



Synthesis and property of 9,9'-spirobifluorene-containing aromatic polyesters as optical polymers with high refractive index and low birefringence

Ryota Seto^a, Takahiro Kojima^b, Katsumoto Hosokawa^b, Yasuhito Koyama^a, Gen-ichi Konishi^a, Toshikazu Takata^{a,*}

^a Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-(H-126), Ookayama, Meguro, Tokyo 152-8552, Japan

^b Canon Inc., Production Engineering Research Laboratory, 70-1, Yanagi-cho, Saiwai, Kawasaki, Kanagawa 212-8602, Japan

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ABSTRACT

C₂-Symmetric 9,9'-spirobifluorene-containing polyesters (**PEs**) were synthesized by polycondensation of 2,2'-dihydroxy-9,9'-spirobifluorene (**1**) with bis(acyl chloride)s (**2**) at 230 °C in diphenylether. The molecular weights of **PEs 3a–3f** were sufficiently high (*M_w* 13,400–41,600). **PEs** displayed high thermal stability. The glass transition temperatures (*T_g*) estimated by differential scanning calorimetry analysis appeared in a range 177–352 °C depending on the spacer structure, while the 5% decomposition temperatures (*T_{d5}*) measured by thermogravimetric analysis were over 416 °C both under nitrogen atmosphere and in air. **PEs** showed good solubility in typical organic solvents such as CHCl₃ and THF easily to afford the tough, transparent, and flexible cast films. The transmittance of the polymer films reached over 90% in the wavelength range from ca. 410–900 nm. In addition, **PEs** exhibited higher refractive index rather than that of commercially available 9,9'-diarylfuorene-containing **PE**, in addition to very low degree of birefringence presumably due to the C₂-symmetric structure.

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1. Introduction

Optically transparent polymers with high refractive index and low birefringence have long been required in a variety of optical material fields such as lenses, functional films for liquid crystal displays, and optical disks, due to their easy processing and light weight [1–4]. Many researchers have devoted to increase the refractive index and to reduce the birefringence of polymers via several approaches such as incorporation of perfluorocyclobutane group [5], adamantane group [6,7], and sulfur atom [8] into polymers in addition to use of organic/inorganic dopants [9–13]. For this reason, *Cardo* structure-containing polymers have attached considerable interests, and polymers with 9,9'-diarylfuorene (DAF) skeleton in the main chain have been extensively studied. DAF-containing polymers shows not only high refractive index and low birefringence but also high solubility, high thermal stability, and high affinity toward fillers enabling fine dispersion in composite materials [14–21]. Namely, the incorporation of many aromatics into polymers produces the high refractive index, while the each aromatic group occupies different plane to cause considerable

decrease of optical anisotropy, eventually rendering the low birefringence. On the other hand, 9,9'-spirobifluorene (SBF) skeleton has the analogous structure to DAF, which contains two fluorene units connected at the tetrahedral spiro carbon, where the two fluorene moieties are perpendicularly crossed each other. There are several reports on polymers containing SBF skeletons for electro luminescence materials [22–31] and gas separation membranes [32–40]. In addition, SBF-containing polymer has been regarded as one of the *Cardo* polymers like DAF-containing polymer from the property similarity, although the SBF and DAF structure are considerably different each other in structure of main chain part, as shown below (Fig. 1).

In fact, we have recently reported the synthesis of SBF-containing polycarbonates as optical materials with high refractive index and low birefringence [41]. The high content of fluorene moieties in the unit structure would attribute to high refractive index, while the perpendicularly crossed two fluorene moieties could afford high optical isotropy. Although the SBF-containing polycarbonates showed good optical properties, there were some problems. The Polycarbonates prepared from diphenolic SBF showed a poor film-forming property, due to their rigid polymer structures. On the other hand, the introduction of alkylene chain in the main chain afforded the tough, transparency, and flexible cast films, however which led to low optical property and thermal

* Corresponding author. Tel.: +81 3 5734 2898; fax: +81 3 5734 2888.

E-mail address: ttakata@polymer.titech.ac.jp (T. Takata).

