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Single-handed helical polyethers synthesized via anionic polymerization of optically active 3-(9-alkylfluoren-9-yl)propene oxides

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ABSTRACT

A series of optically active 3-(9-alkylfluoren-9-yl)propene oxides were synthesized by the reaction of 9-alkylfluoren-9-yllithium with the optically active epichlorohydrin at -70 °C and polymerized using KOH as an initiator. The molecular weight of the poly(3-(9-alkylfluoren-9-yl)propene oxide)s is larger than that of poly(4,4,4-triphenyl-1-butene oxide), which had been proved to take stable helical conformation in solution, and their molecular weight distributions were narrower ($M_w/M_n = 1.02$ to 1.09) than poly(4,4,4-triphenyl-1-butene oxide). By investigating of chiroptical properties of a series of polymers derived from optically active epoxide, it is suggested that the poly(3-(9-alkylfluoren-9-yl) propene oxide)s keep one-handed helical conformation in solution.

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1. Introduction

Synthetic polymers with single-handed helical structure have attracted much attention since it was discovered that the single-handed helical polymer poly(triphenylmethyl methacrylate) (TrMA) had chiral recognizing ability [1–7]. So far, huge amounts of synthetic polymers which keep a single-handed helical conformation in solution have been synthesized from acrylamides [8–12], styrenes [13–18], aldehydes [19,20], isocyanates [21–26], isocyanides [27–30], acetylenes [31–33], N-propargylphosphonamidates [34], N-propargylureas [35] and so on. However, to our knowledge, there was no information about the single-handed helical polymer derived from epoxides until our group prepared successfully optically active helical polyether recently [36,37].

In the polymer of the vinyl compound, there is a common characteristic that the repeated unit of the backbone contains only two atoms and the atoms bearing a bulky pendant responsible for forming helical conformation are isolated from each other only by one atom (see Fig. 1A).

In the polymer of epoxide, the repeated unit contains three atoms and the atoms bearing a bulky pendant are isolated from each other by two atoms. Further more, among the three atoms of the repeated unit of the backbone, there is an oxygen atom, which bears no any other substituent (see Fig. 1B). These characteristics of the polyepoxide backbone make polyepoxide flexible, and therefore result in a difficulty for forming helical polyether. Despite this difficulty, our group have reported that the polymer of optically active 4,4,4-triphenyl-1-butene oxide (TPBO) can keep a prevailing helicity of backbone in solution [36,37]. However, the degree of polymerization (DP) of poly-TPBO is not high and the molecular weight distribution is too wide. Here, we report helical polyepoxides prepared from the polymerization of optically active 3-(9-alkylfluoren-9-yl)propene oxides (AFPOs). When the bulky pendant CPh₃ of poly-TPBO was substituted with 9-alkylfluoren-9-yl group, the polyepoxide not only kept a prevailing helicity of backbone in solution but also had higher molecular weight and narrower molecular distribution.

2. Results and discussion

The optical AFPOs were synthesized with good yield (69 ~ 80%) by the reaction of the corresponding 9-alkylfluoren-9-yllithium with optical epichlorohydrin (ECH) in THF at -70 °C for 30 min and then at room temperature for 3 h (see Scheme 1).

It has been proved [36] that the reaction forming epoxide monomers proceeded in two steps: 1) organolithium attacked CH_2 of the oxirane group of ECH at -70 °C and ring was opened to give intermediate **2**; 2) LiCl was eliminated from intermediate **2** at room temperature to yield epoxide monomer **1**. Therefore, the chiral atom's configuration of the epoxide still remained unchanged in all the processes and the e.e. value of the epoxide monomer was equal to that of the ECH.





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Fig. 1. A: the backbone of the vinyl polymer; B: the backbone of the polyepoxide; R: bulky pendant.

In most case, the polymerization of optical AFPOs was carried out in bulk using KOH as an initiator. (see Scheme 2). In order to obtain higher molecular weight, the solution polymerization of (R)-3-(9ethylfluoren-9-yl)propylene oxide was also conducted in xylene.

The polymerization results are shown in Table 1.

The molecular weight of poly-AFPOs depends on the polymerization conditions and the monomer type. Fig. 2 shows the the GPC trace of poly((R)-3-(9-methylfluoren-9-yl)propylene oxide) (poly-(R)-MFPO) (run 1), poly((R)-3-(9-ethylfluoren-9-yl)propylene oxide) (poly-(R)-EFPO) (run 3), poly((R)-3-(9-propylfluoren-9-yl) propylene oxide) (poly-(R)-PFPO) (run 5), poly((R)-3-(9-butylfluoren-9-yl)propylene oxide) (poly-(R)-BFPO) (run 7) and poly-(R)-EFPO yieded by solution polymerization (run 11).

