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Synthesis of Optically Active Polyarylates Having Axially Chiral Binaphthylene Unit

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Abstract : Novel optically active polyarylates having axially chiral 6,6'-binaphthylene units in the main chain have been synthesized by the reaction of (*R*)- or (*S*)-2,2'-bisalkoxy-6,6'-dibromo-1,1'-binaphthyl (**1a**, **1b**) and aromatic diols with carbon monoxide in the presence of palladium catalyst. The resulting polyarylates had molecular weights up to 20000 and were soluble in a variety of organic solvents including *N,N*-dimethylformamide, 1-methyl-2-pyrrolidone, *m*-cresol, tetrahydrofuran, and pyridine. Circular dichroism (CD) spectra of these polyarylates showed large Cotton effects compared with those of the model compounds and were the complete mirror images of each enantiomer, suggesting the existence of an ordered conformation. The most stable structure of the optically active polyarylates indicated helical conformation by MM2 force field calculation. No change in the specific rotation of the optically active polyarylates was observed on heating at 100°C for 5 h, suggesting thermal stability of the ordered conformation such as helix.

1. Introduction

Many naturally occurring polymers such as proteins, polysaccharides and DNA have helical structures, which are essential to these biological functions such as catalytic activity and transmission of genetic information. Recently, the synthesis of the ordered polymers with higher ordered structure such as helix have attracted much attention as the most challenging works for construction of functional polymeric systems that will be as effective as those in living systems [1-6]. The helical polymers may be effectively applied for the high-performance liquid chromatography (HPLC) stationary phase [7]. The helical polymers may be possibly utilized for other purposes such as asymmetric polymer catalysts [8] and polymer liquid crystals [9-10], in which helical polymer may play a significant role.

The synthetic optically active polymers with a

one-handed helical conformation reported to date are polyquinoxalines [11], polyisocyanides [12], polyisocyanates [13,14], polyaldehydes [15,16], polymethacrylates [1,17-18] with bulky ester groups, polyacetylene [19], and polysilane [20]. Recently, polyarylcarbonates [21,22] with a helical conformation have been synthesized by ring-opening polymerization of optically active aryl carbonates involving axially dissymmetric (C_2 -chiral) units (with atropisomerism). We have reported the synthesis of wholly aromatic polyamides having axially dissymmetric biphenylene and binaphthylene units with C_2 symmetry in their backbone, which assume new types of helical structures [23-26].

In this paper, we demonstrated the synthesis of the optically active polyarylates having the ordered structure like helix by the reaction of aromatic diols with carbon monoxide and (*R*)- or (*S*)-6,6'-

dibromo-2,2'-dimethoxy-1,1'-binaphthyl (**1a**) or (*R*)- or (*S*)-9,14-dibromodinaphto [2,1-*d*: 1'.2'-*f*][1,3]dioxepin (**1b**).

2. Experimental

2.1 Materials

Solvents to be used under anhydrous conditions were purified by distillation and dried by appropriate standard methods. *p*-Benzylphenol, resorcinol, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), bis(4-hydroxyphenyl)methane were purified by recrystallization from benzene. (*R*)- or (*S*)-6,6'-dibromo-2,2'-dimethoxy-1,1'-binaphthyl (**1a**) and (*R*)- or (*S*)-9,14-dibromodinaphto[2,1-*d*: 1'.2'-*f*][1,3]dioxepin (**1b**) were prepared from (*R*)- or (*S*)-2,2'-dihydroxy-1,1'-binaphthyl according to the reported method [27]. 1,8-Diazabicyclo[5,4,0]-7-undecene (DBU) were purified by vacuum distillation. Triphenyl phosphine (PPh₃) was recrystallized. Dichlorobis(triphenylphosphine)-palladium(II) [PdCl₂(PPh₃)₂] was obtained commercially and used as received.

2.2 Polymerization

Polycondensation was carried out in a dry three-necked flask equipped with a stirrer, a carbon monoxide inlet, and a reflux condenser according to previous report [28]. In a flask were placed 0.5mmol of dibromide, 0.5mmol of aromatic diols, 0.03mmol of PdCl₂(PPh₃)₂, 0.12mmol of PPh₃, and 2mL of *N,N*-dimethylformamide (DMF). Carbon monoxide was purged in flask and then the mixture was heated to 115 °C with stirring, following by addition of 1.1mmol of DBU. The reaction mixture was stirred at 115 °C for 8h and the resulting polyester solution was poured into a large volume of methanol. The precipitated polyester was filtered, washed by hot methanol and dried *in vacuo*.