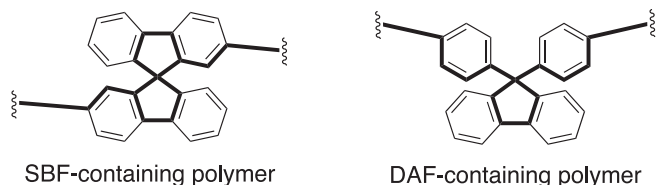


Fig. 1. Structures of SBF-containing polymer and DAF-containing polymer.

stability. To settle such problems, we became intrigued by the usefulness of aromatic polyester (**PE**). Aromatic **PEs** are widely used as fiber, film, and plastic bottle because of their excellent properties such as high mechanical strength, high optical transparency, high thermal stability, and so on. In this article, we describe the synthesis and the evaluation of optical properties of **PEs** containing SBF moiety in the main chain [42].

2. Experimental section

2.1. Materials

Terephthaloyl chloride was purchased from Iharanikkei Chemical Industry Co., Ltd. (Shizuoka, Japan) and purified by recrystallization from hexane. 2,6-Naphthalenedicarboxylic acid and 4,4'-biphenyldicarboxylic acid were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used as received. 9,9-Dimethylfluorene-2,7-dicarboxylic acid and 9,9-dioctylfluorene-2,7-dicarboxylic acid were purchased from Osaka Gas Co. and used without further purification. 2,2'-Dihydroxy-9,9'-spirobifluorene (**1**) [43–45] and 2,2'-dicarboxy-9,9'-spirobifluorene [43,44] were prepared according to the literature. Other commercially available materials were used without further purification.

2.2. Characterization

^1H and ^{13}C NMR spectra were recorded on a JEOL AL-400 spectrometer using CDCl_3 as the solvent and with tetramethylsilane as the internal standard. Molecular weight and its distribution were estimated by size exclusion chromatography (SEC) on a JASCO Gulliver system equipped with two consecutive linear polystyrene

gel columns (Tosoh TSK-gel GMHXL and G5000HXL) at 30 °C (flow rate 0.85 mL/min) on the basis of polystyrene standards using CHCl_3 as the eluent. The glass transition temperatures (T_g) were taken with a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min. The thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min under nitrogen atmosphere and in air atmosphere (flow rate 50 mL/min). Solubility was evaluated by using 3 mg of polymer and 1 mL of solvent. FT-IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Melting points were measured with a Stuart Scientific SMP3. MALDI-TOF MS spectra were taken on a Shimadzu AXIMA-CFR mass spectrometer. Ultraviolet–visible (UV–vis) spectra were recorded on a JASCO V-550 UV–vis spectrometer. Fluorescent spectra were recorded on a JASCO FP-6500 fluorescent spectrometer.

2.3. Transmittance

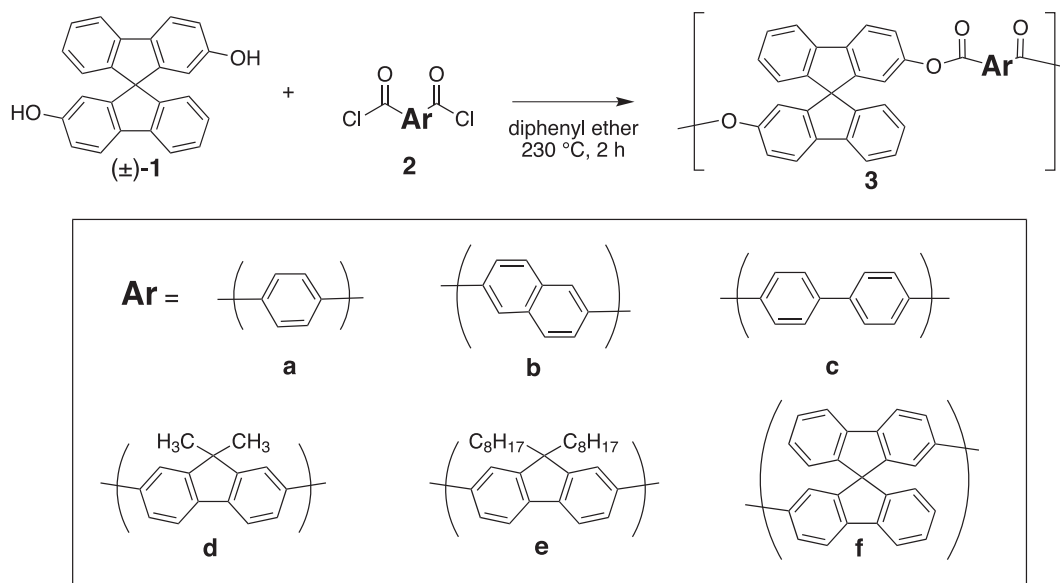
Transmittance of the films was evaluated by a UV–vis spectrophotometer (JASCO V-550) in a scanning range from 200 to 900 nm. The sample films were prepared by a casting method using a solution of the corresponding polymer in THF at 20 °C to arrange to 15 μm thickness.