The bulk polymerization rates of AFPOs are much faster than that of TPBO and the DP of poly-AFPOs are much higher than that of poly-TPBO. For the bulk polymerization of AFPOs at 130 °C, it just took 4 h for the polymeriziton system to solidify with the DPs being 17 while, for that of TPBO at 150 °C, it expended 7 days for the system to solidify [36,37] with its DP being only 7. The molecular weight distribution (M_w/M_n) of poly-TPBO is 1.8. However, that of poly-AFPOs are 1.02–1.09.

The molecular weight of poly-AFPO produced in solution polymerization was larger than that produced in bulk polymerization. The molecular weight of poly-(R)-EFPO produced in bulk polymerization was 4300 (see run 3 and Fig. 2b) while that produced by solution polymerization in xylene under the similar polymerization condition was 5100 (see run 11 and Fig. 2e).

The reason why AFPOs have higher polymerization activity than TPBO is that 9-alkylfluoren-9-yls are smaller than triphenylmethyl and make less hindrance for polymerization.

¹H NMR spectrum of poly-TPBO showed two obvious olefinproton signals at 5.27 ppm and 6.21 ppm (see Fig. 3), indicating that there was a severe chain transfer[37] in the bulk plymerization. It was this chain transfer that resulted in the wide molecular weight distribution. In ¹H NMR spectra of poly-AFPOs, there was no such an olefin-proton signal, indicating that no chain transfer took place in the plymerization. Therefore, the molecular weight distribution of poly-AFPOs was very narrow and the molecular weight of poly-AFPOs was higher than that of poly-TPBO.

By analysing the chiroptical properties of a series of polyepoxides, poly-TPBO was proved to exist in the form of prevailing helicity in solution [36]. In the same way, poly-AFPOs was also proved to exist in the form of prevailing helicity in solution.

The optical rotation sign of AFPOs is opposite to that of TPBO whose configuration is the same as the correponding AFPO. But





Scheme 1. The synthesis of optical 3-(9-alkylfluoren-9-yl)propene oxide.



Scheme 2. The polymerization of 3-(9-alkylfluoren-9-yl)propene oxides.

the optical rotation sign of poly-AFPOs, which is opposite to their monomers', is the same as that of poly-TPBO whose monomer have the same configuration as the corresponding AFPO. This property of optical rotation sign is another evidence for polyepoxides to form helical conformation.

The absolute value of the poly-AFPOs' specific rotation ($[\alpha]$) is 44 times as large as that of the corresponding monomer and this enhance of the $[\alpha]$ from monomer to polymer supports powerfully that poly-AFPOs keep a stable helical conformation.

The CD spectrum properties of poly-AFPO system and poly-TPBO system are similar to their specific rotation properties (see Fig. 4). The Cotton effects of poly-(R)-AFPOs, whose monomers have a negative Cotton effect, are positive, and are the same as that of poly-(R)-TPBO, whose monomer have a positive Cotton effect. Cotton effects of the S-isomer of AFPOs, TPBO and their polymers are opposite to that of the corresponding R-isomer. These properties of the Cotton effect also support intensively that poly-AFPOs keep prevailing helical conformation in solution.

The absolute value of the maximum molar ellipticity $([\theta]_{max},$ referred to one monomeric unit for polymer) of poly-AFPOs is about 40 times as high as that of the corresponding monomers (see Fig. 4). This larger amplification of the maximum molar ellipticity from monomer to polymer are also consistent with the conclusion that poly-AFPOs keep a stable helical conformation.

The amplification times of the $[\theta]_{max}$ from AFPOs to poly-AFPOs is more than 40, which indicates that the helicity poly-AFPOs.is excellent.

The epoxy ring of AFPOs was opened after polymerization and the opening of the epoxy ring should have an impact on the chiroptical properties of poly-AFPOs. However, the experiment data indicated this impact was not much. When the epoxy ring of (R)-3-(9-ethylfluoren-9-yl)propene oxide [(R)-EFPO] was opened by OH⁻ or t-BuO⁻, the [α]₂₆₅³⁶ of the ring-opening product **3a** (-81.2) or **3b** (-106) was not much enough (Scheme 3). Therefore, the change of chiroptical properties after polymerization does not result from the opening of the epoxy ring.

