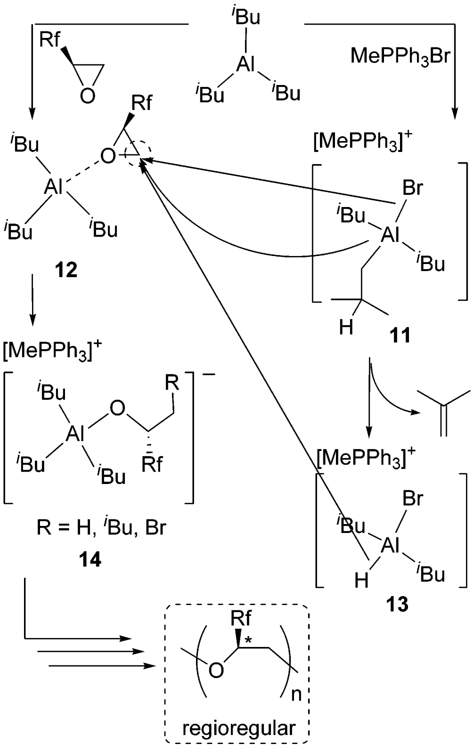
Figure 1. ^{13}C NMR spectra of polymers: (a) the main-chain methylene peak of poly-*rac*-**5**, (b) the main-chain methylene peak of poly-*rac*-**6**, (c) the main-chain methylene peak of poly-(*R*)-**6**, (d) the methylene peak of either main chain or side chain in poly-*rac*-**7**, (e) the methylene peak of either main chain or side chain in poly-(*S*)-**7**, (f) the main-chain methylene peak of poly-*rac*-**8**, (g) the side-chain methylene peak of poly-*rac*-**9**, (h) the side-chain methylene peak of poly-(*R*)-**9**, (i) the methylene peak of either main chain or side chain in poly-*rac*-**10**, and (j) the methylene peak of either main chain or side chain in poly-(*S*)-**10**.

peaks (Figure 1f), while poly-*rac*-**6** had regiorregular structure. This structural difference between *rac*-**6** and *rac*-**8** corresponds to the difference between *rac*-**4** and *rac*-**5**.

Moreover, the production of the regioregular polymer from **9** was also proved by ^{13}C NMR spectra. Poly-*rac*-**9** showed two broad peaks of the methylene carbon in the side chain reflecting the tacticity (Figure 1g). The area ratio was 100:98 from the lower magnetic field to the higher. In contrast, the ^{13}C NMR spectrum of the poly-(*R*)-**9** gave only one methylene carbon peak in the lower magnetic field of the two peaks (Figure 1h). As previously mentioned, poly-(*R*)-**9** was isotactic polyether. Judging from these two charts, the two peaks corresponds to diad (*m* and *r* from lower to higher) and m:r = 51:49 (mm:mr + rm:rr = 26:50:24).

Finally, a polymer obtained from *rac*-**10** also had regioregular structure supported by the sharp ^{13}C NMR spectrum (Figure 1i). Poly-*rac*-**10** showed two broad peaks of the methylene carbon reflecting the tacticity although it is not clear whether it is the one in the main chain or in the side chain. The area ratio was 50:50 from the lower magnetic field to the higher. In contrast, the ^{13}C NMR spectrum of poly-(*R*)-**10** showed only one methylene carbon peak in the lower magnetic field of the two peaks, and it was isotactic polymer (Figure 1j), although low solubility in DMSO led to an unclear spectrum. Comparing the two charts, the two peaks correspond to diad (*m* and *r* from lower to higher) and m:r = 50:50 (mm:mr + rm:rr = 25:50:25).