2.4. Refractive index

Refractive index, birefringence, and Abbe's number of polymer sample were measured by a Kalnew Precision Refractometer (KPR-30, Shimadzu Co., Ltd). The sample films for the refractive index, birefringence, and Abbe's number measurement were prepared by casting an NMP solution of polymer followed by heating at 200 °C to arrange to 700 μm thickness.

2.5. General procedure for synthesis of acylchlorides

A mixture of 2,6-naphthalenedicarboxylic acid (10 mmol) and thionyl chloride (10 mL) in the presence of catalytic amount of DMF was refluxed for 12 h. The resulting solution was cooled to room temperature and excess thionyl chloride was removed under



Scheme 1. Synthesis of **PEs**.

Table 1
Polycondensation of **1** with **2**.^a

Entry	Monomer	Product (%) ^b	M_w^c	M_w/M_n^c
1 ^d	2a	3a' (90)	11,200	3.8
2	2a	3a (85)	41,600	2.5
3	2b	3b (88)	30,200	3.1
4	2c	3c (88)	22,300	5.1
5	2d	3d (90)	35,000	3.1
6	2e	3e (92)	25,800	2.6
7	2f	3f (90)	13,400	3.1

^a 230 °C, 2 h, stirred in diphenylether under argon atmosphere.

^b MeOH-insoluble part.

^c Estimated by SEC on the basis of polystyrene standards (eluent: CHCl₃).

^d Optically active (*R*)-**1** (99% *ee*) was used as the monomer in place of (±)-**1**.

reduced pressure, followed by azeotropic removal with hexane. The crude product was recrystallized from toluene to afford 2,6-naphthalenedicarbonyl dichloride (82% yield): m.p. 189.0–190.0 °C (lit. 189–190 °C) [46].

2.6. Typical procedure for polycondensation reaction of **1** with **2a**

A mixture of 2,2'-dihydroxy-9,9'-spirobifluorene **1** (1.00 g, 2.87 mmol) and terephthaloyl dichloride **2a** (583 mg, 2.87 mmol) in diphenylether (10 mL) was stirred at 230 °C for 2 h under argon atmosphere. The reaction mixture was cooled to room temperature and was poured into MeOH (200 mL) to precipitate white solids. The precipitates were collected by filtration and washed repeatedly with MeOH and water to remove diphenylether. The collected materials were dissolved in CH₂Cl₂ (20 mL) and reprecipitated in MeOH (200 mL). The precipitates were filtered, washed with MeOH, and dried at 100 °C for 24 h to yield the corresponding **PE 3a** as a white solid.

3a: a white solid {1.18 g (2.44 mmol) 85%}; M_w 41,600. M_n 16,600. T_g (N₂) 331 °C. T_{d5} (N₂) 507 °C. ¹H NMR (400 MHz, CDCl₃, 293 K, δ): 8.12 (s, 4H, Ph-H), 7.85 (d, J = 8.0 Hz, 2H, Ph-H), 7.79 (d, J = 8.0 Hz, 2H, Ph-H), 7.36 (dd, J = 8.0, 8.0 Hz, 2H, Ph-H), 7.26 (d,

J = 8.0 Hz, 2H, Ph-H), 7.12 (dd, J = 8.0, 8.0 Hz, 2H, Ph-H), 6.77 (d, J = 8.0 Hz, 2H, Ph-H), 6.62 (s, 2H, Ph-H) ppm. ¹³C NMR (100 MHz, CDCl₃, 293 K, δ): 164.0, 150.4, 149.7, 148.3, 140.8, 139.7, 133.6, 130.1, 128.1, 128.0, 124.2, 121.5, 120.7, 120.0, 117.3, 65.9 ppm. IR (KBr) ν_{max} : 1737 (s, C=O), 1450 (m, C=C), 1233 (s, C-O), 1065 (m, CO-O) cm⁻¹. UV (THF) λ_{max} , nm (ϵ): 251 (46800).

