Polymer Bulletin 59, 481–490 (2007)
DOI 10.1007/s00289-007-0788-3

Polymer Bulletin

Helical Polymers from Optically Active Epoxides with Bulky Pendants

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Received: 15 March 2007 / Revised version: 31 March 2007 / Accepted: 16 May 2007

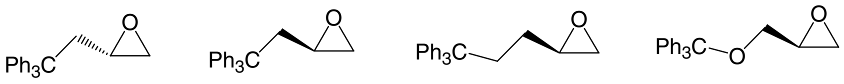
Summary

The backbone of polyethers are often flexible because of inherent characteristics of ether linkage, but polyethers from chiral epoxides could form stable one-handed helical structure in solution state, if the pendants on the chain of polyethers are enough bulky and the distance between pendants and main chain is appropriate.

Introduction

Various polymers with helical conformation have been attracted great attention since Watson and Crick found the double helical structure for DNA in the early 1950s [1]. In recent years, some artificial polymers with one-handed helical conformation such as poly (triphenylmethyl methacrylate) were synthesized. Some of them show excellent chiral recognition ability for many racemic compounds, which encourages chemists to develop new helical polymers [2]. At present, a large amount of polymers with helical conformation have been prepared from achiral and chiral monomers including acrylamides, chloral, isoyanides, isocyanates and so on [3-6]. To our knowledge, some polyethers exist in the form of helical conformation in the solid state. However, there was little information concerning polyethers with stable helical conformation in solution [7-9].

As we know, the ether linkage of polyether has lower barrier to rotation, which makes the chain of polyethers more flexible than polyolefins and results in fast conformationally dynamic interconversion [10]. Therefore, it is very difficult for polyethers to maintain stable helical conformation in solution. Is it possible for polyethers to keep stable helical conformation by introducing elegantly designed functional group like triphenylmethyl that can fix the helix sense through the large interaction between pendants? To answer this question, several optically active polyethers from chiral epoxides with bulky group, such as (*S*)-4,4,4-triphenyl-1-butene oxide ((*S*)-TPBO), (*R*)-4,4,4-triphenyl-1-butene oxide ((*R*)-TPBO)), (*S*)-tritylglycidol ((*S*)-TGE) and (*R*)-5,5,5-triphenyl-1-pentene oxide ((*R*)-TPPO) were synthesized and polymerized in our research work. (**Scheme 1**) We found that polyethers from chiral epoxides could form stable one-handed helical structure in solution if the pendants on the chain of polyethers are enough bulky and the spacers between pendants and main chain are appropriate. Herein, we report our research work.



(*S*)-TPBO (*R*)-TPBO (*R*)-TPPO (*S*)-TGE

Scheme 1. Optically Active Epoxides with Triphenylmethyl Group

Experimental

Materials

All chemicals were bought from Alfar Aesar company except 1.3M *sec*-BuLi in cyclohexane/hexane were purchased from Acros company and they were used as received. THF was distilled under argon protection from benzophenone/Na. The synthesized monomers were purified several times until the purity was not less than 99% (check by HPLC) before they were used in polymerization.

Instruments

NMR were recorded on a Bruker 400 spectrometer with $CDCl_3$ solvent and tetramethylsilane (TMS) as internal standard. GPC was measured on Waters 1515 GPC instrument with polystyrene as a standard and chloroform as eluent. Optical rotations were measured using a Perkin-Elmer 341 LC polarimeter. Enantiomeric excesses (ee's) were determined by chiral HPLC analysis using a Dionex P680 HPLC. The following HPLC column was employed: Chiracel® OD (Daicel Chemical Ind., Ltd) Inc., (25 cm × 0.46 cm) (conditios 97.5:2.5 hexanes: *i*-PrOH, 0.8 mL / min, 220 nm). CD spectrums were performed on Jasco J-810 CD instrument (CH_2Cl_2 as solvent and samples's concentration equal to 1g. dm^{-3}). Purity of monomers was also checked by Dionex P680 HPLC.

