Synthesis and Structure of Optically Active Polyesters Containing C_2 Chiral Spirobifluorene Moieties in the Main Chain

Ryota SETO, Takeshi MAEDA, Gen-ichi KONISHI, and Toshikazu TAKATA[†]

*Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
Ookayama, Meguro, Tokyo 152-8552, Japan*

(Received May 1, 2007; Accepted September 8, 2007; Published October 23, 2007)

ABSTRACT: Three optically active polyesters possessing C_2 chiral spirobifluorene moieties in the main chains were prepared and their structural feature was discussed mainly by the UV-vis and CD spectral characteristics. Polycondensation of optically active (*R*)-(+)-2,2'-dihydroxy-9,9'-spirobifluorene **1** and terephthaloyl dichloride **2a** in THF in the presence of triethylamine yielded the corresponding polyester as methanol-insoluble part (**3a**, 89%, M_w 5400, M_w/M_n 3.5). The polymerizations with 2,6-naphthaloyl dichloride **2b** and 4,4'-azodibenzoyl dichloride **2c** also afforded polyesters **3b** (95%, M_w 20000, M_w/M_n 2.3) and **3c** (95%, M_w 6200, M_w/M_n 2.2), respectively. In the solvent-free polymerization, the corresponding polyester **3a** was obtained in 40% yield (M_w 16000). In the case of racemic **1**_{rac}, similar yield and molecular weight for **3a** were achieved. Although no clear glass transition point was observed in all three polymers, these polymers had high thermal decomposition temperature over 480°C. In the UV-vis and CD spectra of the polymers **3**, bisignate Cotton effect was observed in the UV-vis absorption region of optically inactive diacid part of the repeating unit in all three polymers. Further, CD intensity of **3** depended upon temperature: the temperature increase corresponded to the decrease in CD intensity. Both the results obtained and the structure simulation of **3** suggested their helical conformation. [doi:10.1295/polymj.PJ2007026]

KEY WORDS Spirobifluorene / Optically Active Polymer / C_2 Chiral / Polycondensation / Helical Structure /

A variety of artificial helical polymers,^{1,2} excluding bio-related polymers, such as polymethacrylate, polyisocyanide, polyisocyanate, polyacetylene, poly(*m*-arylene-ethynylene), and so on^{3–9} have been developed to attract interests of many scientists, whereas polymers consisting of C_2 chiral moieties in the main chains have also occupied part of helical polymers.^{10–15} We had first found that optically active polycarbonate having binaphthyl groups as C_2 chiral repeating units takes one-handed helix according to the chirality of the binaphthyl or biphenyl group.^{16–23} We also showed that repeated alternative binding of binaphthyl moiety as the chiral twisted block and metallosalen complex as the planar block results in the formation of very rigid helix of which groove is applicable as an asymmetric catalysis center.^{24–26} From these reports, we have concluded that suitable successive connection of chirally twisted units gives rise to the formation of polymer with helical conformation even in molecular level. Among C_2 chiral structures, spirobifluorene is a fascinating building block because it takes an extraordinary rigid C_2 chiral conformation^{27,28} which requires the rectangular two fluorene planes strongly fixed at the sp^3 spiro carbon, when the fluorene skeleton is substituted with some groups. Such rigid conformation is expected to reduce the uncertainty of the helix formation during the polymer-

ization. Recently many papers on synthesis of polymers involving spirobifluorene moiety have been reported mainly in the electroluminescence materials field.^{29–34} However, only a report utilizing C_2 chirality of the spirobifluorene moiety has recently appeared so far as we know.³⁴ This paper deals with the successive connection of a homoditopic C_2 chiral dihydroxy-spirobifluorene possessing 90°-twisted two fluorene planes and a few homoditopic arene carboxylic acid chlorides to yield polyesters of which structures are also discussed.

EXPERIMENTAL SECTION

General

Triethylamine (Wako Pure Chemical Industries, Ltd.) was dried overnight over calcium hydride and distilled prior to use. Commercially available materials and solvents including terephthaloyl dichloride **2a** were used without further purification. Optically active ((*R*)-(+)) and inactive 2,2'-dihydroxy-9,9'-spirobifluorene **1**,³⁵ 2,6-naphthaloyl dichloride **2b**,³⁶ and 4,4'-azobenzoyl dichloride **2c**³⁷ were prepared according to the literatures.

¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a JEOL GTX-400 spectrometer using CDCl₃ as the solvent and tetramethylsilane as

[†]To whom correspondence should be addressed (Tel: +81-3-5734-2898, Fax: +81-3-5734-2888, E-mail: takata.t.ab@m.titech.ac.jp).

the internal standard. Molecular weight and its distribution were measured by gel permeation chromatography (GPC) on a JASCO Gulliver system equipped with two consecutive liner polystyrene gel columns (TOSOH TSKgel G2000H_{XL} and GMH_{XL}) at 30 °C, eluted with CHCl₃ at a flow rate of 0.085 mL/min, and calibrated using polystyrene standards. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Thermogravimetry (TG) was performed on a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min under N₂ atmosphere (flow rate of 50 mL/min) to determine decomposition temperature T_{d5} at which 5% weight loss was observed. Differential scanning calorimetry (DSC) was carried out using a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under N₂ atmosphere (flow rate of 50 mL/min) to determine glass transition temperature T_g . Melting points were measured with a Stuart Scientific SMP3. UV-vis spectra were taken on a JASCO V-550 UV/VIS spectrophotometer. CD spectra were taken on a JASCO J-820 spectropolarimeter. Specific optical rotations were measured on a JASCO DIP-1000 digital polarimeter in a 10 cm cuvette. The conformational analysis of polymers were carried out by using CAChe version 6.1.12 for Windows.

Polycondensation of 1 and 2. A Typical Polycondensation Procedure for Synthesis of 3a. 2,2'-Dihydroxy-9,9'-spirobifluorene (**1**, optically active: $[\alpha]_D^{25} +18.7$ ($c = 0.10$, CHCl₃)) (100 mg, 0.287 mmol), dry tetrahydrofuran (THF, 1 mL), and dry triethylamine (0.0798 mL, 0.574 mmol) were charged in a 10 mL Schrenck tube equipped with a magnetic stirrer under argon atmosphere. The mixture was cooled and stirred at 0 °C for 10 min. To the mixture was added dropwise a solution of terephthaloyl dichloride (**2a**, 58.9 mg, 0.287 mmol) in dry THF (1 mL) with stirring. The temperature was kept at 0 °C for 1 h. After an additional stirring for 1 h the turbid mixture was added to hexane (100 mL) to precipitate white powdery polymer. The precipitated polymer was collected by filtration, and then purified by precipitation from THF solution into water. The precipitated polymer was collected by filtration, and purified again by reprecipitation from THF solution into methanol. The precipitated polymer **3a** collected by filtration was dried *in vacuo* at 60 °C for 0.5 h (122 mg, 0.255 mmol, 89%).

Polyester 3a

$[\alpha]_D^{25} +77.5$ ($c = 0.10$, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 8.11 (s, 4H, Ar-H), 7.84 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.79 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.35 (dd, $J = 7.2$, 7.2 Hz, 2H, Ar-H), 7.25 (d, $J = 8.4$ Hz, 2H, Ar-H), 7.11 (dd, $J = 7.2$, 7.2 Hz, 2H, Ar-H), 6.70 (d, $J = 7.2$ Hz, 2H, Ar-H), 6.60 (s, 2H,

Ar-H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 164.0, 150.4, 149.7, 148.2, 140.7, 139.6, 133.6, 130.0, 128.1, 128.0, 124.1, 121.5, 120.7, 120.0, 117.3, 65.8 ppm. IR (KBr): 1740 (C=O), 1450 (Ar), 1235 (Ar-O), 1067 (O=C-O), 1016 (O=C-O), 720 (Ar) cm⁻¹.

Polyester 3b

Yield 95% (methanol-insoluble part). $[\alpha]_D^{25} +301$ ($c = 0.10$, CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ 8.67 (s, 2H, Ar-H), 8.11 (d, $J = 10.8$ Hz, 2H, Ar-H), 7.93 (d, $J = 10.8$ Hz, 2H, Ar-H), 7.87 (d, $J = 9.2$ Hz, 2H, Ar-H), 7.81 (d, $J = 7.4$ Hz, 2H, Ar-H), 7.35 (dd, $J = 7.4$, 7.4 Hz, 2H, Ar-H), 7.31 (d, $J = 9.2$ Hz, 2H, Ar-H), 7.12 (dd, $J = 7.4$, 7.4 Hz, 2H, Ar-H), 6.79 (d, $J = 7.4$ Hz, 2H, Ar-H), 6.69 (s, 2H, Ar-H). IR (KBr): 1735 (C=O), 1449 (Ar), 1172 (Ar-O), 1054 (O=C-O), 754 (Ar) cm⁻¹.