3b: a white solid {1.33 g (2.53 mmol) 88%}; M_w 30,200. M_n 9700. T_g (N₂) 346 °C. T_{d5} (N₂) 511 °C. ¹H NMR (400 MHz, CDCl₃, 293 K, δ): 8.67 (s, 2H, Ph-H), 8.11 (d, J = 8.1 Hz, 2H, Ph-H), 7.93 (d, J = 8.1 Hz, 2H, Ph-H), 7.87 (d, J = 8.2 Hz, 2H, Ph-H), 7.80 (d, J = 8.2 Hz, 2H, Ph-H), 7.37 (dd, J = 8.2, 8.2 Hz, 2H, Ph-H), 7.31 (d, J = 8.2 Hz, 2H, Ph-H), 7.12 (dd, J = 8.2, 8.2 Hz, 2H, Ph-H), 6.79 (d, J = 8.2 Hz, 2H, Ph-H), 6.69 (s, 2H, Ph-H) ppm. ¹³C NMR (100 MHz, CDCl₃, 293 K, δ): 164.6, 150.7, 149.8, 148.3, 140.9, 139.6, 134.7, 131.3, 129.7, 129.0, 128.1, 128.0, 126.2, 124.2, 121.6, 120.7, 120.0, 117.4, 65.9 ppm. IR (KBr) ν_{max} : 3062 (w, C-H), 1736 (s, C=O), 1450 (m, C=C), 1240 (s, C-O), 1057 (m, CO-O) cm⁻¹. UV (THF) λ_{max} , nm (ϵ): 291 (45200).

3c: a white solid {1.40 g (2.53 mmol) 88%}; M_w 22,300. M_n 4400. T_g (N₂) 352 °C. T_{d5} (N₂) 507 °C. ¹H NMR (400 MHz, CDCl₃, 293 K, δ): 8.13 (d, J = 8.1 Hz, 4H, Ph-H), 7.86 (d, J = 8.2 Hz, 2H, Ph-H), 7.80 (d, J = 7.6 Hz, 2H, Ph-H), 7.63 (d, J = 8.1 Hz, 4H, Ph-H), 7.35 (dd, J = 7.6, 7.6 Hz, 2H, Ph-H), 7.28 (d, J = 8.2 Hz, 2H, Ph-H), 7.11 (dd, J = 7.6, 7.6 Hz, 2H, Ph-H), 6.77 (d, J = 7.6 Hz, 2H, Ph-H), 6.66 (s, 2H, Ph-H) ppm. ¹³C NMR (100 MHz, CDCl₃, 293 K, δ): 164.6, 150.7, 149.7, 148.3, 144.6, 140.8, 139.5, 130.6, 129.0, 128.1, 128.0, 127.3, 124.1, 121.6, 120.6, 120.0, 117.5, 65.9 ppm. IR (KBr) ν_{max} : 3040 (w, C-H), 1736 (s, C=O), 1605 (m, C=C), 1450 (m, C=C), 1240 (s, C-O), 1065 (m, CO-O) cm⁻¹. UV (THF) λ_{max} , nm (ϵ): 291 (47500).

3d: a white solid {1.54 g (2.58 mmol) 90%}; M_w 35,000. M_n 11,300. T_g (N₂) 349 °C. T_{d5} (N₂) 492 °C. ¹H NMR (400 MHz, CDCl₃, 293 K, δ): 8.18 (s, 2H, Ph-H), 8.12 (d, J = 7.6 Hz, 2H, Ph-H), 7.88 (d, J = 8.4 Hz, 2H, Ph-H), 7.82 (d, J = 5.6 Hz, 2H, Ph-H), 7.80 (d, J = 5.6 Hz, 2H, Ph-H), 7.38 (dd, J = 7.6, 7.6 Hz, 2H, Ph-H), 7.31 (dd, J = 8.4, 2.0 Hz, 2H, Ph-H), 7.13 (dd, J = 7.6, 7.6 Hz, 2H, Ph-H), 6.80 (d, J = 7.6 Hz, 2H, Ph-H), 6.70 (d, J = 2.0 Hz, 2H, Ph-H), 1.50 (s, 6H, -CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃, 293 K, δ): 165.0, 154.8, 150.8, 149.8, 148.4, 143.0, 140.9, 139.5, 129.7, 129.1, 128.0, 127.9, 124.6,