Monomer synthesis

(R)-TPBO and (S)-TPBO

n-BuLi solution in hexane (15ml, 1.6M) was gradually dropped into a solution of triphenylmethane (5g, 20mmol) in THF(30ml) under nitrogen atmosphere with stirring. The reaction mixture was stirred at 0°C for 2 hrs to give a dark red triphenylmethyllithium solution, then a solution of chiral epichlorohydrin (2.4 ml) in dry THF (6ml) was slowly added in at –70°C. The mixture was stirred for 20 minutes after the addition finished. The mixture was then warmed to room temperature and stirred at this temperature for 3 hours before distilled water (10ml) was carefully added. The mixture was exacted with diethyl ether (2×15ml). The extracts were successively washed with diluted H_2SO_4 (10%) and water, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the residue was recrsytalized from ethanol to give pure product (colorless crystal, 4.2g, yield 68%). M.p. 127.6-128.0°C. ee%=98%. Specific optical rotation of (*S*)-TPBO $[\alpha]^{20}_{589} = -28°$; (*R*)-TPBO $[\alpha]^{20}_{589} = +28°$ (c 0.2, THF). Anal. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71. Found C, 87.94; H, 6.75.

(S)-TGE

(R)-Glycidol (4.8g, 0.065mol) was dropped into a solution of triphenylmethylchloride (13.9g, 0.05mol), 4-(N, N-dimethylamino) pyridine (DMAP) (0.125g, 0.001mol) and triethylamine (6ml) in THF (50ml) under nitrogen atmosphere. The reaction mixture was stirred at 25°C overnight, and then poured into ice-water mixture. The mixture was exacted with dichloromethane. The combined organic phase was dried over anhydrous Na_2SO_4, concentrated, and precipitated in alcohol to give crude product (11.3g, yield 72%). The pure (*S*)-tritylglycidol could be obtained by redissolving the crude product in CH_2Cl_2 and precipitating again in alcohol for 2-3 times. M.p. 101.5-101.9°C (literature 97.0-97.5°C [11]). $[\alpha]_{589}^{20}$=-11° (c 0.2, THF), ee%=100%. Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found C, 83.52; H, 6.41.

(R)-TPPO

2-Chloro-1, 1, 1-triphenylethane was prepared according to the method used by E Grovenstein [12]. (colorless product, mp 100-101°C, ^{1}H NMR ($CDCl_3$): δ=7.23-7.33 (m, 15H, Ar), 4.63 (s, 2H, CH_2); ^{13}CNMR ($CDCl_3$): 144.82, 129.38, 127.95, 126.66, 57.98, 52.90).

2-chloro-1, 1, 1-triphenylethane (1g, 3.4mmol) was dissolved in THF (10ml) and reacted with Mg turnings (0.72g, 30mmol) to give a solution of corresponding Girnard reagent under N_2. The excess of unreacted Mg was removed by filtration. Then, fresh prepared CuBr (20mg) was added to the solution of Girnard reagent and the reaction mixture was cooled to -10°C. A solution of (*R*)-(-)-epichlorohydrin (0.6ml) in THF (5ml) was slowly dropped in within 30 min. then the reaction mixture was warmed to 25°C and stirred at this temperature for another 30 min. NaOH solution (20ml, 50%) was then 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 (2×10ml). The organic phase was combined and successively washed with diluted H_2SO_4 (10%) and brine, and then dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the residue was recrystallized from hexane and then from ethanol to give pure (*R*)-(+)-5,5,5–triphenyl-1-pentene oxide, yield 61%, mp106.1-106.7°C. $[\alpha]_{589}^{20}$= +14° (c 0.2, THF). ee%=95%. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found C, 87.85; H, 7.06.

Polymerization

Typical Process for Bulk Polymerization of Optically Active TPBO Using t-BuOK or KOH as initiator

TPBO (0.3g, 1mmol) and *t*-BuOK (11.2mg, 0.1mmol) was placed in a tube under argon. The tube was sealed and placed in thermostatic bath at 150°C and the reaction mixture was stirred for 7 days. At the end of the polymerization, the reaction mixture was cooled to room temperature and the tube was then carefully opened. THF (3ml) was added to give a homogenous solution. This solution was poured into methanol (15ml). The formed precipitation was filtered and washed with methanol, then dried on vacuum at 60°C to obtain crude poly((*S*)-TPBO), yield 58%. The obtained polymer could be further purified by redissolved in THF and precipitated in methanol again.