Polyester 3c

Yield 95% (methanol-insoluble part). $[\alpha]_D^{25} -462$ ($c = 0.10$, CHCl₃). The specific rotation value was very unstable and changed in a range of +2000–−2000. ¹H NMR (400 MHz, CDCl₃): δ 8.24 (d, $J = 7.4$ Hz, 4H, Ar-H), 7.97 (d, $J = 7.4$ Hz, 4H, Ar-H), 7.88 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.82 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.38 (dd, $J = 7.2$, 7.2 Hz, 2H, Ar-H), 7.31 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.15 (dd, $J = 7.2$, 7.2 Hz, 2H, Ar-H), 6.80 (d, $J = 7.2$ Hz, 2H, Ar-H), 6.67 (s, 2H, Ar-H). IR (KBr): 1736 (C=O), 1450 (Ar), 1239 (Ar-O), 1061 (O=C-O), 768 (Ar) cm⁻¹.

Polycondensation of 1 and 2 without Solvent. A Typical Polycondensation Procedure for Synthesis of 3a. 2,2'-Dihydroxy-9,9'-spirobifluorene (**1**, 200 mg, 0.574 mmol) and terephthaloyl dichloride (**2a**, 118 mg, 0.580 mmol) were charged in a 10 mL Schrenck tube equipped with a magnetic stirrer under argon atmosphere. The solid mixture was stirred at 85 °C for 10 min and then at 250 °C for 30 min. The resulting mixture was cooled, dissolved in CH₂Cl₂ (5 mL), and poured into hexane (100 mL) to precipitate white powdery polymer. The precipitated polymer was purified similarly to the polymer obtained in *Polycondensation of 1 and 2* mentioned above (117 mg, 0.230 mmol, 40%).

Synthesis of Model Compounds

2-Hydroxy-2'-tert-butylldimethylsiloxo-9,9'-spirobifluorene. A solution of 2,2'-dihydroxy-9,9'-spirobifluorene (**1**, optically active) (200 mg, 0.575 mmol), 4-dimethylaminopyridine (23.2 mg, 0.190 mmol), and triethylamine (0.08 mL, 58.0 mg, 0.575 mmol) in dry THF (1 mL) in a 20 mL Schrenck tube was stirred at room temperature for 10 min under argon atmosphere. To the mixture was added dropwise a solution of *tert*-butylldimethylchlorosilane (95.4 mg, 0.633 mmol) dis-

solved in dry CH₂Cl₂, and the mixture was stirred for 30 min. After 1 h the solvents were evaporated to dryness. The resulting material was subjected to the separation by column chromatography on silica gel with hexane/ethyl acetate (4:1, v/v) as eluent. The pure product was obtained as a white, amorphous, resinous solid (76.5 mg, 0.166 mmol, 29%).

mp 78.2~80.5 °C. $[\alpha]_D^{25} = +6.6$ ($c = 0.50$, CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 7.72 (d, $J = 3.4$ Hz, 1 H, Ar-H), 7.70 (d, $J = 3.4$ Hz, 1 H, Ar-H), 7.68 (d, $J = 6.9$ Hz, 1 H, Ar-H), 7.65 (d, $J = 6.9$ Hz, 1 H, Ar-H), 7.31 (ddd, $J = 7.5, 7.5, 1.0$ Hz, 1 H, Ar-H), 7.30 (ddd, $J = 7.5, 7.5, 1.0$ Hz, 1 H, Ar-H), 7.03 (ddd, $J = 7.5, 7.5, 1.0$ Hz, 1 H, Ar-H), 7.02 (ddd, $J = 7.5, 7.5, 1.0$ Hz, 1 H, Ar-H), 6.83 (dd, $J = 4.7, 2.3$ Hz, 1 H, Ar-H), 6.81 (dd, $J = 4.7, 2.3$ Hz, 1 H, Ar-H), 6.69 (d, $J = 6.7$ Hz, 1 H, Ar-H), 6.68 (d, $J = 6.7$ Hz, 1 H, Ar-H), 6.20 (d, $J = 2.2$ Hz, 1 H, Ar-H), 6.17 (d, $J = 2.3$ Hz, 1 H, Ar-H), 4.89 (1 H, OH), 0.86 (s, 9 H, CH₃), 0.05 (s, 6 H, Si-CH₃) ppm.

2-(4-Methoxycarbonylbenzoyloxy)-2'-tert-butyltrimethylsiloxy-9,9'-spirobifluorene 5a. A solution of 2-hydroxy-2'-tert-butyltrimethylsiloxy-9,9'-spirobifluorene (32 mg, 0.069 mmol) and triethylamine (10 μ L, 6.98 mg, 0.069 mmol) in dry CH₂Cl₂ (0.5 mL) was stirred at 0 °C for 10 min in a 30 mL two necked round-bottom flask under argon atmosphere. To the mixture was added dropwise a solution of 4-methoxycarbonylbenzoyl chloride (14.0 mg, 0.069 mmol) dissolved in dry CH₂Cl₂ (0.5 mL), and the mixture was stirred for 40 min. After 1 h the reaction was quenched by pouring into water (100 mL). The organic layer was separated, while the aqueous layer was extracted three times with dichloromethane. The combined organic layer was washed with water three times and brine and dried over anhydrous MgSO₄. The solvents were evaporated to dryness. The product was purified by column chromatography on silica gel with hexane/ethyl acetate (8:1, v/v) as eluent. The pure product was obtained as a white, amorphous, resinous solid (6.2 mg, 0.01 mmol, 14%).