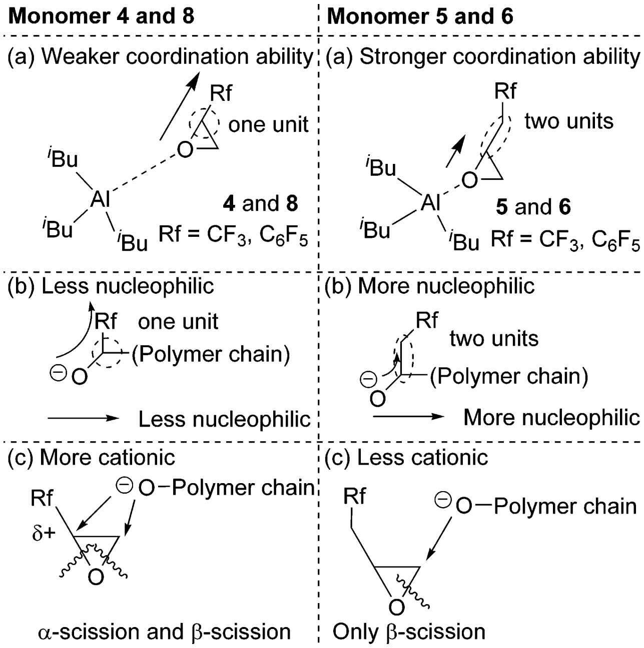
Scheme 3. Previously Proposed Mechanism of Fluorine-Containing Epoxides



Reaction Mechanism and Scope of Substrate. A working mechanistic hypothesis[19,26] was previously proposed as shown in Scheme 3. At first, aluminate complex **11** was formed from MePPh$_3$Br and Al^{i}Bu$_3$. On the other hand, an epoxide was activated by coordination on Al^{i}Bu$_3$ (complex **12**) through an oxygen atom. This epoxide complexed with Al^{i}Bu$_3$ induced exclusive nucleophilic attack to methylene carbon by ^{i}Bu, Br, or hydride derived from ate complex **13**, which reproduced new aluminate complex **14** and sequentially regioselective ring-opening reaction of the epoxide. Repeated exclusive nucleophilic attacks on the methylene carbon yielded regioregular polyethers. This hypothesis based on previous reports[19] is also supported by the fact that isotactic polyethers were obtained from enantiopure epoxides.[26]

Judging from this reaction mechanism, the lower activities and the regioirregularities of poly-*rac*-**4** and poly-*rac*-**8** are reasonably explained as follows (Scheme 4). While methylene carbon units are inserted between the epoxide rings and the electron-withdrawing groups (C_6F_5 and CF_3) in epoxides **5** and **6**, those in epoxides **4** and **8** are adjacent to ethylene oxide directly. These neighboring electron-withdrowing groups decreased the coordinating ability of the oxygen atom to Al^{i}Bu$_3$ and nucleophilicity of the chain-end alkoxide, which resulted in the decrease of polymerization activity (Scheme 4a,b). This hypothesis is probably supported by previous reports on the electronic effects of perfluoroalkyl groups in trialkylphosphines[55,56] that insertion of two or more methylene spacers between the phosphorus atom and the perfluoroalkyl groups was essential as a buffer to insulate efficiently the electron-withdrawing effects on the phosphorus atom. Similarly, such an insulation of the electron-withdrawing effect on polymerization activity was discussed in copolymerization of carbon monoxide and fluorine-containing olefin.[4,5]

Scheme 4. Elucidation of Lower Activities and Regioirregularities of Epoxides 4 and 8: (a) Coordinating Ability, (b) Nucleophilicity, and (c) Cationic Methine Carbon



On the other hand, regioirregularities of polymers from **4** and **8** would be due to the more cationic property of methine carbon of the epoxide ring as follows (Scheme 4c). Neighboring electron-withdrawing groups forced methine carbon to be more strongly cationic and induced nucleophilic attack of polymer chain ends to the methine carbon. As a result, both α-scission (cleavage between methine and oxygen) and *β*-scission (cleavage between methylene and oxygen) took place for **4** and **8** in spite of steric hindrance. In contrast, the other epoxides **5** and **6** had methylene units to alleviate effects of the electron-withdrowing groups to induce exclusively nucleophilic attack on methylene carbon and cause only *β*-scission for steric hinderence. Normally regioregular polyethers resulted from successive *β*-scission initiated by KOH and Zn alkoxide,[57] while regioregular poly-*rac*-**4** was obtained by exclusive α-scission initiated by KOH and Zn alkoxide.[22,23] On the basis of this fact and the proposed mechanism above, it is reasonable to assume that epoxides *rac*-**4** and *rac*-**8** would polymerize through α-scisson by nature and that Lewis acid Al^{i}Bu$_3$ activated methylene carbons of *rac*-**4** and *rac*-**8** to cause both α-scission and *β*-scission.