Typical Process for Solution Polymerization of Optically Active TPBO Using t-BuOK

A solution of (*S*)-TPBO (0.3g, 1mmol) and *t*-BuOK (11.2mg, 0.1mmol) in THF (1 ml) was added in tube under argon. Then, the tube was sealed and placed in thermostatic bath at 60°C, the reaction mixture was stirred at this temperature for 2days. At the end of the polymerization, the reaction mixture was cooled to room temperature and then the tube was carefully opened. A little drop of methanol was added to cease the polymerization. The solution was precipitated in 8ml methanol. The formed precipitation was filtered and washed with methanol, then dried on vacuum at 60°C, yield 60%. The obtained polymer could be further purified by redissolved in THF and precipitated in methanol again.

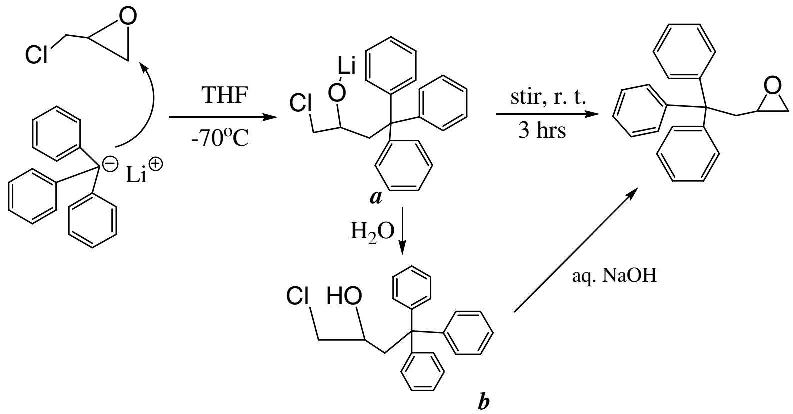
Typical Process for Solution Polymerization of Optically Active Epoxides Using sec-BuLi/t-BuP$_4$

A solution of (*S*)-TPBO (0.3g, 1mmol) in THF (1ml) was placed in tube under argon and cooled to -78°C, 1.3M sec-BuLi solution in cyclohexane/hexane (25µl, 0.033mmol) was added through syringe. The reaction mixture was warmed to room temperature and then heated to 45-55°C. The mixture stood at this temperature for 10 min, 1.1 M t-BuP$_4$ solution in hexane (35µl, 0.038mmol) was added in. The tube was sealed and placed in thermostatic bath at 50°C and the reaction mixture was stirred for 7 days. At the end of the polymerization, the reaction mixture was cooled to room temperature and then the tube was opened. A drop of acetic acid was added into reaction mixture to terminate the polymerization, then reaction mixture was poured into acetic acid-methanol solution (10ml, v:v=1:3). The formed precipitation was filtered and washed with methanol, then dried on vacuum at 60°C to obtain poly((*S*)-TPBO), yield 43%.

Results and discussion

Synthesis of chiral terminal epoxides

(*S*)-TPBO and (*R*)-TPBO were prepared by reaction of triphenyllithium with (*R*)-epichlorohydrin or (*S*)-epichlorohydrin in THF at –70°C, then the reaction mixture was warmed to r.t. and stirred several hours to provide the desired epoxides without the presence of additional base and catalysts. The chiral epoxides were obtained with good yields (68%) and excellent e.e. (98%, similar to that of the original epichlorohydrin). We found that the formation of epoxides via the reaction of organolithium with epichlorohydrin proceeded in two steps: 1) organolithium attacked oxirane group of epichlorohydrin at -70°C and ring was opened to give a intermediate (***a***, scheme 2); 2) the reaction of closing-ring occurred and gave the desired products



