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Anionic Polymerization of Optically Active Propene Oxides Bearing Substituted *N*,*N*-Diphenylamino Moiety

Jin Zhang, Chun-Hui Zhao, Li-Wen Yang, and Nian-Fa Yang*
Key Laboratory of Environmentally Friendly Chemistry and Applications, Ministry of Education,
College of Chemistry, Xiangtan University, Hunan 411105, P. R. China

(E-mail: nfyang@xtu.edu.cn)

A series of novel chiral propene oxides bearing substituted *N*,*N*-diphenylamino moiety were synthesized and anionically polymerized. Most of propene oxides gave polymers possessing high specific rotation and intensive circular dichroism (CD) signals, which were attributed to the helical conformation of the main chain. Poly(3-(4,4′-dimethoxy)diphenylaminopropene oxide) exhibited the highest specific rotation ($[\alpha]^{20}_{365} = -5400$).

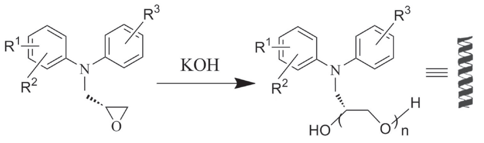
Synthetic polymers with main-chain helical chiralities have attracted long-standing interest for their wide applications in chiral recognition toward racemic compounds, liquid crystal formation, chiral catalytic activity, and biological mimics.[1] So far, a variety of helical polymers have been synthesized. Examples include poly(triphenylmethyl methacrylate),[2] polyacrylamides,[3] polyaldehydes,[4] polyisocyanides,[5] polystyrenes,[6] polyisocyanates,[7] polyacetylenes,[8] and so on. But there are still very few reports available about chiral helical polyethers from the polymerization of epoxides due to a low barrier to rotation for carbon–oxygen bonds, especially for helical polyether with pendant containing nitrogen atoms.[9]

The helical polyacrylamides including the series of *N*,*N*-diphenylacrylamides have been prepared.[10] Although the stereocontrol in the polymerization of acrylamides was difficult, the bulky *N*,*N*-diphenyl side chains of polyacrylamides help the polymers maintain stable helical conformation in solution, which encourage us to design, synthesize, and polymerize chiral epoxides with bulky *N*,*N*-diphenyl moiety.

In this study, chiral epoxides bearing an *N*,*N*-diphenyl moiety (DPOs) were synthesized from the corresponding *N*,*N*-diphenylamine with (*R*)- or (*S*)-epichlorohydrin. Anionic polymerization of DPOs were performed with potassium hydroxide as initiator (Scheme 1). Chiroptical properties of the polymers were investigated by specific optical rotations, circular dichroism (CD) measurements, and *g*-value.

The anionic polymerization of DPOs bearing methyl groups at the ortho, meta, and para position of benzene have been investigated, from 4- to 2-position, the polymerization seems to decrease and the poly(4-MeDPO) possessed a high optical rotation (Table 1, Runs 11 and 12). Interestingly, the phenomenon that the pendant groups on the polyacrylamides with bulky *N*,*N*-diphenyl side chain had a similar influence as reported in the literature.[10]

The results of the anionic polymerization of para-disubstituted DPOs are also summarized in Table 1 (Runs 3–8). The bulkiness of the substituents is in the order of DPO < 4,4′-Me$_2$DPO < 4,4′-(MeO)$_2$DPO < 4,4′-(α,α-dimethylbenzyl)$_2$DPO, and the specific rotation of polymer is increased with that of the substituent except for poly(4,4′-(α,α-dimethylbenzyl)$_2$DPO), since the degree of polymerization of poly(4,4′-(α,α-dimethylbenzyl)$_2$DPO) is too low.



Monomer	R^1	R^2	R^3
DPO	H	H	H
4,4′-Me$_2$DPO	4-Methyl	H	4-Methyl
4,4′-(MeO)$_2$DPO	4-Methoxy	H	4-Methoxy
4,4′-(α,α-dimethylbenzyl)$_2$DPO	4-(α,α-dimethyl)benzyl	H	4-(α,α-dimethyl)benzyl
3-MeDPO	3-Methyl	H	H
4-MeDPO	4-Methyl	H	H
3,4-Me$_2$DPO	3-Methyl	4-Methyl	H
3-MeODPO	3-Methoxy	H	H
2-Me-4-MeODPO	2-Methyl	4-Methoxy	H

Scheme 1. The polymerization of optically active DPOs.

As Table 1 shows, most of the poly(DPO)s obtained showed large specific rotation in solution and the optical rotation sign is opposite to their monomers'. The absolute value of the poly(DPO)s' specific rotation ($[\alpha]^{20}_{365}$) is 45 times as large as that of the corresponding monomer (Table 1, Run 11), which implies that the poly(DPO)s keep a stable helical conformation.