ORD and CD Spectra of Optically Active Isotactic Polymer. To investigate the structural insights of isotactic polyethers (poly-(*R*)-**1**, poly-(*R*)-**3**, poly-(*R*)-**6**, poly-(*S*)-**7**, poly-(*R*)-**9**, poly-(*S*)-**10**) in solution state, ORD and CD spectroscopy were used. At first, poly-(*R*)-**1**, poly-(*R*)-**3**, and their monomers (*R*)-**1** and (*R*)-**3** which were previously synthesized[26] were studied (Figure 2a). Fluorous solvent AK-225 (CF_2ClCF_2CFHCl: $CF_3CF_2CFHCl_2$ = 11:9, v/v) was selected as a solvent because of good solubility of both polymers to detect plane curves of both polymers (Figure 2a). On the other hand, monomer (*R*)-**1** showed slightly detected peak top (peak $[\alpha]_{278}$ +8.59), while clearly distorted curve (peak $[\alpha]_{373}$ +7.24) was seen in the ORD spectrum of monomer (*R*)-**3** (Figure 2a). Enantiopure propylene oxide showed both plane curve in benzene and distorted curve in chloroform, while enantiopure 1,2-diethoxypropane which was a model compound of repeating unit of optically active isotactic poly(propylene oxide) gave a plane curve in these solvents.[44] This meant that there was no unambiguous information for helical structure of optically active isotactic poly(propylene oxide).[44] Hence, it is reasonable to assume that no