It is possible that the large optical rotation and the large CD intensity of poly-AFPOs may arise from the chiral carbons in the polymer main chain. To rule out this posiblity, (*R*)-4-(9-propyl-fluoren-9-yl)-1-butene oxide [(*R*)-PFBO] (see Fig. 5) was synthesized and polymerized. The $[\alpha]_{365}^{20}$ of (*R*)-PFBO is +14.6 and that of its polymer +27.0. Fig. 3 shows that CD intensity of (*R*)-PFBO and that of its polymer is almost the same. This small chiroptical property differences between (*R*)-PFBO and its polymer implies that the large optical rotation and the large CD intensity of poly-AFPOs by no means arise from the chiral carbons in the polymer main chain.

The chiroptical property differences also depend on the distance between the chromophore and the backbone which contains chiral atom. But, the study on the chiroptical properties of (*R*)-4,4diphenyl-1-hexene oxide [(*R*)-DPHO] (see Fig. 5) and its polymer negated that the large optical rotation and the large CD intensity of poly-AFPOs result from the right distance between the chromophore and the backbone. Although this distance in (*R*)-DPHO is the same as that in (*R*)-AFPOs, the chiroptical property differences between (*R*)-DPHO and its polymer are not much. $[\alpha]_{365}^{20}$ of (*R*)-DPHO is +108 and that of its polymer +229. The CD intensity of (*R*)-DPHO is also close to its polymer's (see Fig. 6).

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Table	1

The	polymerization	of AFPOs ^a .

run	monomer			polymer				
	R	Cnf. ^b	[α] ²⁰ ₃₆₅ ^c	Y ^d /%	[α] ²⁰ ₃₆₅ ^c	$M_n^e / \times 10^3$	DP ^e	$M_{\rm w}/M_{\rm n}^{\rm e}$
1 ^f	CH ₃	R	-14.2 ± 0.2	71.7	$+786\pm10$	3.7	16	1.04
2^{f}	CH ₃	S	$+14.1\pm0.2$	72.6	-793 ± 10	3.7	16	1.04
3	C_2H_5	R	-21.2 ± 0.3	84.4	$+934\pm14$	4.3	17	1.02
4	C_2H_5	S	$+21.0\pm0.3$	83.1	-970 ± 14	4.3	17	1.03
5	n-C ₃ H ₇	R	-21.6 ± 0.3	77.9	$+1346\pm18$	4.8	18	1.06
6	n-C ₃ H ₇	S	$+21.6\pm0.3$	78.6	-1361 ± 18	4.8	18	1.04
7	$n-C_4H_9$	R	-16.0 ± 0.2	81.4	$+734\pm10$	4.7	17	1.05
8	$n-C_4H_9$	S	$+16.0\pm0.2$	81.0	-758 ± 10	4.7	17	1.05
9^{g}	C ₂ H ₅	R	-21.2 ± 0.3	53.8	$+424\pm8$	2.3	9	1.12
10 ^h	C_2H_5	R	-21.2 ± 0.3	67.3	$+836\pm12$	3.8	15	1.03
11 ⁱ	C_2H_5	R	-21.2 ± 0.3	61.7	$+994\pm14$	5.1	20	1.09

^a Conducted in bulk, initiator: KOH, the molar ratio of monomer to initiator (*M*₀/Int): 25, polymerization temperature (*T*): 130 °C, polymerization time (*t*): 4 h ^b the configuration of monomers.

the configuration of monomers.

^c measured in THF (c = 10.00 g/L).

^d Isolated yields

^e Determined by GPC (polystyrene as standard, THF as solvent).

^f T: 120 °C.

^g M₀/Int: 30, T: 90 °C, t: 24 h

^h *M*₀/Int: 30, *T*: 120 °C, *t*: 10 h

ⁱ *M*₀/Int: 30, *T*: 125 °C, *t*: 48 h, xylene (50% wt) was added.

Since the opening of the epoxy ring, the chiral carbons in the main chain of the polymer and the distance from the backbone to the bulky group in pendant do not result in the large optical rotation and the large CD intensity of poly-AFPOs, there must be another factor which is responsible for this chiroptical properties, and this factor should be the one-handed helical backbone.

The reason why the optical rotation and the maximum molar ellipticity of poly-(R)-PFBO are not large is that the bulky 9-alkyl-fluoren-9-yl group is far from the polymer backbone, which makes the backbone too flexible to form a stable helical conformation.