Polymers with single-handed helical conformation often show Cotton effect in circular dichroism (CD) spectra.[11] For almost all of the obtained poly(DPO)s, obvious Cotton effect also emerges in the spectrum, which supports that poly(DPO)s keep prevailing helical conformation in solution. There are also great differences between poly(DPO)s and the corresponding monomer in the CD spectrum. The CD signals of most of the poly(DPO)s are much stronger than the corresponding monomers. Poly((*R*)-DPO)s and poly((*S*)-DPO)s exhibited mirror images in CD spectra (Figure 1).

Perhaps the large optical rotation and CD intensity of poly(DPO)s may arise from the chiral carbons in the polymer main chain. Based on this hypothesis, all the poly(DPO)s should have large specific rotation and CD intensity. This seems not to be favored since the chiroptical properties of poly((*S*)-2-Me-4-MeODPO) and poly((*S*)-3-MeODPO) show no great difference with their corresponding monomers (Figure 1d; Table 1, Runs 14 and 18), while chiral carbons are also present in these polyethers.

The epoxy ring of DPOs was opened after polymerization and the opening of the epoxy ring should have an impact on the chiroptical properties of poly(DPO)s. However, the experimental data indicated this impact was not much. When the epoxy ring of (*S*)-DPO was opened by OH$^-$, the $[\alpha]^{20}_{365}$ of the ring-opening product was not enough (Scheme 2). Therefore, the change of

Table 1. Anionic polymerizations of epoxides[a]

Run	Monomer		Polymer			
	Compounds	$[\alpha]^{20}_{365}$	Yield[b]/%	$M_n \times 10^{-3}$	PDI[c] (M_w/M_n)	$[\alpha]^{20}_{365}$[d]
1	(*R*)-DPO	−78	71.9	2.1	1.28	+714
2	(*S*)-DPO	+78	70.5	2.2	1.21	−702
3	(*R*)-4,4′-Me_2DPO	−85	53.2	2.9	1.11	+1196
4	(*S*)-4,4′-Me_2DPO	+84	51.6	2.7	1.12	−1227
5[e]	(*R*)-4,4′-$(MeO)_2$DPO	+973	70.0	2.8	1.18	+5344
6[e]	(*S*)-4,4′-$(MeO)_2$DPO	−972	71.2	2.9	1.16	−5400
7	(*R*)-4,4′-(α,α-dimethylbenzyl)$_2$DPO	−76	40.2	2.7	1.15	+178
8	(*S*)-4,4′-(α,α-dimethylbenzyl)$_2$DPO	+76	40.3	2.8	1.13	−188
9	(*R*)-3-MeDPO	−80	42.7	2.4	1.16	+880
10	(*S*)-3-MeDPO	+80	41.8	2.3	1.15	−872
11	(*R*)-4-MeDPO	−25	71.2	2.6	1.14	+1140
12	(*S*)-4-MeDPO	+26	70.8	2.7	1.12	−1090
13	(*R*)-3-MeODPO	−190	40.8	2.3	1.20	+203
14	(*S*)-3-MeODPO	+192	38.7	2.2	1.19	−237
15	(*R*)-3,4-Me_2DPO	−44	46.3	2.7	1.16	+1121
16	(*S*)-3,4-Me_2DPO	+44	45.2	2.7	1.17	−1092
17	(*R*)-2-Me-4-MeODPO	−130	25.1	2.6	1.20	+95
18	(*S*)-2-Me-4-MeODPO	+130	24.9	2.5	1.18	−103

[a]The polymer was obtained by bulk polymerization for 24 h at 150 °C using KOH as an initiator. [b]THF-soluble part. [c]Determined by GPC against polystyrene standards, [M]/[I] = 20/1. [d]$C = 4.0\,\mathrm{mg\,mL^{-1}}$ in THF. [e]$C = 0.25\,\mathrm{mg\,mL^{-1}}$ in THF.