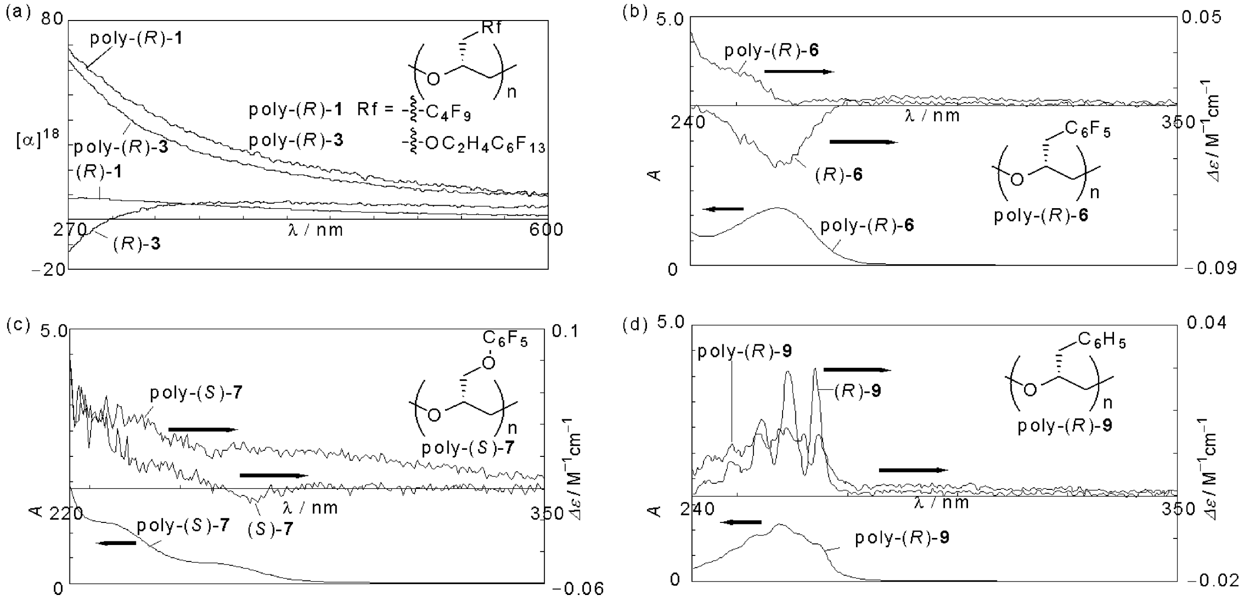


Figure 2. ORD or CD spectra of optically active isotactic polymers and their monomers. All concentration values of polymers were disclosed as concentration values of monomer-unit: (a) ORD spectra of poly-(*R*)-**1** (*c* 1.06, AK-225, 18 °C), poly-(*R*)-**3** (*c* 1.06, AK-225, 18 °C), (*R*)-**1** (*c* 5.26, AK-225, 18 °C), and (*R*)-**3** (*c* 1.06, AK-225, 18 °C). (b) CD spectra of poly-(*R*)-**6** and (*R*)-**6** and UV/vis spectrum of poly-(*R*)-**6** (3.21×10^{-3} mol/L, THF, 25 °C). (c) CD spectra of poly-(*S*)-**7** and (*S*)-**7** and UV/vis spectrum of poly-(*S*)-**7** (1.27×10^{-3} mol/L, THF, 25 °C). (d) CD spectra of poly-(*R*)-**9** and (*R*)-**9** and UV/vis spectrum of poly-(*R*)-**9** (5.96×10^{-3} mol/L, THF, 25 °C).

data to support the helical structures of poly-(*R*)-**1** and poly-(*R*)-**3** were obtained from their ORD measurements.

Next, C_6F_5-substituted poly-(*R*)-**6**, poly-(*S*)-**7**, and C_6H_5-substituted poly-(*R*)-**9** were evaluated by CD spctroscopy and UV spctroscopy in comparison with their monomers at the same concentration (Figure 2b−d). Unfortunately, although UV absorption of these polyethers ranged from 220 to 290 nm, these polyethers were insoluble in the solvents which are used for UV/CD measurements in the short wavelength region such as CH_3CN, $^cC_6H_{12}$, 1,4-dioxane, and EtOH. Of good solvents (THF, $CHCl_3$, CH_2Cl_2, and toluene), THF was chosen for the most sufficient solubility and the smallest abosorption from 350 to 220 nm to detect CD spectra of these three polymers. However, it should be noted that THF also has strong absorbance at short wavelength region. Poly-(*S*)-**10** was insoluble in any solvents at room temperature.

At first, CD spectra of poly-(*R*)-**6** showed slight positive Cotton effects, while monomer (*R*)-**6** exhibited a negative Cotton effect (Figure 2b). Compared with circular dichroism values $\Delta\epsilon$ of helical polymers,[31−34] $\Delta\epsilon$ of poly-(*R*)-**6** disclosed much smaller than $\Delta\epsilon$ of normal helical polymers.

CD spectra of poly-(*S*)-**7** and its monomer (*S*)-**7** were obtained in THF solution (Figure 2c). Strong UV absorption derived from THF at low wavelength region forced us to measure CD spectra of monomer (*S*)-**7** and poly-(*S*)-**7** at low concentration because the measurement device has the limitation for absorbance to obtain unclear CD spectra. However, it seemed that the CD spectrum of poly-(*S*)-**7** showed a plane curve. Incidentally, it should be noted that the plane curve of the polyether CD spectrum indicated helical structure in the previous literature in spite of the lack of evidence.[52]

Monomer (*R*)-**9** gave a vibrational curve, while poly-(*R*)-**9** showed more moderately oscillating curve (Figure 2d). Since optically active 1-phenyl-2-propanol which can be regarded as a model compound of repeating unit of poly-(*R*)-**9** also showed a vibrational curve,[58] moderate oscillating curves of poly-(*R*)-**9** would derive from unit structure of poly-(*R*)-**9**.

Conclusively, different curves between polymers and their monomers may result from structural differences of polymers and epoxides, but essentially no information was given for helical structures of the polymers in solution states through CD and ORD spectra.

Conclusion

The substrate scope and generality of our reaction system were investigated, and it was proved that fluoroaryl-substituted epoxides and the corresponding H-substituted epoxides were polymerized easily. Additionally, optically active isotactic polyethers were obtained by using enantiopure epoxides. Structures of the obtained polymers were clearly assigned by ^{13}C NMR spectra. Side-chain methylene was regarded as a buffer of perfluoro functions for alleviating their influence of the electron-withdrawing effect to polymerize regioregularly. Structures of obtained optically active isotactic polymers were indicated in both solution state and bulk state. None of them showed any proof for helical structures in solution state by CD and ORD spectra.