Nakano reported that the polymer of dibenzofulvene (DBF) possess a novel " π -stacked structure" in which the aromatic groups in the side chain are stacked on top of each other [38] and π -stacked structure consisting of three or more fluorene units lead to a helical structure [39]. Perhaps there are π -stacked structure in poly-AFPO and, besides bulkiness of the side-chain groups, these π -stacked fluorene groups are the driving force that lead to helical conformation. In order to confirm this guess, poly-(R)-EFPO (n = 18) was drawn in "ChemDraw Ultra 8.0" software, then the poly-(R)-EFPO drawn in "ChemDraw Ultra 8.0" was pasted in "Chem3D Ultra 8.0" software, and a beautiful helical conformation figure came out (see Fig. 7).

From the 3D helical figure, one can find that three monomeric units form one turn with all of oxygen atoms locating in the inner of



Fig. 2. The GPC trace evolution of the polyethers. GPC was measured with polystyrene as a standard and THF as eluent. The elution time "t_r" was used to express the peak position: a, run 1 in Table 1, $t_r = 15.406$ min; b, run 3, $t_r = 15.211$ min; c, run 5, $t_r = 15.103$ min; d, run 7, $t_r = 15.274$ min; e, run 11, $t_r = 14.925$ min.

the helical pipe. There are four groups of π -stacked structure which consist of three fluorene rings in the helical column. At each end of helial column, there are three fluorene rings, with tow of fluorene rings forming π -stacked structure. In the "Chem3D Ultra 8.0", Poly-(*R*)-DPHO (n = 18) cannot form helical conformation and also have not such a π -stacked structure.

To exclude further the possibility that the change of chiroptical properties resulted from the chiral carbons in the main chain of the polymer, the relation between chiroptical properties of poly-(R)-EFPO and its degree of polymerizations (DP) was studied. The poly-(R)-EFPO with different DP were obtained by changing polymerization condition. DP of **3a** is 1. The relation between chiroptical properties of poly-(R)-EFPO and its DP are shown in Fig. 8.

As being shown in Fig. 8, the $[\alpha]_{365}^{20}$ and the $[\theta]_{max}$ of poly-(*R*)-EFPO increase with the increase of DP linearly when DP is less than 17, and their come to maximum and become constant when DP is more than 19. This relation between the chiroptical property characteristic of poly-(*R*)-EFPO and its DP indicates that the tremendous $[\alpha]_{365}^{20}$ and the $[\theta]_{max}$ of the polymer does not come from the chiral carbons in the main chain of the polymer but from the stable helical conformation.

3. Conclusion

In summary, a series of optical active AFPO was synthesized and anionically polymerized. The molecular weight of poly-AFPOs is higher than that of poly-TPBO, and molecular weight distribution of poly-AFPOs is narrower than that of poly-TPBO, which has been proved to keep a stable one-handed helical conformation in solution. The specific optical rotation ($[\alpha]_{365}^{20}$) and the maximum molar ellipticity ($[\theta]_{max}$) of poly-AFPOs is 44 times as large as that of the corresponding monomer. This enhance of the $[\alpha]$ and the $[\theta]$ from monomer to polymer results from the formation of a stable helical conformation.

4. Experimental

4.1. Synthesis of 9-alkylfluorene

9-Alkylfluorene (alkyl = methyl, ethyl, n-propyl and n-butyl) were prepared using the method proposed by Kurt L. Schoen and E. I. Becker [40].



Fig. 3. ¹H NMR spectra of polymers: A, poly-TPBO; B, poly-PFPO.

4.2. Synthesis of (R)- or (S)-3-(9-alkylfluoren-9-yl)propylene oxide

To a solution of 9-methylfluorene (9.00g, 0.05 mol) in THF (40 mL), was dropped n-BuLi solution in hexane (20.0 mL, 2.5 M) at 0 °C with stirring under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h to give a dark red solution of 9-methylfluoren-9-yllithium. A solution of (*R*)-(–)-epichlorohydrin (ECH) (2.4 mL) in dried THF (10 mL) was added dropwise at -70 °C with stirring within 30 min. The mixture was warmed to room temperature after the addition of ECH and stirred at room temperature for 3 h before distilled water (10 mL) was added. The mixture was extracted with diethyl ether $(3 \times 15 \text{ mL})$ and the combined extract was washed with water and dried over anhydrous Na₂SO₄. The solvent was evaporated in vacuo and the residue was recrystallized from ethanol to obtain 9.23g of (R)-3-(9-methylfluoren-9-yl)propylene oxide [(R)-MFPO]. Yield 78.3%, white crystal, m.p.: 41-42 °C. $[\alpha]_{365}^{20} = -14.2^{\circ}(c = 0.0100 \text{ g/mL}, \text{THF}), e.e.:$ 98.8% ($t_{(R)} = 13.817 \text{ min}$); Anal. Calcd for C₁₇H₁₆O: C, 86.40; H, 6.82; O, 6.77; Found C, 86.34; H, 6.85. ¹H NMR(CDCl₃, 400 MHz) δ (ppm): 7.73 (d, I = 6.8 Hz, 2H, Ar-H), 7.48 (d, I = 6.2 Hz, 1H, Ar-H), 7.32-7.40 (m, 5H, Ar-H), 2.38-2.41 (m, 1H, CH), 2.30-2.33 (m, 2H,