mp 69.3 ~ 71.0 °C. $[\alpha]_D^{27} = -2.7$ ($c = 0.062$, CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 8.13 (d, $J = 6.7$ Hz, 2 H, Ar-H), 8.10 (d, $J = 6.7$ Hz, 2 H, Ar-H), 7.88 (d, $J = 8.2$ Hz, 1 H, Ar-H), 7.83 (d, $J = 7.7$ Hz, 1 H, Ar-H), 7.71 (d, $J = 7.7$ Hz, 1 H, Ar-H), 7.65 (d, $J = 8.2$ Hz, 1 H, Ar-H), 7.38 (ddd, $J = 7.6, 7.6, 0.8$ Hz, 1 H, Ar-H), 7.32 (ddd, $J = 7.6, 7.6, 0.8$ Hz, 1 H, Ar-H), 7.27 (dd, $J = 8.3, 2.2$ Hz, 1 H, Ar-H), 7.12 (ddd, $J = 7.6, 7.6, 0.8$ Hz, 1 H, Ar-H), 7.05 (ddd, $J = 7.6, 7.6, 0.8$ Hz, 1 H, Ar-H), 6.84 (dd, $J = 8.3, 2.3$ Hz, 1 H, Ar-H), 6.75 (d, $J = 7.6$ Hz, 1 H, Ar-H), 6.72 (d, $J = 7.6$ Hz, 1 H, Ar-H), 6.60 (d, $J = 2.2$ Hz, 1 H, Ar-H), 6.22 (d, $J = 2.3$ Hz, 1 H, Ar-H), 3.94 (s, 3H, O-CH₃), 0.87 (s, 9 H, CH₃), 0.05 (s, 6 H, Si-

CH₃) ppm. IR ν (KBr): 2950 (CH₃), 1725 (C=O), 1450 (Ar), 1241 (CO-OC), 1105 (COO-C), 724 (Si-CH₃) cm⁻¹.

2,2'-Bis(4-methoxycarbonylbenzoyloxy)-9,9'-spirobifluorene 6a. A solution of 2,2'-dihydroxy-9,9'-spirobifluorene (**1**) (112 mg, 0.322 mmol), and triethylamine (0.098 mL, 71.7 mg, 0.708 mmol) in dry CH₂Cl₂ (1.0 mL) in a 30 mL two necked round-bottom flask was stirred at 0 °C for 10 min under argon atmosphere. To the mixture was added dropwise a solution of 4-methoxycarbonylbenzoyl chloride (141 mg, 0.708 mmol) dissolved in dry CH₂Cl₂ (2.0 mL), and the mixture was stirred for 40 min. After 1 h the reaction was quenched by pouring into water (100 mL). The organic layer was separated, while the aqueous layer was extracted three times with CH₂Cl₂. The combined organic layer was washed with water three times and brine and dried over anhydrous MgSO₄. The solvents were evaporated to dryness to afford a solid material which was purified by column chromatography on silica gel with hexane/ethyl acetate (6:1, v/v) as eluent. The pure product was obtained as a white, amorphous, and resinous solid (100 mg, 0.149 mmol, 46%).

mp 96.7 ~ 98.3 °C. $[\alpha]_D^{27} = +5.8$ ($c = 0.067$, CHCl₃). ¹H NMR (CDCl₃, 400 MHz): δ 8.14 (d, $J = 8.5$ Hz, 4 H, Ar-H), 8.09 (d, $J = 8.5$ Hz, 4 H, Ar-H), 7.87 (d, $J = 8.3$ Hz, 2 H, Ar-H), 7.82 (d, $J = 7.6$ Hz, 2 H, Ar-H), 7.38 (ddd, $J = 7.5, 7.5, 1.0$ Hz, 2 H, Ar-H), 7.29 (dd, $J = 8.3, 2.1$ Hz, 2 H, Ar-H), 7.14 (ddd, $J = 7.6, 7.6, 1.0$ Hz, 2 H, Ar-H), 6.79 (d, $J = 7.5$ Hz, 2 H, Ar-H), 6.65 (d, $J = 2.1$ Hz, 2 H, Ar-H), 3.94 (s, 6 H, CH₃) ppm. IR ν (KBr): 2957 (CH₃), 1728 (C=O), 1451 (Ar), 1261 (CO-OC), 1105 (COO-C), 809 (Ar-H) cm⁻¹.