Scheme 2. The Process of TPBO’s Formation

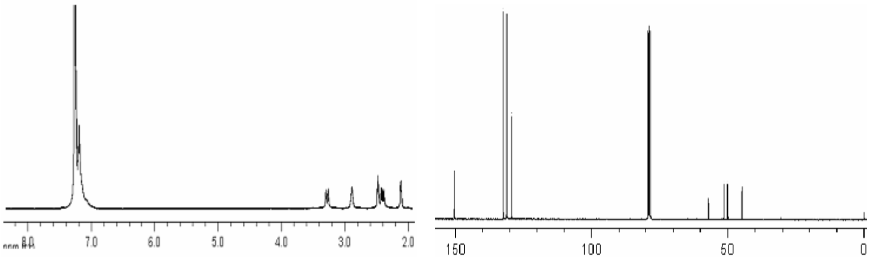


Figure1. ^{1}HNMR and ^{13}CNMR of Chiral TPBO

when the temperature of reaction rise to room temperature after the addition of organolithium was completed.

This mechanism was proved by the hydrolysis of intermediate ***a***. When water was added into the reaction mixture before the reaction mixture was warmed from –70°C to room temperature, the hydrolysis product, which is not TPBO, was obtained. The reaction of the hydrolysis product with aqueous NaOH gave TPBO. The ^{1}HNMR of the hydrolysis product is given as following: δ=7.17-7.37(m, 15H), 3.76-3.79(m, 1H), 3.14(dd, J_1=4.1Hz, J_2=14.8Hz), 3.00-3.05(m, 1H), 2.83-2.86(m, 1H), 2.66(dd, 1H, J=5.2Hz, J=14.8Hz, 1H), 1.90(m,1H). Combining the product of its reaction with aqueous NaOH and the NMR data, the hydrolysis product should be 1-chloro-4, 4, 4-triphenyl-2-butanol (***b***).

Figure 1 was NMR spectras of chiral TPBO. The NMR data of chiral TPBO was given as following: ^{1}HNMR, δ=7.21-7.45(m, 10H, Ph), 3.30 (dd, 1H, J=3.5Hz, J=14.5Hz, $-CH_2CPh_3$), 2.90-2.93 (m, 1H, -CHO-), 2.49-2.51 (m, 1H, $-CH_2O-$), 2.42 (dd, 1H, J=6.8Hz, J=14.4Hz, $-CH_2CPh_3$), 2.14 (m, 1H, $-CH_2O-$); ^{13}CNMR, δ=146.8 (Ph), 129.0 (Ph), 127.9 (Ph), 126.2 (Ph), 55.8 (CPh_3), 50.2 (-CHO-, carbon of epoxy group), 48.9 ($-O-CH_2$, carbon of epoxy group), 43.7 ($-CH_2CPh_3$). The optical purity of (*S*)-TPBO and (*R*)-TPBO were checked by HPLC with chiral column. Eluent was the mixtures of hexane and *i*-PrOH (v:v= 97.5:2.5), we found that the peak of (*S*)-TPBO appeared at 7.71min and (*R*)-TPBO at 8.15 min. The optical purity was determined to be 98% from the integration of peaks area.

However, (*R*)-TPPO could not be synthesized by the similar method as that of chiral TPBO because the corresponding organolithium was difficultly obtained and less stable. 2-Chloro-1, 1, 1-triphenylethane reacted with Mg turnings to give the corresponding Girnard reagent, which reacted with (*R*)-(-)-epichlorohydrin to give ring-opening intermediate and then formed ring-closed product in the presence of KOH or NaOH solution. Figure 2 was NMR spectra of (*R*)-TPPO. The NMR data of chiral (*R*)-TPPO was given as following: ^{1}HNMR, δ=7.27-7.08 (m, 15H, Ph), 2.90-2.85 (m, 2H, $-CH_2-CPh_3$(1H)); -CH(O)-(1H)), 2.73-2.70 (m, 1H, 1H, $-CH_2O-$), 2.64-2.61 (m, 1H, $-CH_2-CPh_3$(1H)), 2.42-2.40 (m, 1H, $-CH_2O-$), 1.36-1.27 (m, 2H, methylene adjacent to epoxy group); ^{13}CNMR($CDCl_3$): δ= 147.04 (Ph), 129.16 (Ph), 127.90 (Ph), 125.95 (Ph), 56.47 (CPh_3), 53.53 (-CHO-, carbon of epoxy group), 46.58 ($-O-CH_2$, carbon of epoxy group), 36.86 ($-CH_2-$, adjacent to triphenylmethyl), 28.46 ($-CH_2-$, adjacent to epoxy group).