Experimental Section

General Method. All manipulations involving air-sensitive and/or moisture-sensitive compounds were carried out using the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11. All NMR spectra of obtained polymers were recorded in hexafluorobenzene (C_6F_6), chloroform-*d* ($CDCl_3$), and DMSO-d_6 (CD_3SOCD_3) on a JEOL JNM-ECP500 (^1H: 500 MHz; ^{13}C: 125 MHz; ^{19}F: 471 MHz) spectrometer. Chemical shifts are reported in ppm from following internal standards: tetramethylsilane (0 ppm) for ^1H and ^{13}C, $CF_3C_6H_5$ (−64.0 ppm) for ^{19}F. Size exclusion chromatography (SEC) analyses for polymer molecular weight were carried out using two columns (Shodex KF-804L) and tetrahydrofuran as an eluent at 40 °C at 1 mL/min calibrated by polystyrene standard (Table 1, runs 1, 2−10). Exceptionally, the molecular weight and the molecular weight distribution of the polymer sample (Table 1, run 11) were determined at 120 °C by high-temperature size exclusion chromatography (HT-SEC) on a HLC-8121SEC/HT apparatus

(Tosoh Corp.), and 1,2-dichlorobenzene was employed as an eluent at a flow rate of 1.0 mL/min calibrated by polystyrene standard. Differential scanning calorimetry (DSC) measurements of polymers were performed on a Mettler DSC 30. Heating rates were 5 °C/min. The reported T_g and T_m values were determined from the second heating scan except for poly-(*R*)-**9**, whose reported T_m value was measured from the first heating scan (Table 1, run 9). Circular dichroism (CD) spectra were recorded on a Jasco J-700 spectropolarimeter fitted with a Jasco PTC-423 L temperature controller in 1 cm rectangular quartz cells. Optical rotatory dispersion (ORD) spectra were recorded on a Jasco J-820 spectropolarimeter fitted with a Jasco PTC-423 L temperature controller in 1 cm rectangular quartz cells. Optical rotations were measured on a JASCO DIP-360 spectrometer using a 10 cm cell. All solvents and epoxides used for reactions were distilled under argon after drying over an appropriate drying reagent. Most of the reagents were purchased from Aldrich Chemical Co. Inc., Tokyo Kasei Kogyo Co. Ltd., Kanto Kagaku Co. Ltd., Daikin Industries, and Matrix Scientific Co. Ltd. and were used without further purification unless specified. Phosphonium salt was purified through reprecipitation under mixture solvents (hexane:CH_2Cl_2 = 2:1, v/v).

Representative Polymerization Procedure of Epoxides. A 20 mL Schlenk flask equipped with a magnetic stirring bar was charged with $MePPh_3Br$ as an initiator (0.0250 mmol), solvent (2.00 mL), and an epoxide (2.80 mmol) under Ar at room temperature. The mixture was cooled to 0 °C, and trialkylaluminium (0.250 mmol, 0.250 mL of 1 M toluene solution) was added in one portion.

Typical Isolation Procedure for Obtaining Polymers. After stirring at described temperature for desired period, the reaction was stopped by adding methanol/water (ca. 5 mL, MeOH:H_2O = 4:1, v/v), and the mixture was dried off under reduced pressure. Then, dichloromethane (3 × 30.0 mL) was added to this mixture, and the resulting suspension was filtered through Celite to remove aluminum residue. The filtrate was dried off to give crude polymer. Obtained crude polymer was dissolved into CH_2Cl_2 (20.0 mL). Successively, hexane (100 mL) was added into this solution. The mixture was evaporated until the amount of solvent was ca. 10 mL. The supernatant was removed to exclude small amount of oligomers (M_n < 1500) and initiator residue. Obatined material was dried off to isolate polymer.