Fig. 4. The CD spectra of chiral epoxides and their polymer (molar ellipticity [θ] referred to one monomeric unit for polymers). a: 3-(9-meth-ylfluoren-9-yl)propylene oxide; b: 3-(9-ethylfluoren-9-yl)propylene oxide; c: 3-(9-n-propylfluoren-9-yl) propylene oxide; d: 3-(9-n-butyl-fluoren-9-yl)propylene oxide; e: 4,4,4-triphenyl-1-butene oxide.

CH₂), 2.11–2.13(m, 1H, CH*H*), 1.97–2.02 (m, 1H, CHH), 1.55 (s, 3H, Me). ¹³C NMR (CDCl₃, 100 MHz) δ : 151.18, 150.92, 139.94, 139.79, 127.39, 127.38, 127.35, 127.27, 123.20, 122.90, 120.11, 120.09, 49.46, 49.17, 47.09, 43.36, 26.34.

(*S*)-3-(9-methylfluoren-9-yl)propylene oxide [(*S*)-MFPO] was synthesized as (*R*)-MFPO except that (*R*)-(–)-ECH was replaced by (*S*)-(+)-ECH. (*S*)-MFPO, yield, 77.6%, $[\alpha]_{365}^{20} = +14.1^{\circ}(c = 0.0100 \text{ g/mL, THF})$, *e.e.*: 98.7% ($t_{(S)} = 13.900 \text{ min}$). The m.p., element analysis and the NMR spectrum data was the same as (*R*)-MFPO.

When 9-methylfluorene was replaced by 9-ethylfluorene, 9-propylfluorene and 9-butylfluorene, respectively, to react with (R)-(-)-ECH or (S)-(+)-ECH, the corresponding monomers had been obtained.

(*R*)-3-(9-ethylfluoren-9-yl)propylene oxide [(*R*)-EFPO]: yield 80.2%, white crystal, m.p.: 76–77 °C. [α]₃₆₅²⁰ = -21.2° (*c* = 10.0 g/L, THF), *e.e.*: 98.8% ($t_{(R)}$ = 13.275 min); (S)-EFPO: yield, 79.8%, [α]₃₆₅²⁰ = +21.0° (*c* = 10.0 g/L, THF), *e.e.*: 98.7% ($t_{(S)}$ = 11.667 min). Anal. Calcd for C₁₈H₁₈O: C, 86.36; H, 7.25; Found C, 86.34; H, 7.27. ¹H NMR(CDCl₃, 400 MHz) δ (ppm): 7.73 (d, *J* = 5.6 Hz, 2H, Ar), 7.44 (d, *J* = 7.2, 1H, Ar–H), 7.29–7.39 (m, 5H, Ar–H), 2.41–2.45 (m, 1H, CH), 2.25–2.28 (m, 2H, CH₂), 1.99–2.12 (m, 4H, 2CH₂), 0.33 (t, *J* = 7.4 Hz, 3H, Me). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 149.20, 148.96, 141.12, 140.94, 127.30, 127.26, 127.17, 127.12, 123.29, 123.00, 119.93, 119.90, 54.05, 49.01, 47.21, 42.87, 32.60, 8.02.