2.3 Synthesis of model compound

(*R*)-Bis(*p*-benzylphenyl)-dinaphto[2,1-*d*: 1'.2'-*f*][1,3]dioxepin-9,14-dicarboxylate(**4f**) as the model compound for analysis of chiroptical properties was synthesized by the reaction 2mmol of (*R*)-**1a** and 4mmol of *p*-benzylphenol using a method similar to that employed for polymerization. The reaction mixture was poured into methanol. The precipitated solid product was collected by filtration, recrystallized from tetrahydrofuran (THF)-methanol, and dried at 40 °C

under vacuum. (*R*)-**4f**: 77% yield; mp 232 °C; [α]_D²⁵ -320° (c 1.0, in THF); IR (KBr) 2900, 2775, 1735, 1668, 1181, 1070, 810, cm⁻¹; ¹H NMR (DMSO-*d*₆) 3.78 (s, 4H), 5.75 (s, 2H), 6.90-7.50 (m, 18H), 7.52 (d, 2H), 7.66 (d, 2H), 7.80 (dd, *J* = 1.7, 9Hz, 2H), 8.18 (d, *J* = 9Hz, 2H), 8.46 (d, 2H) ppm.

2.4 Spectroscopic and gel permeation

chromatography (GPC) measurements

IR spectra were recorded on a HORIBA FT-210 spectrometer. UV-vis spectra were recorded on a SHIMAZU UV-2000 spectrometer in THF solution. Specific optical rotations were measured in THF or dimethylacetamide (DMAc) solution at 25 °C by use of a JASCO DIP-1000 polarimeter. CD spectra were measured in DMAc solution at 25 °C using a JASCO J-720 WI. CD spectral data are presented in molecular ellipticity ([θ]), with degree cm²/repeating-unit-dmol (or deg cm²/dmol), which was calculated by the following equation:

$$[\theta] = \theta / \{0.1 \times (m/M)\} = 3300 \Delta \epsilon$$

where *M* is the repeating-unit molecular weight of the polyarylate or the molecular weight of the model compound; *m* is the sample weight per unit area (g/cm²), and θ is the measured ellipticity (deg), and $\Delta \epsilon$ is the molecular circular dichroism (cm²/mmol).

NMR spectra were measured on sample solutions in dimethylsulfoxide-*d*₆ (DMSO-*d*₆) with tetramethylsilane as an internal standard by using a JEOL EX 270 spectrometer. Molecular weights were determined by the combination of gel permeation chromatography (GPC) and low angle laser light scattering using a JASCO HPLC equipped with a TOSOH HLC-8120GPC/TOSOH LS-8000 instrument.

2.5 Computational studies

The geometry of repeating units was calculated by use of the PM3 HAMILTONIAN in the molecular orbital package (MOPAC). The most stable conformation of the polyarylates consisting of axially chiral binaphthylene units was obtained using a MM2 force field calculation by CAChe system and also calculated with a MD universal force field (UFF-1.02) at 300 K by Cerius 2 system.

3. Results and Discussion

Polyarylates with axially dissymmetric binaphthylene units were synthesized by the reaction of (*R*)- or (*S*)-**1a**, (*R*)- or (*S*)-**1b** and aromatic diols

with carbon monoxide in the presence of palladium catalyst according to the method of Yoneyama *et al* [28] (Scheme 1).

Scheme 1 Synthesis of polyarylates with axially chiral binaphthylene units

The results are summarized in Table 1. The polymers obtained were confirmed to be polyarylates by the IR spectra, exhibiting a carbonyl absorption at 1740 cm⁻¹ which was the characteristic absorption of ester bond. The optically active polyarylates thus obtained had the weight-average molecular weight ($\overline{M}_w$) of up to 20000,

Table 1 Synthesis and Properties of Polyarylates with Axially Chiral Binaphthylene Units^{a)}