Other Isolation Procedures for Obtaining Polymers. *Run 2 in Table 1.* After stirring at described temperature for the desired period, the reaction was stopped by adding methanol/water (ca. 5 mL, MeOH:H_2O = 4:1, v/v), and the mixture was dried off under reduced pressure. Then, AK-225 (2 × 30.0 mL) was added to the mixture. The resulting suspension was filtered through Celite to remove residue of initiator and aluminum residue. The filtrate was dried off to give poly-*rac*-**5**.

Run 6 in Table 1. After stirring at the described temperature for the desired period, the reaction was stopped by adding methanol/water (ca. 5 mL, MeOH:H_2O = 4:1, v/v), and the mixture was dried off under reduced pressure. Then, hot toluene (50.0 mL, 90 °C) was added to this mixture until solid polymer was completely dissolved. To remove aluminum residue, the resulting suspension was filtered through Celite. Additional dichloromethane (150 mL) was added to the suspension to be filtered through Celite. The filtrate was dried off to give a white solid polymer. The obtained crude polymer was dissolved into CH_2Cl_2 (100 mL). Successively, hexane (100 mL) was added into this solution. The mixture was evaporated until the amount of solvents was ca. 30 mL. The mixture was filtered to remove a small amount of oligomer (M_n < 1500) and initiator. The collected solid material was dried off to isolate polymer.

Run 11 in Table 1. At first, dichloromethane (10.0 mL) was added to this mixture, and the resulting supernatant was removed. Additional dichloromethane (10.0 mL) was added into this mixture again, and the resulting supernatant was removed again to obtain white powder. The collected powder was dried off to obtain polymer.

NMR Data of Polymers. Atactic poly(3-trifluoromethyl-1,2-epoxypropane) (Table 1, run 2, poly-*rac*-**5**). ^{1}H NMR ($CDCl_3$): δ 2.31 (m, 2H), 3.39 to 3.56 (m, 1H), 3.57 to 3.77 (m, 2H). ^{13}C NMR (C_6F_6): δ 40.96, 75.65, 75.83, 76.09, 76.23, 79.00, 131.19; ^{19}F NMR ($CDCl_3$) δ −64.82 to −65.22 (m, 3F).

Atactic poly(3-pentafluorophenyl-1,2-epoxypropane) (Table 1, run 3, poly-*rac*-**6**). ^{1}H NMR ($CDCl_3$): δ 2.77 (br, 2H), 3.15 to 3.55 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 24.95, 25.02, 25.14, 25.31, 71.24, 71.44, 71.66, 71.81, 72.09, 72.20, 72.38, 78.44, 78.66, 111.93, 137.51, 140.02, 145.57. ^{19}F NMR ($CDCl_3$): δ −144.09 (br, 2F), −158.23 (br, 1F), −164.41 (br, 2F).

Isotactic poly(3-pentafluorophenyl-1,2-epoxypropane) (Table 1, run 4, poly-(*R*)-**6**). ^{1}H NMR ($CDCl_3$): δ 2.78 (m, 2H), 3.35 (m, 1H), 3.41 to 3.57 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 25.29, 72.18, 78.40, 111.76, 137.50, 140.01, 145.53. ^{19}F NMR ($CDCl_3$): δ −144.09 to −144.24 (m, 2F), −158.23 (m, 1F), −164.40 (m, 2F).

Atactic poly(glycidyl pentafluorophenyl ether) (Table 1, run 5, poly-*rac*-**7**). ^{1}H NMR ($CDCl_3$): δ 3.77 (br, 3H), 4.15 (br, 1H), 4.28 (br, 1H). ^{13}C NMR ($CDCl_3$): δ 68.95, 69.09, 74.99, 75.11, 78.59, 133.80, 137.53, 138.10, 141.68. ^{19}F NMR ($CDCl_3$): δ −158.28 to −158.71 (m, 2F), −164.34 to −165.04 (m, 3F).

Isotactic poly(glycidyl pentafluorophenyl ether) (Table 1, run 6, poly-(*S*)-**7**). ^{1}H NMR ($CDCl_3$): δ 3.77 (br, 3H), 4.09 to 4.19 (m, 1H), 4.22 to 4.32 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 69.16, 75.13, 78.62, 133.81, 137.56, 138.09, 141.74. ^{19}F NMR ($CDCl_3$): δ −156.70 to −156.89 (m, 2F), −162.79 (m, 1F), −163.09 (m, 2F).