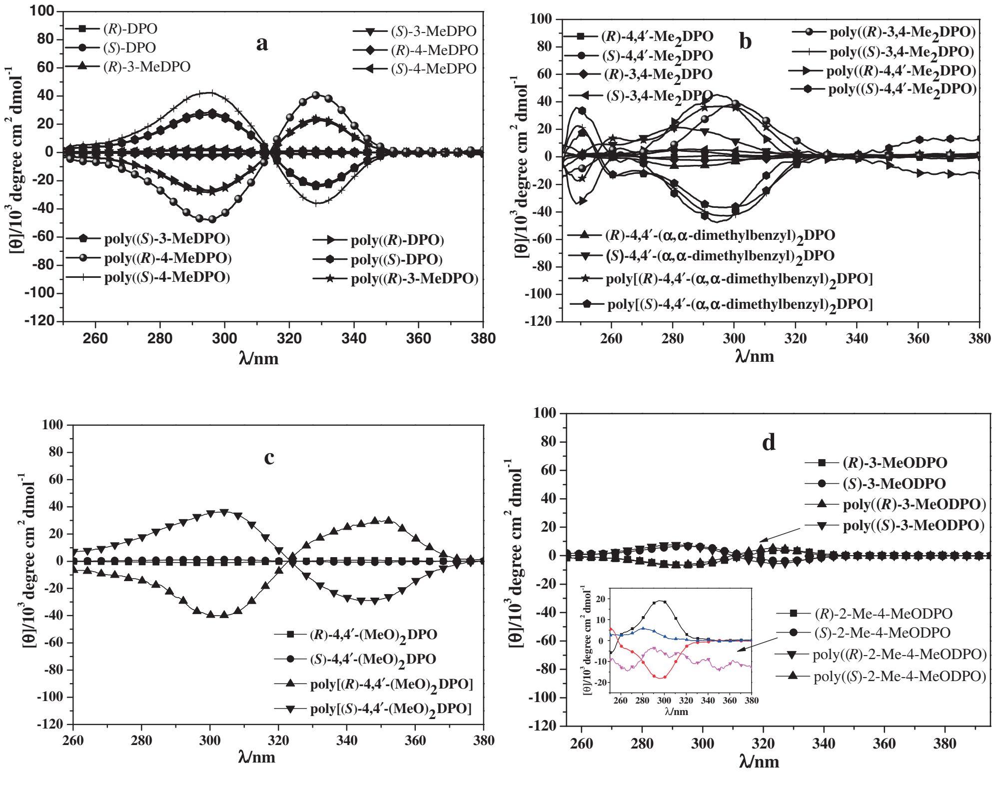
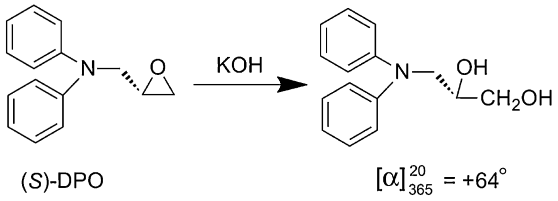


Figure 1. The CD spectra of chiral epoxides and their polymers in $CHCl_3$ at 25 °C. Concentration: $3.9 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ (referred to one monomeric unit) for all of CD.

specific rotation after polymerization does not result from the opening of the epoxy ring.

The conformations of biomolecules and optically active helical polymers are usually sensitive to temperature variation.[12] When the temperature exceeds their "tolerable" limit, their unique helical conformations can be destroyed and random coils formed. Thus, the CD spectra of the poly((*S*)-4-MeDPO) was measured at different temperature to study their conformational stability. Figure 2 shows temperature-variable CD spectra of poly((*S*)-4-MeDPO) in $CHCl_3$ in the range from 25 to 45 °C.



Scheme 2. Opening of the epoxy ring of (*S*)-DPO.

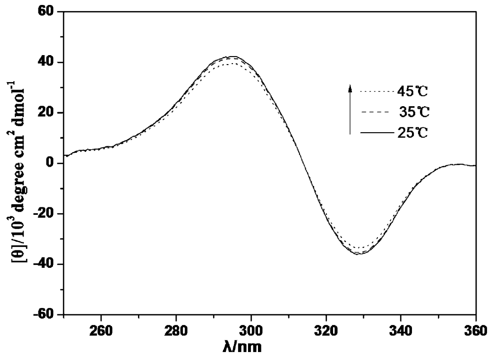


Figure 2. Temperature-variable CD spectra of poly((*S*)-4-MeDPO) which was obtained by bulk polymerization for 24 h at 150 °C using KOH as an initiator in $CHCl_3$ at 3.90×10^{-5} mol L^{-1} (referred to one monomeric unit).

It was obvious that though the intensity of the Cotton effects at 45 °C was a little weaker than those at 25 °C the pattern of CD spectra remained almost unchanged. Moreover, upon cooling to 25 °C again, the signals returned to the original values. The results revealed that the helical conformation of poly((*S*)-4-MeDPO) was quite stable in the temperature region tested.

In summary, a series of novel chiral epoxides bearing an *N*,*N*-diphenyl moiety (DPOs) have been prepared from the corresponding *N*,*N*-diphenylamine with (*R*)- or (*S*)-epichlorohydrin. DPOs were polymerized anionically using potassium hydroxide as initiator to obtain optically active poly(DPO)s. Most of the obtained poly(DPO)s exhibited very large specific rotation in solution. Significant cotton effects were observed in circular dichroism (CD) absorption bands of poly(DPO)s. All these suggested that poly(DPO)s kept stable single-handed helical conformation in solution.

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Supporting Information is available electronically on J-STAGE.

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