The reaction process of Girnard reagent with epichlorohydrin was similar to that of organolithium with epichlorohydrin except that additional alkaline solution must be added to promote the formation of ring. The optical purity of (*R*)-TPPO was checked

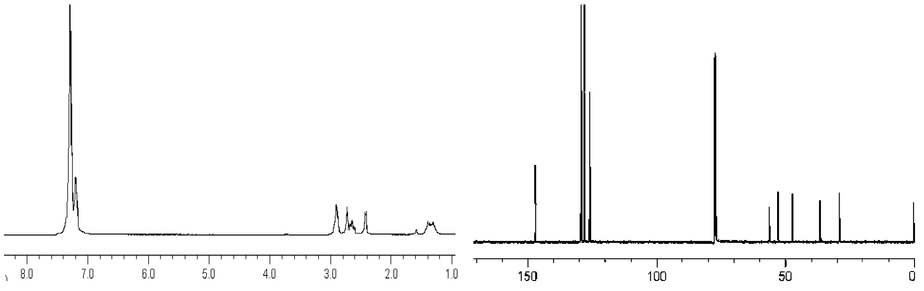
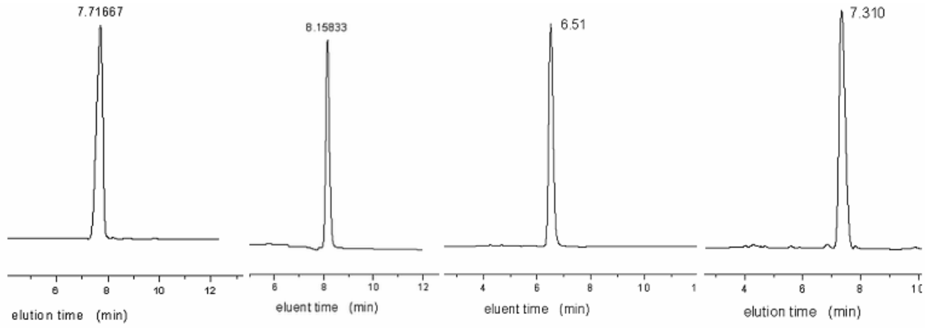


Figure2. ^{1}HNMR and ^{13}CNMR of (*R*)-TPPO



(a) (b) (c) (d)

Figure3. Chiral HPLC of (*S*)-TPBO (a), (*R*)-TPBO (b), (*S*)-TGE (c) and (*R*)-TPPO (d)

by HPLC with chiral column. we found that the peak of (*R*)-TPBO appeared at 7.31min (Figure 3(d)). The optical purity was determined to be 95% from the integration of peaks area.

(*S*)-TGE was easily synthezied by reacting triphenylmethylchloride with (*R*)-glycidol in the presence of weak base such as triethylamime. Figure 4 was NMR spectra of (*S*)-TGE. The NMR data of (*S*)-TGE was given as following: δ=7.20-7.51 (m, 15H, Ph), 3.21(d, 1H, J=8Hz, $-O-CH_2-$), 3.10-3.15 (m, 2H, -CHO- (1H); $-O-CH_2-$ (1H)), 2.75-2.79 (m, 1H, $-O-CH_2$, proton of epoxy), 2.60-2.63 (m, 1H, $-O-CH_2$, proton of epoxy); ^{13}CNMR($CDCl_3$): δ=143.89 (Ph), 128.71 (Ph), 127.87 (Ph), 127.09 (Ph), 86.80 (CPh_3), 64.83 ($-OCH_2-$), 51.04 (-CHO-, carbon of epoxy group), 44.6 ($-O-CH_2$, carbon