RESULTS AND DISCUSSION

Synthesis of Optically Active Polyesters

Optically active (*R*)-(+)-2,2'-dihydroxy-9,9'-spirobifluorene **1** was chosen as a C₂ chiral biphenol monomer for polyester synthesis. According to Prelog's method,²⁸ racemic **1**_{rac} was prepared in six steps in 24% yield from 2-aminobiphenyl and its optical resolution³⁵ was carried out using a tartaric acid derivative to give optically active (*R*)-(+)-**1** in 17% yield.

Among possible spirobifluorene-containing polymers from **1**, polyester was selected since no polyester has been reported so far, from viewpoint of more stable helical structure expected from the lowered freedom of ester bond in comparison with carbonate bonds. Polycondensation of (*R*)-(+)-**1** with homoditopic acid chlorides **2** such as terephthaloyl dichloride **2a** was conducted in THF in the presence of triethyl-

Scheme 1.

Figure 1. Partial ^1H NMR spectrum of polyester **3a** (M_w 11400, 400 MHz, CDCl_3 , 295 K). The asterisk reveals the end group signal of **3a**.

amine for 1 h at 0°C (Scheme 1). The polymerization **1** with **2a** yielded the corresponding polyester as methanol-insoluble part (**3a**, 89%, M_w 5400, M_w/M_n 3.5) (run 1). Small peaks at low molecular weight region in the GPC trace seemed to reveal the formation of oligomeric cyclic polyesters. Although the yield was low (29%), the polymer molecular weight reached M_w 11400, when acetone was used as a precipitation solvent (run 2). Since the polymer molecular weight was not high enough, the solvent-free polycondensation was examined in the absence of triethylamine. A solid mixture of **1** and **2a** was heated without solvent at 250°C for 1 h to give the corresponding polyester **3a** in 40% yield as the acetone-insoluble part, of which molecular weight was M_w 16000 (M_w/M_n 1.7) (run 3). The acetone-soluble part contained lower-molecular weight polyester (26% yield, M_w 7600, M_w/M_n 5.2), in which oligomeric cyclic polyesters were little included as suggested by the single modal GPC trace. This result indicates that the solvent-free polymerization suppressed the formation of oligomeric product. In the case of **1_{rac}** similar polyester **3a_{rac}** was obtained in 44% yield (run 4). Thus, it was concluded that the solvent-free polycondensation yielded slightly higher molecular weight polyesters.

The polymerizations with 2,6-naphthaloyl dichloride **2b** and 4,4'-azodibenzoyl dichloride **2c** also afforded polyesters **3b** (95%, M_w 20000, M_w/M_n 2.3) and **3c** (95%, M_w 6200, M_w/M_n 2.2), respectively (runs 5 and 6). The polymerization behaviors were little dependent on the structure of **2**, although somewhat higher molecular weight polymer was obtained with **2b**.

The structure determination of polyester **3** was performed by ^1H NMR and IR spectra. Figure 1 illustrates ^1H NMR of **3a** (run 1, Table I) in which all aromatic signals were assignable as depicted on the spectrum. The signal around 8.2 ppm was assigned as that of the terminal acid chloride moiety, while the molecular weight determined by the quantitative end group analysis was M_n 6000 which corresponded to that estimated by GPC (run 2). IR spectrum of **3a** showed a typical aromatic ester carbonyl absorption at 1700 cm^{-1} in addition to 1100 cm^{-1} for C-O vibration.

Thermal Property. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of **3** were examined. DSC indicated no clear glass transition point (T_g) in all three polymers. TGA showed high 5% weight loss point (T_{d5}) over 480°C in all three polymers, being consistent with their all

Table I. Synthesis and Property of Polyesters **3** from **1**¹ and **2**

run	2	temp.[°C]	solvent	base	product	yield[%]	<i>M_w</i>	<i>M_n</i>	<i>M_w</i> / <i>M_n</i>	<i>T_{ds}</i> [°C]	[α] _D ²
1 ³	2a	0	THF	Et ₃ N	3a	89	5400	1600	3.5	—	—
2 ⁴	2a	0	THF	Et ₃ N	3a	29	11400	6700	1.7	480	+77.5
3 ⁴	2a	250	none	none	3a	40	16000	9600	1.7	495	+149
4 ^{4,5,6}	2a	250	none	none	3a	44	14000	8200	1.7	—	—
5 ³	2b	0	THF	Et ₃ N	3b	95	20000	8800	2.3	—	—
6 ⁴	2b	0	THF	Et ₃ N	3b	80	20400	10200	2.0	508	+301
7 ³	2c	0	THF	Et ₃ N	3c	95	6200	2800	2.2	—	—
7 ⁴	2c	0	THF	Et ₃ N	3c	53	6500	5000	1.3	488	−462