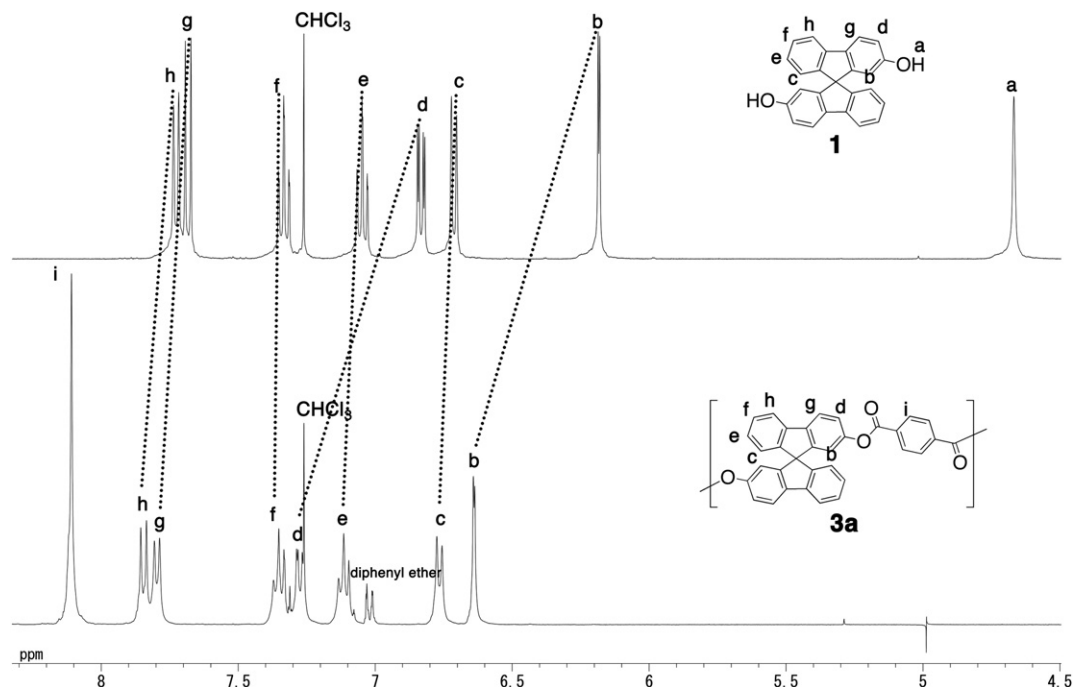


Fig. 2. Partial ¹H NMR spectra of **1** and **3a** (Table 1, Entry 2) (400 MHz, 293 K (**1**) and 333 K (**3a**), CDCl₃).

Table 2
Thermal property of **3**.

Polymer	T_g^a (°C)	T_{d5}^b (°C) N ₂	T_{d5}^b (°C) Air
3a	331	507	497
3b	346	511	512
3c	352	507	482
3d	349	492	447
3e	177	443	416
3f	334	507	517

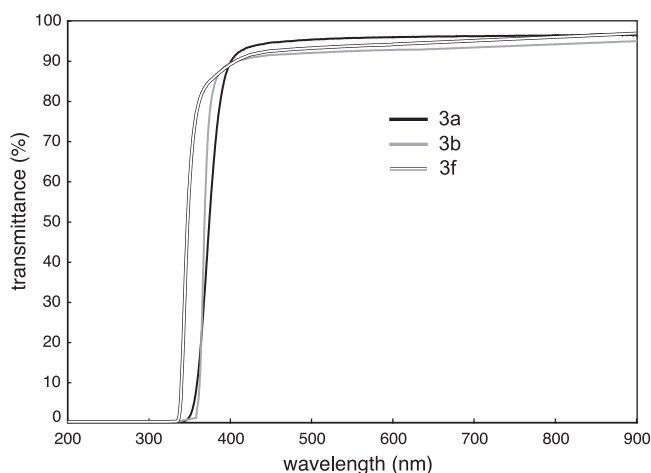
^a DSC was conducted at a heating rate 10 °C/min under N₂ and air atmospheres.^b TGA was carried out at a heating rate of 10 °C/min.**Table 3**
Solubility of **PE 3** toward organic solvents.