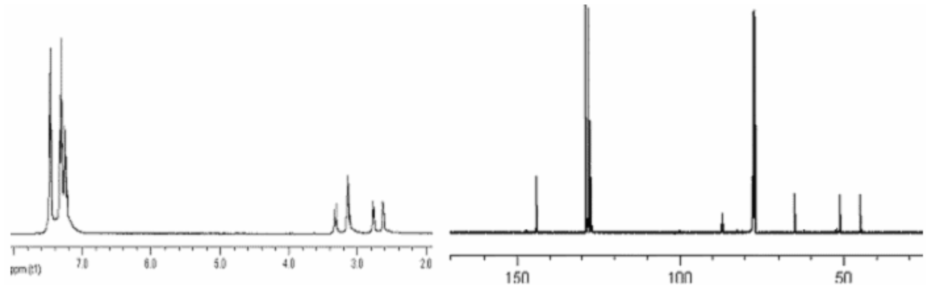


Figure4. ^{1}HNMR and ^{13}CNMR of (*S*)-TGE

of epoxy). HPLC chromatogram showing the optical purity was given in Figure 3(c). Enantiomeric excesses of (*S*)-TGE could also be estimated by comparison of the reported result in literature [11].

Anionic Polymerization of Epoxides

Alkali metal hydroxides and alkali metal alkoxides are the common initiators for the anionic polymerization of epoxides. In our experiment, KOH or *t*-BuOK were used as an initiator of the polymerization of chiral epoxides. The results were shown in table 1. The rate of the polymerization was very slow when amount of initiator was not enough. For example, the degree of polymerization (DP) of poly ((*S*)-TPBO) was about 8 and yield was only14% after keeping the polymerization for 7 days ([M]/[I]=20, run *2* in table 1). It indicated that the bulky side group blocked the chain propagation of polyethers. Recently, Eβwein et al. reported that *sec*-BuLi/tBuP$_4$ was a good kind of initiator for the anionic polymerization of epoxides [13]. In our research work, *sec*-BuLi/tBuP$_4$ was also tried as an initiator for the polymerization of chiral epoxides. The results of polymerization were given in **table 1**.

Table 1. Anionic Polymerization of Optically Active Epoxides

			reaction conditions			produced polymers			
Run	initiator	monomer	[M]/[I]^{a}	Temp (°C)^{b}	Time (day)^{c}	Yield (%)	$[\alpha]^{20}_{589}$ ^{d}	M$_w$^{e} (×10^3)	M$_w$/M$_n$^{e}
1	KOH	(*S*)-TPBO	7	150	7	85	-105	2.2	1.6
2	KOH	(*S*)-TPBO	20	150	7	14	-94	2.2	1.8
3	KOH	(*S*)-TPBO	20	200	7	22	-87	2.1	1.8
4	*t*-BuOK	(*S*)-TPBO	10	150	7	58	-121	2.4	1.6
5	*t*-BuOK	(*S*)-TPBO	20	150	7	37	-117	2.4	1.7
6	*t*-BuOK^{f}	(*S*)-TPBO	10	60	2	62	-122	2.1	1.5
7	*t*-BuOK^{f}	(*S*)-TPBO	20	60	6	47	-128	2.4	1.5
8	*sec*-BuLi/Bu^{t}P$_4$^{g}	(*S*)-TPBO	30	20	7	10	-103	1.5	1.5
9	*sec*-BuLi/Bu^{t}P$_4$^{g}	(*S*)-TPBO	30	50	7	43	-121	1.5	1.5
10	*sec*-BuLi/Bu^{t}P$_4$^{g}	(*S*)-TPBO	30	80	7	80	-112	1.3	1.7
11	*sec*-BuLi/Bu^{t}P$_4$^{g}	(*R*)-TPPO	40	60	5	86	+16	10	1.1
12	*sec*-BuLi/Bu^{t}P$_4$^{g}	(*S*)-TGE	30	20	2	51	+9.6	8.6	1.1
13	*sec*-BuLi/Bu^{t}P$_4$^{g}	(*R*)-TPBO	30	80	5	45	+126	1.9	1.6

a) [M]/[I] = the ratio of molar of monomer to that of initiator; when *sec*-BuLi / Bu^{t}P$_4$ system as intiator, [I] was caculated on molar amount of *sec*-BuLi; the molar amount of monomers used in polymerization was 1mmol. b) Temperature of polymerization; c) Time of polymerization. d) Optical rotation was measured in THF (c=0.2). e) M$_w$ and M$_w$/M$_n$ were determined by GPC and polystyrene as standard. solvent was THF. g) Polymerization was performed in THF solution. f) The ratio of molar of *sec*-BuLi to that Bu^{t}P$_4$ equal to 1:1.1 and polymerization was performed in THF solution.