Regioirregular poly(pentafluorostyrene oxide) (Table 1, run 7, poly-*rac*-**8**). ^{1}H NMR ($CDCl_3$): δ 3.32 to 3.96 (m, 2H), 4.70 to 4.93 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 69.80 to 70.40, 70.83 to 71.59, 72.41 to 73.79, 111.52, 137.61, 141.38, 145.49. ^{19}F NMR ($CDCl_3$): δ −143.11 to −144.46 (m, 2F), −153.9 to −154.71 (m, 1F), −161.93 to −163.51 (m, 2F).

Atactic poly(3-phenyl-1,2-epoxypropane) (Table 1, run 8, poly-*rac*-**9**). ^{1}H NMR ($CDCl_3$): δ 2.60 (br, 1H), 2.70 (br, 1H), 3.10 to 3.55 (m, 3H), 7.02 to 7.30 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 38.21, 38.39, 70.93, 71.05, 71.39, 71.49, 80.59, 80.67, 126.13, 128.21, 129.65, 138.89.

Isotactic poly(3-phenyl-1,2-epoxypropane) (Table 1, run 9, poly-(*R*)-**9**). ^{1}H NMR ($CDCl_3$): δ 2.60 (dd, J = 7.1, 11.3 Hz, 1H), 2.69 (dd, J = 4.9, 13.7 Hz, 1H), 3.20 (dd, J = 4.9, 9.8 Hz, 1H), 3.28 to 3.45 (m, 2H), 7.00 to 7.28 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 38.37, 71.44, 80.67, 126.13, 128.23, 129.61, 138.89.

Atactic poly**(**glycidyl phenyl ether) (Table 1, run 10, poly-*rac*-**10**). ^{1}H NMR (DMSO-d_6, 120 °C): δ 3.61 to 3.81 (m, 3H), 3.91 to 4.07 (m, 2H), 6.83 (m, 3H), 7.16 (m, 2H). ^{13}C NMR (DMSO-d_6, 120 °C): δ 67.71, 67.75, 68.71, 68.85, 77.28, 77.37, 77.45, 114.30, 120.05, 128.60, 158.16.

Isotactic poly**(**glycidyl phenyl ether) (Table 1, run 11, poly-(*S*)-**10**). ^{1}H NMR (DMSO-d_6, 120 °C): δ 3.63 to 3.78 (m, 3H), 3.88 to 4.06 (m, 2H), 6.83 (br, 3H), 7.15 (br, 2H). ^{13}C NMR (DMSO-d_6, 120 °C): δ 67.73, 68.85, 77.44, 114.32, 120.08, 128.64, 158.17.

Optical Rotations of Polymers. Poly-(*R*)-**6**: $[\alpha]_D^{22}$ = +5.69° (*c* 1.54 in $CHCl_3$). Poly-(*S*)-**7**: $[\alpha]_D^{21}$ = +3.01° (*c* 0.308 in THF). Poly-(*R*)-**9**: $[\alpha]_D^{22}$ = +5.45° (*c* 0.400 in $CHCl_3$). Poly-(*S*)-**10** (insoluble in any organic solvent at room temperature).

Acknowledgment. This work was financially supported by Asahi Glass Co. Research Collaboration Project. The authors thank Prof. T. Kato, Dr. Y. Yoshio, and Dr. T. Nishimura (The University of Tokyo) for DSC and CD measurements. The authors also acknowledge Prof. T. Aida and Dr. A. Tsuda (The University of Tokyo) for ORD measurements. Additionally, the authors also thank Prof. Z. Hou, Dr. M. Nishiura, and Mr. K. Mori (The Institute of Physical and Chemical Research) for molecular weight measurement. Last, the authors also thank Dr. M. Yamashita (The University of Tokyo), Dr. T. Sasamori, and Prof. N. Tokitoh (The University of Kyoto) for X-ray crystallographic analyses and their helpful discussions.

Supporting Information Available: All syntheses of monomers, determinations of absolute configurations, ^{13}C NMR spectra charts of obtained polymers, and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA070428J