Polymer	Binaphthyl dibromide	Aromatic diol	Yield %	$\overline{M}_w^b$ 10 ³	$[\alpha]_D^{25}$ degree
(R)-3aa	(R)(+)-1a	2a	74	14	-54
(S)-3aa	(S)(-)-1a	2a	70	13	+60
(R)-3ab	(R)(+)-1a	2b	63	10	-66
(S)-3ab	(S)(-)-1a	2b	72	12	+69
(R)-3ac	(R)(+)-1a	2c	66	9	-64
(S)-3ac	(S)(-)-1a	2c	70	11	+65
(R)-3ba	(R)(-)-1b	2a	80	20	-531
(S)-3ba	(S)(+)-1b	2a	75	18	+523
(R)-3bb	(R)(-)-1b	2b	70	10	-515
(S)-3bb	(S)(+)-1b	2b	73	13	+504
(R)-3bc	(R)(-)-1b	2c	85	13	-375
(S)-3bc	(S)(+)-1b	2c	80	12	+383

^{a)}Polymerization was carried out with 0.5 mmol of binaphthyl dibromide, 0.5 mmol of aromatic diol, 1.1 mmol of DBU, 0.03 mmol of Pd(PPh₃)₂Cl₂ and 0.12 mmol of PPh₃ in 2ml of DMF at 115 °C under carbon monoxide

^{b)}Molecular weight were determined by combination of GPC and low angle laser light scattering.

^{c)}Specific optical rotations of polymers were measured in DMAc at 25 °C

which were determined by combination of GPC and low angle laser light scattering. The polyarylates obtained from binaphthylene monomers **1a** and **1b** showed approximately the same molecular weights. The optical rotation signs of the polyarylates **3aa**, **3ab** and **3ac** produced from binaphthylene monomer **1a** were the opposite to those of monomer **1a**, whereas the polyarylates **3ba**, **3bb** and **3bc** from binaphthylene monomer **1b** were the same as the optical rotation sign of **1b**. The optical rotation values of the polyarylates obtained from monomer **1b** exhibited 6 to 9 times as large as those of the polyarylates from monomer **1a**. This result may be due to a rigid structure of monomer **1b** relative to monomer **1a**. The specific optical rotation of polyarylate (R)-**3bb** is higher than that of model compound [(R)-**4f**] ($[\alpha]^{25} = -320^\circ$) prepared from (R)-**1b** and 4-benzylphenol as shown in Scheme 2, being expected for the existence of an ordered conformational structure in this polyarylate. Circular dichroic (CD) spectroscopy is an effective method for the study of ordered conformations in solution [29]. Generally, the random conformation of a polymer result in weaker Cotton effects at the same wavelength range than those of the corresponding model compound. However, the appearance of new CD bands

Scheme 2 Synthesis of model compound (R)-**4f**.

or stronger intensities than that of the corresponding model compound can be attributed to the formation of some kind of ordered conformation [30-32]. CD and UV spectra of **3bb** with R and S-type axially dissymmetric naphthylene units are shown in Fig. 1 as typical examples, together with those of the corresponding model compound (R)-**4f**. The UV absorption bands around 270nm and 320nm are attributable to the $\pi-\pi^*$ and $\sigma-\pi^*$ electronic transitions of the aromatic rings, in the region of which the CD spectra exhibit dichroic bands of positive and negative signs, respectively. Cotton effects for (R)-**3bb** were observed negatively at 309.5nm and positively at 270.5nm. The CD spectra of

Fig. 1 CD and UV spectra of polyarylates (*R*)-**3bb**, (*S*)-**3bb** and model compound (*R*)-**4f**.

other polyarylates were very similar to those of (*R*)- and (*S*)-**3bb** as shown in Fig. 2. The CD spectrum of (*R*)-**3bb** is the complete mirror image of that of (*S*)-**3bb** and their Cotton effect intensities are relatively larger than those of the model compound (*R*)-**4f**, suggesting the existence of an ordered conformational structure in this polyarylate. These polyesters are considered to have a kind of helical structure in solution, because the main chain consisting of rigid segment are twisted in one direction by C_2 -axially chiral binaphthylene unit. Therefore, the polyarylate (*R*)-**3bb** was optimized with a MM2 force field by CAChe system. The resulting top and side views on the most stable conformation for

Fig. 2 CD spectra of polyarylates (*R*)-**3aa**, (*R*)-**3ab**, (*R*)-**3ba** and (*R*)-**3bc**.