¹(*R*)-(+)-**1**: *M_w* 348, [α]_D = +18.7 (*c* 0.1, CHCl₃) at 25 °C. ²(*c* 0.1, CHCl₃) at 25 °C. ³Reprecipitation from THF solution into methanol. ⁴Reprecipitation from THF solution into acetone. ⁵Polymer obtained as acetone-insoluble part (yield 26%) showed *M_w* 7600, *M_n* 1500, and *M_w*/*M_n* 5.1. ⁶(*rac*)-**1** was used as monomer.

aromatic polyester structures. The high thermal stability of **3** seems to come from the rigid spirobifluorene skeleton in the main chain, since the high thermal stability of polymers containing spirobifluorene moieties has been reported.^{29–33}

Optical and Spectroscopic Characteristics. Specific rotation values of **1** and **3** (25 °C, *c* = 0.10, CHCl₃) are indicated in Table I. The value of optically active monomer **1** ([α]_D +18.7° (25 °C, *c* = 1.0, CHCl₃))³⁵ was changed to +77.5° (run 1) or +149° (run 2) when converted to **3a**, suggesting the polymerization degree-dependent specific rotation. As for **3b** the specific rotation value [α]_D²⁵ +301 (run 6) was obtained, while **3c** indicated [α]_D²⁵ −462 (run 7), although the experimental error was so big (+2000–−2000). The unstable specific rotation value is probably caused by the absorption of **3c** extended to 600 nm.

Since a CD spectrum has been measured only for an optically active polymer containing chiral spirobifluorene moieties in the main chain (polyaryrene),³⁴ we have studied the CD spectral characteristics of **3** in detail. UV-vis and CD spectra (THF, 25 °C, 20 μM) of monomer **1**, dimethyl esters of **4**, polyesters **3**, and unit models **5** and **6** were measured (Figures 2–7).

As shown in Figure 2, UV-vis spectrum of **3a** was approximately superimposition of those of **1** and dimethyl terephthalate **4a** having a UV absorption maximum at 240 nm. Although the monomer **1** has some UV absorption at 220–330 nm, **1** showed rather weak Cotton effect around such absorption region in the CD spectrum (Figure 2). On the other hand, clear bisignate Cotton effect was confirmed at 247 nm which is the absorption maximum of the corresponding terephthaloyl part of **3a**. This CD spectral feature is similar to that reported for a polyaryrene in which bisignate

Figure 2. CD and UV-vis spectra of monomer **1**, polyester **3a**, dimethyl terephthalate **4a** (20 μM, THF, 295 K).

Cotton effect was observed around 320 nm corresponded to the absorption of the conjugated polyaryrene main chain unit.³⁴

Similar spectral characteristics were observed in both UV-vis and CD spectra of **3b** and related com-

Figure 3. CD and UV-vis spectra of monomer **1**, polyester **3b**, dimethyl 2,6-naphthalenedicarboxylate **4b** (20 μ M, THF, 295 K).

Figure 4. CD and UV-vis spectra of monomer **1**, polyester **3c**, and 4,4'-bis(methoxycarbonyl)azobenzene **4c** (20 μ M, THF, 295 K).

Scheme 2.

pounds (Figure 3). Meanwhile, in the case of **3c**, main CD signal moved to a region around 325 nm which was red-shifted in comparison with the cases of **3a** and **3b**, because the UV-vis absorption maximum of **3c** appeared at 330 nm where the additivity rule was still kept, as shown in Figure 4. Namely, the absorption band and the CD Cotton effect around 325 nm are based on the optically inactive azobenzene moiety.

Similar bisignate Cotton effect in the CD spectrum of **3c** to those of **3a** and **3b** seemed to suggest similar

structural characteristics of these three polyesters possessing C_2 chiral spirobifluorene moieties in the main chains. Then, two unit models of **3a** (**5a** and **6a**) were synthesized by reacting 4-methoxycarbonylbenzoyl chloride with **1** and monoprotected **1** (**1_{si}**), respectively, in the presence of a base (Scheme 2). CD and UV-vis spectra of **3a**, monosubstituted model **5a**, and **6a** are shown in Figure 5. It is obvious by comparing Figures 5 and 6 that UV-vis spectra of both **5a** and **6a** are similar each other and further similar to that

Figure 5. CD and UV-vis spectra of **4a**, model compounds **5a** and **6a** (20 μ M, THF, 295 K).

of **1**, whereas Cotton effect in the CD spectrum of **5a** is not similar to that of **6a**. Namely, the rectangular terephthaloyl moieties produced by the rigid C_2 chiral structure of **1** are probably necessary for the occurrence of the Cotton effect, similarly to the case of polyester **3a**.