Chiroptical Properties of Polymers

All obtained poly ((*S*)-TPBO) or poly ((*R*)-TPBO) show large specific optical rotation in solution. For example, with *t*-BuOK as an initiator, the value of specific optical rotation of poly ((*S*)-TPBO) is -128°, about 3-5 times of that of starting monomer whose specific optical rotation is -28° (see table 1, run 7). The large specific optical rotation implies the poly ((*S*)-TPBO) in the solution should exist in the form of one-handed helical structure.

The opening of epoxide ring changes the polarity and the bond angles of the four bonds of chiral carbon in the chiral epoxide and subsequently causes the change of the specific optical rotation. Is it possible that the large optical rotation of optically active poly (TPBO) is resulted from the opening of the ring? In order to answer this question, ring opening products of (*S*)-TPBO, chiral 4, 4, 4-triphenyl-1, 2-butanediol and chiral 4, 4, 4-triphenyl-1-tert-butoxyl-2-butanol, were prepared by solvolysis of (*S*)-TPBO in the presence of large amount of potassium hydroxide and potassium *tert*-butoxide respectively. As our expectation, the specific optical rotations of chiral 4, 4, 4-triphenyl-1, 2-butanediol and 4, 4, 4-triphenyl-1-tert-butoxyl-2-butanol were -38° and -37° [14-15], nearly the same as that of (*S*)-TPBO. These suggested that large optical rotation of poly ((*S*)-TPBO) did not come from the change of structure due to ring-opening of epoxides, and it should be resulted from helical conformation of the polymers.

Perhaps large specific optical rotation of optically active poly (TPBO) may be attributed to chiral carbons of polymer. However, when the distance between bulky triphenylmethyl group and main-chain carbon was farer than that of poly (TPBO), the specific optical rotation of polyethers are almost the same as their monomers, which suggests chiral carbons on polymer chain are not responsible to the large specific optical rotation of optically active poly (TPBO). For instance, the specific optical rotation of (*R*)-TPPO is +14° (see table 1, *run 11*) and that of poly ((*R*)-TPPO) is +16°, almost the same! Another example is (*S*)-TGE and poly ((*S*)-TGE): $[\alpha]_{589}^{20}$ of (*S*)-TGE is –11° and that of poly ((*S*)-TGE) is +9.6° (see table 1, run *12*). These indicated that increase of the distance between bulky group and main-chain would make decrease of the rigidity of polymer chain and then steric repulsion between pendants became weak, which were very important for the polymers to maintain stable helical conformation in solution. Thus, those polymers exhibit poor specific optical rotation.

A similar phenomenon was observed in CD spectrums of optically active poly (TPBO), poly ((*R*)-TPPO) with corresponding epoxides (Figure5). The CD signal intensity of poly ((*R*)-TPBO) is much stronger than (*R*)-TPBO while that of poly ((*R*)-TPPO) is very close to that of (*R*)-TPPO. Thus, the further evidence that optically active poly (TPBO) in solution as helical structure comes out.