Fig. 3 Most stable conformation of polyarylate (*R*)-**3bb** optimized with a MM2 force field (CAChe system).

polyarylate (*R*)-**3bb** show in Fig. 3, in which the main chain takes an ordered structure like helix. A pitch of this helix is 28.4 Å containing three repeating units and the length between the chiral axes of the binaphthylene units on the cross-section of the helix rod is 17.3 Å. On the other hand, the most stable conformations computed for polyarylate (*R*)-**3ab** with no bridge structure in binaphthylene unit resulted in zigzag-type helix feature as shown in Fig. 4. In addition, the conformations computed for polyarylates **3ba** and **3bc** without methylene joint in diphenol units were same zigzag-type helix features as **3ab** (data not shown). Therefore, the presence of diphenol containing methylene joint and of binaphthylene containing the bridge structure in the axially chiral polyarylate suggest to play an important role in a formation of more stable helical conformation. Further, a model hexamer of polyarylate (*R*)-**3bb** was optimized with a MD universal force field (UFF) at 300 K by Cerius 2 system. The resulting stable conformation remained the ordered structure like helix (Fig. 5). The helical polymers originated by central chirality on carbon atom of the main chain units as exemplified by proteins and genes commonly undergo distortion of the helix (mutarotation) or denaturation on heating [1]. Therefore, thermal stability is invaluable when

Fig. 4 Most stable conformation of polyarylate (*R*)-**3ab** optimized with a MM2 force field (CACH system).

Fig. 5 A model hexamer of polyarylate (*R*)-**3bb** optimized with a MD universal force field at 300 K (Cerius 2 system).

evaluating the properties of helical polymers. Fig. 6 shows the change of specific optical rotation of polyarylate (*S*)-**3bb** on heating temperatures in DMAc. The ordered structure like helix seems quite stable up to 100 °C because the rotation values little change even after 5 h at this temperature. Although the specific

Fig. 6 Changes of specific optical rotations of polyarylate (*S*)-**3bb** in DMAc on heating at 80 °C (●), 100 °C (□), 120 °C (Δ) and 140 °C (×).

rotation value of (*S*)-**3bb** decreased by heating at 120 °C or 140 °C. IR and ¹H-NMR spectral patterns of **3bb** after heating were entirely the same as those of untreated **3bb**. These results indicate that no chemical changes occur during the heating treatment and the decrease in the optical rotation may be ascribed to partial racemization of the chiral naphthylene units in polyarylate. Table 2 shows the solubility behaviour of the optically active polyarylates. Wholly aromatic polyesters are generally insoluble in ordinary solvents, however, all the polymers obtained were highly soluble in polar solvents such as N-methyl-2-pyrrolidone (NMP), DMF, DMSO, DMAc and *m*-cresol, and even in less polar pyridine and THF. Thus, the solubilities of polyarylates were greatly improved by the

Table 2 Solubility of Optically Active Polyarylates^{a)}

Solvent	Polymer					
	(<i>R</i>)-3aa	(<i>R</i>)-3ab	(<i>R</i>)-3ac	(<i>R</i>)-3ba	(<i>R</i>)-3bb	(<i>R</i>)-3bc
	(<i>S</i>)-3aa	(<i>S</i>)-3ab	(<i>S</i>)-3ac	(<i>S</i>)-3ba	(<i>S</i>)-3bb	(<i>S</i>)-3bc
DMF	++	++	++	++	++	++
DMAc	++	++	++	++	++	++
NMP	++	++	++	++	++	++
DMSO	++	++	++	++	++	++
<i>m</i> -Cresol	++	++	++	++	++	++
Pyridine	++	++	++	++	++	++
THF	+	+-	+-	++	++	++
CHCl ₃	-	+-	+-	-	-	-

^{a)} ++, Soluble at room temperature; +, soluble on heating; +-, swelling on heating; -, insoluble.

introduction of the bulky, kinked and cranked 1,1'-binaphthylene-2,2'-dialkoxy-6,6'-diyl unit into polymer backbone.

In conclusion, novel optically active polyarylates having axially chiral 6,6'-binaphthylene units in the main chain have been synthesized. These polyarylates were soluble in a variety of organic solvents and didn't show the change of the specific rotations even on heating at 100°C. In addition, **3bb** among those polyarylates was suggested to take the ordered structure like helix in solution by comparison with CD spectra of model compound and the computational studies of most stable conformation of it.

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