There is no strong absorption around 250 nm in UV-vis spectrum of **1**, although **4a** has some UV absorption around 250 nm where Cotton effect was observed in its CD spectrum. Accordingly, the Cotton effect around 250 nm in the CD spectrum of **3a** would be supposed to come from the terephthaloyl moiety in the polymer main chain, although it has not a chiral structure. From similar Cotton effect of polyester **3a** and model **6a** and the CD intensity of **6a** weaker than that of **3a**, the terephthaloyl moieties should be regularly arranged in polymer **3a** in solution state. This conclusion well coincides with the observation of the Cotton effect around 330 nm in the CD spectrum of achiral azobenzene-containing polyester **3c**.

Figure 6 collects the CD and UV-vis spectra of polyesters **3** along with that of monomer **1**. Bisignate Cotton effect appeared around the UV-vis absorption maximum originated from the comonomer unit of **2**

Figure 6. CD and UV-vis spectra of polyesters **3** and monomer **1** (20 μ M, THF, 295 K).

was observed in all three polymers. Since the strongest CD intensity was confirmed in the case of **3b**, temperature dependency of CD intensity was examined. Figure 7 unambiguously revealed the decrease of CD intensity of **3b** around 250 nm according to the temperature increase (0–60 °C in THF), probably suggesting a typical decrease in helical conformation. This result suggests that **3b** has a regular structure like helix, judging from the previous reports^{4,5} which describe helical polymers based on the C_2 chiral moiety in the main chain.

Structure simulation of **3** was carried out by MM2. As shown in Figure 8 (for **3a**), a helical conformation was calculated as the energy minimum structure in which left-handed helix was suggested from the *R*-spirobifluorene skeleton, like the result of *R*-binaphthyl skeleton-based polycarbonate.^{16–23} Both of them involve *R*-forms of the C_2 chiral repeating units in the main chain. Meanwhile, the inside size of the calculated helix was as big as 17 Å x 17 Å which reveals potential utility of the inner cavity. Similar helical structures were simulated for **3b** and **3c** by the MM2 calculation. The helical structure of **3** should be the main structure of C_2 chiral *R*-spirobifluorene skele-

Figure 7. Temperature-dependent CD spectral change of polyester **3b** (0, 20, 40, 60 °C, 20 μ M, THF).

Figure 8. MM2-simulated structure of polyester **3a** (15mer, left: side View and right: top view).

ton-containing polyesters in solution, because all data obtained in this work are consistent with it, although there is no data ruling out other possible conformations besides helix.

CONCLUSIONS

This work has demonstrated the synthesis of three optically active polyesters possessing C_2 chiral spirobifluorene moieties in the main chains of which structural feature was discussed based on the UV-vis and CD spectral data. The polycondensation of optically active (*R*)-(+)-2,2'-dihydroxy-9,9'-spirobifluorene **1** and aromatic acid dichlorides **2** afforded the corresponding polyesters **3** with M_w 5400–20000. In the

solvent-free polymerization, the corresponding polyester **3a** with M_w 16000 was obtained. These polymers had high thermal decomposition temperature T_{d5} over 480 °C presumably due to the presence of the spirobifluorene moiety, whereas they showed no clear T_g . The intense bisignate Cotton effect appeared around the absorption region of the optically inactive diacid part of **3**, the CD intensity decrease connected with the temperature increase, the simulated structure of **3**, and so on suggested their helical conformation. The results obtained in this work seem to indicate that the spirobifluorene moiety with the marked skeletal rigidity promises the helical conformation of polymers constructed by the successive connection of C_2 chiral units because of its low degree of mobility, in comparison with other C_2 chiral structures such as biphenyl and binaphthyl groups.