The temperature of anionic polymerization of ((*S*)-TPBO) seems to show slight influence on the optical rotation of polyepoxides since polyepoxides obtained in bulk polymerization under high temperature still exhibit large optical rotation (run 1-3 in

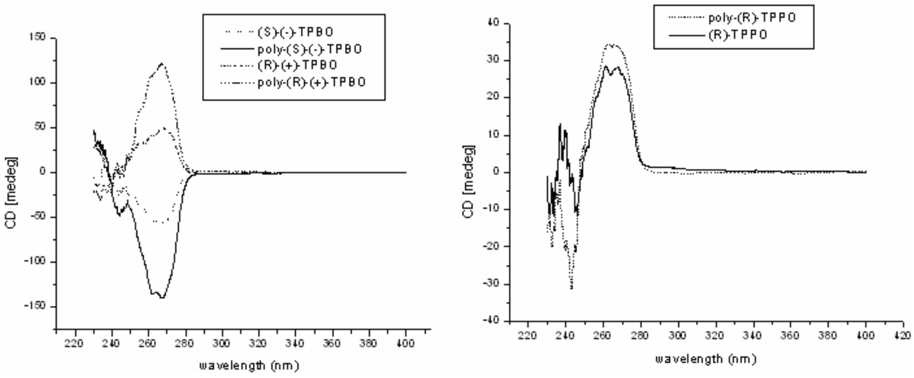


Figure5. CD Curves of Optically Active TPBO and TPPO with Their Polymers

table 1). This should be attributed to quite stable helical conformation caused by the great steric hindrance of bulky pendant.

As we mentioned above, poly ((*S*)-TPBO) possess of helical conformation in solution, however, despite many efforts have been taken to improve DP of poly ((*S*)-TPBO), we found all obtained polymers were mainly oligomers. With separation of poly ((*S*)-TPBO), the maximal polymer degree (DP) of oligomer was not over 12. Comparison of poly ((*S*)-TPBO), DP of obtained poly ((*R*)-TPPO) or poly ((*S*)-TGE) was much larger (DP≈30) (run11, 12 table1). These suggested that the repulsion between pendants showed strong impact on length of polymer-chain.

Conclusion

In summary, we have found that in spite of the backbone of polyether from epoxide was flexible, it was possible for polyepoxides to form one-handed helical conformation in solution with furnishing elegantly designed pendant, which can fix the helix sense through the large interaction between bulky pendants. The results of polymerization of optically active TPBO gave good illustrations. Although only oligomers were obtained in the polymerization of optically active TPBO, further designing of new chiral epoxides with bulky group for producing helical polyethers with satisfactory molecular weight are currently under investigation.

Acknowledgement. We thank the National Natural Science Foundation of China (grant nos. 20572090) for financial support.

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14. Optically active 4,4,4-triphenyl-1,2-butanediol, ^{1}HNMR ($CDCl_3$): δ=7.18-7.37 (m, 15H, PhH), 3.75-3.80 (m, 1H, - CH-), 3.14 (dd, J_1-4.1Hz, J_2=14.8Hz 1H,- CH_2-), 3.01-3.05 (m, 1H, -CH_2-), 2.82-2.86 (m, 1H, -CH_2-), 2.67 (dd, J_1-5.2 Hz, J_2=14.8Hz, 1H, -CH_2-CPh_3), 1.86 (m, 1H, -OH), 1.25 (m, 1H, -OH); ^{13}CNMR($CDCl_3$): δ=146.63, 129.02, 128.21, 126.36, 69.46, 56.05, 50.88, 45.13. $[\alpha]_{589}^{20}$=-38° (c 0.2, THF)
15. Optically active 4,4,4-triphenyl-1-tert-butoxyl-2-butanol, ^{1}HNMR ($CDCl_3$): δ=7.12-7.35 (m, 15H, PhH), 3.61-3.64(m, 1H, -CH-), 2.99 (dd, 1H, J1=2.8Hz, J2=14.7Hz, -CH_2-CPh_3), 2.76-2.81 (m, 1H, -CH_2-), 2.54 (dd, 1H, J=5.3Hz, J=14.6Hz, -CH_2-CPh_3), 2.36 (dd, 1H, m, 1H, -CH_2-), 2.16 (m, 1H, -OH), 0.98 (s, 9H, -$C(CH_3)_3$); ^{13}CNMR($CDCl_3$): δ=146.26, 128.92, 128.33, 126.15, 69.22, 68.13, 55.92, 50.35.88, 45.13, 29.56.$[\alpha]_{589}^{20}$=-37° (c 0.2, THF)