(*R*)-3-(9-propylfluoren-9-yl)propylene oxide [(*R*)-PFPO]: yield 77.3%; white crystal, m.p.: 87–88 °C; $[\alpha]_{265}^{20} = -21.6^{\circ}$ (*c* = 10.0 g/L, THF); *e.e.*: 98.6% ($t_{(R)} = 12.408$ min); (*S*)-PFPO: yield 78.1%, $[\alpha]_{265}^{20} = +21.6^{\circ}(c = 10.0 \text{ g/L}, \text{THF});$ *e.e.*: 98.7%, ($t_{(S)} = 11.183$ min); Anal. Calcd for C₁₉H₂₀O: C, 86.32; H, 7.63; O, 6.05; Found C, 86.27; H, 7.65. ¹H NMR(CDCl₃, 400 MHz) δ (ppm): 7.72 (d, *J* = 7.2 Hz, 2H, Ar–H), 7.45 (d, *J* = 6.8 Hz, 1H, Ar–H), 7.30–7.37 (m, 5H, Ar–H), 2.40–2.45 (m, 1H, CH), 2.25–2.27 (m, 2H, CH₂), 1.97–2.10 (m, 4H, 2CH₂), 0.65–0.67 (m, 5H, Et). ¹³C NMR (CDCl₃) δ (ppm, 100 MHz): 149.62, 149.38, 140.90, 140.72, 127.26, 127.25, 127.22, 127.11, 123.28, 122.98, 119.93, 119.90, 53.68, 48.94, 47.19, 43.10, 42.25, 16.89, 14.32.



Scheme 3. Opening of the epoxy ring of (R)-EFPO.



Fig. 5. The structure of (*R*)-PFBO and (*R*)-DPHO.

(*R*)-3-(9-butylfluoren-9-yl)propylene oxide [(*R*)-BFPO]: yield 69.4%, white crystal, m.p.: 46–47 °C; $[\alpha]_{20}^{26} = -16.0^{\circ}(c = 10.0 \text{ g/L}, THF); e.e: 98.3%, (<math>t_{(R)} = 11.858 \text{ min}$); (*S*)-BFPO: yield 68.7%, $[\alpha]_{20}^{26} = +16.0^{\circ}(c = 10.0 \text{ g/L}, THF); e.e: 98.3%, (<math>t_{(S)} = 10.717 \text{ min}$); Anal. Calcd for C₂₀H₂₂O: C, 86.29; H, 7.97; O, 5.75; Found C, 86.29; H, 7.99. ¹H NMR(CDCl₃, 400 MHz) δ (ppm): 7.73 (d, J = 6.4 Hz, 2H, Ar–H), 7.45 (d, J = 6.8 Hz, 1H, Ar–H), 7.30–7.37 (m, 5H, Ar–H), 2.39–2.44 (m, 1H, CH), 2.24–2.26 (m, 2H, CH₂), 2.01–2.09 (m, 4H, CH₂CH₂), 1.04–1.12 (m, 2H, CH₂), 0.59–0.69 (m, 5H, Et). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 149.62, 149.37, 140.92, 140.74, 127.26, 127.25, 127.21, 127.11, 123.27, 122.97, 119.93, 119.90, 53.56, 48.94, 47.18, 43.21, 39.58, 25.62, 22.92, 13.75.

4.3. Synthesis of 3a and 3b

4.3.1. Synthesis of 3a

To a solution of (R)-PFPO (0.50 g, 0.002 mol) in THF 15 mL, was added aqueous solution of KOH (1 mL, 50% wt) with stirring. The mixture was refluxed for 24 h and extracted with diethyl ether $(3 \times 5 \text{ mL})$ after cooling to room temperature. The extract was washed with water, dried over anhydrous MgSO₄ and evaporated in vacuo. The residue was separated by column chromatography $(hexane/CH_2Cl_2 = 4/1)$ to obtain **3a**, yield 44.8%. (*R*)-3a: $[\alpha]_{365}^{20} = -81.2$; (c = 10.0 g/L, THF). ¹H NMR(CDCl₃, 400 MHz) δ (ppm): 7.68 (d, J = 6.2 Hz, 2H, Ar), 7.20–7.41 (m, 6H, Ar), 3.64 (s, 1H, CH), 3.09-3.13 (m, 1H, CHH), 2.90-3.04 (m, 1H, CHH), 2.83-2.87 (m, 1H, CHH), 2.57-2.62 (m, 1H, CHH), 1.94 (q I = 5.8, 2H, CH₂), 0.53 $(t, J = 6.2 \text{ Hz}, 3\text{H}, \text{CH}_3)$. ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 149.61, 149.22, 141.16, 140.91, 127.13, 127.05, 127.01, 126.87, 123.48, 123.06, 119.74, 119.71, 67.74, 64.45, 51.33, 41.27, 32.06, 9.41. Anal. Calcd for C₁₈H₂₀O₂: C, 80.56; H, 7.51; O, 11.92; found C, 80.49; H, 7.55; O, 11.95.

4.3.2. Synthesis of 3b

To a solution of (R)-PFPO (0.50 g, 0.002 mol) in THF 15 mL, was dropped t-BuOK solution in THF (1.7 mL, 1.2 M) at r.t. with stirring



Fig. 6. The CD spectra of (*R*)-PFBO, (*R*)-DPHO and their polymers.