REFERENCES

1. T. Nakano and Y. Okamoto, *Chem. Rev.*, **101**, 4013 (2001).
2. L. Pu, *Chem. Rev.*, **98**, 2405 (1998).
3. a) Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, and H. Yuki, *J. Am. Chem. Soc.*, **101**, 4763 (1979).
b) A. K. M. F. Azam, M. Kamigaito, and Y. Okamoto, *Polym. J.*, **38**, 1035 (2006).
4. A. J. M. Van Beijnen, R. J. M. Nolte, W. Drenth, and A. M. F. Hezemans, *Tetrahedron*, **32**, 2017 (1976).
5. T. Patten and B. M. Novak, *J. Am. Chem. Soc.*, **113**, 5065 (1991).
6. a) E. Yashima, K. Maeda, and Y. Okamoto, *Nature*, **399**, 449 (1999).
b) T. Hasegawa, K. Maeda, H. Ishiguro, and E. Yashima, *Polym. J.*, **38**, 912 (2006).
7. J. C. Nelson, J. G. Saven, J. S. Moore, and P. G. Wolynes, *Science*, **277**, 1793 (1997).
8. K. Akagi, G. Piao, S. Kaneko, K. Sakamaki, H. Shirakawa, and M. Kyotani, *Science*, **282**, 1683 (1998).
9. M. Fujiki, *J. Am. Chem. Soc.*, **116**, 6017 (1994).
10. T. Takata, Jasco Report, JPN, 2001.
11. T. Takata, in "Precision Polymers and Nano-Organized Systems" T. Kunitake, S. Nakahama, S. Takahashi, N. Toshima, Ed., Kodansha, Tokyo, 2000, pp 85–88.
12. L. A. Howe and G. D. Jaycox, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 2827 (1998).
13. F. Kondo, D. Takahashi, H. Kimura, and M. Takeishi, *Polym. J.*, **30**, 161 (1998).
14. Q. S. Hu, D. Vitharana, G. Y. Liu, V. Jain, M. W. Wagaman, L. Zhang, T. R. Lee, and L. Pu, *Macromolecules*, **29**, 1082 (1996).
15. a) K. Maeyama, K. Ogura, A. Okamoto, K. Ogino, H. Saito, and N. Yonezawa, *Polym. J.*, **37**, 736 (2005).
b) K. Maeyama, S. Maeda, H. Saito, and N. Yonezawa, *Polym. J.*, **39**, 342 (2007).
16. T. Takata, H. Matsuoka, and T. Endo, *Chem. Lett.*, 2091 (1991).
17. T. Takata, H. Matsuoka, T. Hirasa, J. Matsuo, T. Endo, and Y. Furusho, *Kobunshi Ronbunshu*, **54**, 684 (1997).

18. T. Takata, Y. Furusho, K. Murakawa, T. Endo, H. Matsuoka, T. Hirasa, J. Matsuo, and M. Sisido, *J. Am. Chem. Soc.*, **120**, 4530 (1998).
19. K. Murakawa, Y. Furusho, and T. Takata, *Chem. Lett.*, 94 (1999).
20. T. Takata, K. Murakawa, and Y. Furusho, *Polym. J.*, **31**, 1051 (1999).
21. T. Takata, M. Goto, Y. Furusho, and T. Kato, *Kobunshi Ronbunshu*, **59**, 778 (2002).
22. M. Goto, Y. Furusho, and T. Takata, *ITE Letters*, **3**, 597 (2002).
23. Y. Ikari, R. Seto, T. Maeda, and T. Takata, *Kobunshi Ronbunshu*, **63**, 512 (2006).
24. Y. Furusho, T. Maeda, T. Takeuchi, N. Makino, and T. Takata, *Chem. Lett.*, 1020 (2001).
25. T. Maeda, Y. Furusho, and T. Takata, *Chirality*, **14**, 587 (2002).
26. T. Maeda, T. Takeuchi, Y. Furusho, and T. Takata, *J. Polym. Sci., A: Polym. Chem.*, **42**, 4693 (2004).
27. A. M. Sargeson, *Pure Appl. Chem.*, **50**, 893 (1978).
28. V. Prelog and D. Bedekovic, *Helv. Chem. Acta*, **62**, 2285 (1979).
29. D. S. Reddy, C. Shu, and F. Wu, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 262 (2002).
30. C. Chou, D. S. Reddy, and C. Shu, *J. Polym. Sci., Part A: Polym. Chem.*, **40**, 3615 (2002).
31. S. Wu and C. Shu, *J. Polym. Sci., A: Polym. Chem.*, **41**, 1160 (2003).
32. D. S. Reddy, C. Chou, C. Shu, and G. Lee, *Polymer*, **44**, 557 (2003).
33. Y. Kim, H. Kim, and S. Kwon, *Macromolecules*, **38**, 7950 (2005).
34. J. Yan, X. Cheng, Q. Zhou, and J. Pei, *Macromolecules*, **40**, 832 (2007).
35. F. Toda and K. Tanaka, *J. Org. Chem.*, **53**, 3607 (1988).
36. J. Liu and P. H. Geil, *J. Polym. Sci., Part B: Polym. Phys.*, **35**, 1575 (1997).
37. B. Philip and K. Sreekumar, *J. Mater. Sci.*, **38**, 1573 (2003).