Fig. 7. Poly-(*R*)-EFPO was simulated in "Chem3D Ultra 8.0" software.

under nitrogen atmosphere. The mixture was refluxed for 5 h and extracted with diethyl ether (3 × 5 mL) after cooling to room temperature. The extract was washed with water and dried over anhydrous MgSO₄. The solvent was evaporated in vacuo and the residue was separated by column chromatography (hexane/ CH₂Cl₂ = 5/1) to obtain **3b**, yield 32.5%. (*R*)-**3b**: $[\alpha]_{205}^{205} = -108$ (*c* = 10.0 g/L, THF).; ¹H NMR(CDCl₃, 400 MHz) δ (ppm): 7.70 (d, *J* = 6.4 Hz, 2H, Ar), 7.28–7.47 (m, 6H, Ar), 3.02 (s, 1H, OH), 2.69–2.73 (m, 1H, CH), 2.60–2.64 (m, 1H, CHH), 2.31–2.34 (m, 1H, CH), 2.02–2.19 (m, 4H, 2CH₂), 0.94 (s, 9H, 3CH₃), 0.28 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (CDCl₃, 100 MHz) δ /ppm: 149.69, 149.27, 141.20, 140.98, 127.21, 127.13, 127.03, 126.92, 123.55, 123.14, 119.83, 119.81, 72.86, 68.20, 66.15, 53.79, 43.27, 33.78, 27.31, 7.97. Anal. Calcd for C₂₂H₂₈O₂: C, 81.44; H, 8.70; O, 9.86; found C, 81.40; H, 8.75; O, 9.91.

4.4. Synthesis of (R)-4-(9-ethylfluoren-9-yl)butylene oxide

To a solution of 9-ethylfluorene [40] (9.70 g, 0.05 mol) in THF (50 mL), was dropped n-BuLi solution in hexane (20.0 mL, 2.5 M) at 0 °C with stirring under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h to give a dark red solution of 9-ethylfluoren-9-yllithium. A solution of dibromomethane (0.05 mol) in dried THF (5 mL) was added dropwise at -10 °C with stirring within 20 min. The mixture was warmed to room temperature with stir for 3 h before distilled water (10 mL) was



Fig. 8. The function of the $[\alpha]_{365}^{20}$ and the $[\theta]_{max}$ of poly-(*R*)-EFPO vs DP.

added. The mixture was extracted with diethyl ether (3 × 10 mL) and the combined extract was washed with water and dried over anhydrous CaCl₂. The solvent was evaporated in vacuo and the residue was recrystallized from ethanol to obtain 12.10 g of 9-ethylfluoren-9-yl bromomethane. Yield 84.2%, white crystal, m.p.: 69–70 °C. Anal. Calcd for C₁₆H₁₅Br: C, 66.91; H, 5.26; Br, 27.82; found C, 66.87; H, 5.32. ¹H NMR(CDCl₃, 400 MHz) δ (ppm): 7.76 (d, *J* = 7.4 Hz, 2H, Ar), 7.52 (d, *J* = 7.3 Hz, 2H, Ar), 7.34–7.44 (m, 6H, Ar), 3.76 (s, 2H, CH₂Br), 2.23 (q, *J* = 7.3 Hz, 2H, CH₂), 0.43 (t, *J* = 7.3 Hz, 3H, Me). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 147.43, 141.08, 127.93, 127.20, 123.55, 119.96, 55.05, 41.86, 29.86, 8.57.

9-ethylfluoren-9-yl bromomethane (2.86g, 10 mmol) was dissolved in THF (30 mL) and reacted with Mg (0.48 g, 20 mmol) under N₂ to give a solution of corresponding Grignard reagent. The excess of unreacted Mg was removed by filtration. Then, CuI (15 mg) was added to the solution and the reaction mixture was cooled to -15 °C. A solution of (R)-ECH (0.12 mmol) in THF (5 ml) was dropped into the reaction mixture. 30 min later, the reaction mixture was warmed to r.t. and stirred for another 2 h. KOH aqueous solution (4 mL, 50% wt) was added with stirring. The reaction was monitored by TLC and stopped when no further reaction progress was observed. The organic layer was separated and water layer was exacted with diethyl ether (3 \times 5 mL). The organic phase was dried over anhydrous MgSO₄. The solvent was removed under reduce pressure and the residue was separated by column chromatography (elution hexane/ $CH_2Cl_2 = 5/1$) to obtain (R)-4-(9-ethylfluoren-9-yl) butylene oxide. yield 47.6%, white crystal, m.p. 76 ~ 77 °C e.e.: 98.1 (8.103 min), $[\alpha]_{365}^{20} = +14.6$; Anal. Calcd for C₁₉H₂₀O: C, 86.32; H, 7.63; O, 6.05; found C, 86.27; H, 7.65; O, 6.08. ¹H NMR(CDCl₃, 400 MHz) δ (ppm): 7.71 (d, J = 6.8 Hz, 2H, Ar), 7.30-7.35 (m, 6H, Ar), 2.60-2.62 (m, 1H, CHHO), 2.50-2.52 (m, 1H, CHHO), 2.21-2.28 (m, 2H, CH₂), 2.13-2.14 (m, 1H, CH), 2.03–2.08 (m, 2H, CH₂), 0.83–0.89 (m, 2H, CH₂), 0.34 (t, J = 7.2 Hz, 3H, CH₃). ¹³C NMR (CDCl₃, 100 MHz) δ(ppm): 149.51, 149.33, 141.44, 141.34, 127.26, 127.19, 127.08, 127.06, 122.93, 122.82, 119.77, 119.73, 55.08, 52.29, 46.89, 35.83, 33.17, 27.24, 8.32.

4.5. Synthesis of (R)-2-(2,2-diphenylbutyl)oxirane

To a solution of 1,1-diphenyl ethylene [41] (3.60 g, 0.02 mol) in THF (50 mL), was dropped MeLi solution in diethyl ether (2.0 mL, 1.0 M) at -10 °C with stirring under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 h to give a dark red solution of 1,1-diphenyl ethyllithium. A solution of (R)-ECH (0.02 mol) in dried THF was added dropwise at -70 °C with stirring within 20 min. The mixture was warmed to room temperature with stir for 3 h before distilled water (10 mL) was added. The mixture was extracted with diethyl ether (3 \times 10 mL) and the combined extract was washed with water and dried over anhydrous CaCl₂. The solvent was evaporated in vacuo and the residue separated by column chromatography (elution hexane/ $CH_2Cl_2 = 5/1$). Yield 54.6%, colorless iol-like. *e.e.*: 98.2% (7.608 min); $[\alpha]_{365}^{20} = +108$; Anal. Calcd for C₁₈H₂₀O: C, 85.67; H, 7.99; O, 6.34; Found C, 85.63; H, 8.03. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.15-7.29 (m, 10H, ph); 2.59-2.62 (m, 1H, CH); 2.49-2.55 (m, 2H, CH₂); 2.33–2.39 (m, 1H, CHH); 2.20–2.25 (m, 2H, CH₂); 2.10–2.15 (m, 1H, CHH); 0.68 (t, 3H, J = 7.3 Hz, Me).¹³C NMR (CDCl₃, 400 MHz) δ (ppm): 148.00, 147.96, 128.02, 127.98, 127.96, 127.94, 125.91, 125.88, 49.55, 49.46, 47.01, 40.28, 30.85, 8.72.

4.6. Polymerization

4.6.1. Bulk anionic polymerization

A test tube with stir bar was charged with 10.00 mmol of epoxide monomer and a desired amount (0.4 mmol for example) of

KOH under argon atmosphere, and then sealed with flame of Bunsen burner. The test tube was put into an oil bath thermostated at the desired temperature (such as 130 °C). The reaction mixture was stirred for 4 h. During this time, the mixture turned to auburn and got more and more viscous until the magnetic bar could not move. The reaction mixture was cooled to room temperature and the tube was opened. THF (10 mL) was added to give a homogenous solution. The THF solution was poured into methanol (100 mL). The formed precipitation was filtered and washed with methanol. The above-mentioned process, solving and precipitating, was repeated, then the obtained precipitation was dried in vacuo at 50 °C to obtain polymer, yield 71.7–84.4%.

4.6.2. Solution anionic polymerization

A test tube with stir bar was charged with 10.00 mmol of (R)-EFPO, a desired amount (0.34 mmol for example) of KOH and 1.25 mL xylene under argon atmosphere and then sealed with flame of Bunsen burner. The test tube was put into an oil bath thermostated at the desired temperature (such as 125 °C). The reaction mixture was stirred for 48 h. During this time, the mixture turned to auburn and got more and more viscous. The treatment was the same as that in bulk anionic polymerization and polymer was obtained, yield 61.7%.

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Appendix. Supporting information

The supplementary data associated with this article can be found in the on-line version at doi:10.1016/j.polymer.2010.10.017.

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