Solvent	Polymer					
	3a	3b	3c	3d	3e	3f
DMF	++	±	±	±	±	±
DMAc	±	±	±	±	++	±
DMSO	±	±	±	±	±	±
Nitrobenzene	+	±	+	+	+	±
MeOH	–	–	–	–	–	–
NMP	+	±	+	++	++	±
Acetone	–	–	–	–	±	–
CH ₂ Cl ₂	++	++	++	++	++	++
THF	++	++	++	++	++	++
CHCl ₃	++	++	++	++	++	++
Toluene	–	–	–	–	++	–
Benzene	+	+	–	++	++	++
<i>n</i> -Hexane	–	–	–	–	–	–

Key: ++, soluble; +, slowly soluble; ±, partially soluble on heating; –, insoluble. Solubility test was carried out using 3 mg of polymer and 1 mL of solvent.

124.2, 121.7, 120.9, 120.6, 120.0, 117.5, 65.9, 47.2, 26.6 ppm. IR (KBr) ν_{\max} : 2960 (w, C–H), 1735 (s, C=O), 1609 (m, C=C), 1450 (m, C=C), 1232 (s, C–O), 1059 (m, CO–O) cm^{–1}. UV (THF) λ_{\max} , nm (ϵ): 332 (48200).

3e: a white solid {1.08 g (1.36 mmol) 92% (monomer 1.47 mmol was used)}; M_w 25,800, M_n 9900. T_g (N₂) 177 °C. T_{d5} (N₂) 443 °C. ¹H NMR (400 MHz, CDCl₃, 293 K, δ): 8.13 (d, J = 8.0 Hz, 2H, Ph–H), 8.06 (s, 2H, Ph–H), 7.90 (d, J = 8.0 Hz, 2H, Ph–H), 7.83 (d, J = 7.6 Hz, 2H, Ph–H), 7.79 (d, J = 7.9 Hz, 2H, Ph–H), 7.40 (dd, J = 7.6, 7.6 Hz, 2H, Ph–H), 7.33 (d, J = 7.9 Hz, 2H, Ph–H), 7.15 (dd, J = 7.6, 7.6 Hz, 2H, Ph–H), 6.82 (d, J = 7.6 Hz, 2H, Ph–H), 6.71 (s, 2H, Ph–H), 2.10–1.90 (m, 4H, –CH₂–), 1.25–0.90 (m, 22H, –CH₂–), 0.78 (t, J = 7.0 Hz, –CH₃), 0.55–0.40 (m, 4H, –CH₂–) ppm. ¹³C NMR (100 MHz, CDCl₃, 293 K, δ): 165.2, 152.0, 150.8, 150.0, 148.3, 144.9, 140.9, 139.4, 129.5,

**Fig. 3.** Transmittance of **3a** in film state (film thickness: 15 μ m).**Table 4**
The cut off wavelength of **3**.

Polymer	90% ^a (nm)	50% ^a (nm)	10% ^a (nm)
3a	402	374	359
3b	408	368	362
3c	389	362	348
3d	378	354	346
3e	397	370	361
3f	409	348	340

^a Transmittance of **3** in film state. The sample films were prepared by casting a THF solution of polymer to arrange to 15 μ m thickness.

128.9, 128.1, 127.9, 124.5, 124.2, 121.8, 120.6, 120.5, 120.0, 117.6, 55.7, 40.0, 31.7, 29.8, 29.1, 29.0, 23.7, 22.5, 14.0 ppm. IR (KBr) ν_{\max} : 2926 (m, C–H), 1736 (s, C=O), 1450 (m, C=C), 1227 (s, C–O), 1060 (m, CO–O) cm^{–1}. UV (THF) λ_{\max} , nm (ϵ): 329 (54900).

3f: a white solid {1.85 g (2.58 mmol) 90%}; M_w 13,400, M_n 4300. T_g (N₂) 334 °C. T_{d5} (N₂) 507 °C. ¹H NMR (400 MHz, CDCl₃, 293 K, δ): 8.10 (s, 2H, Ph–H), 7.86 (s, 2H, Ph–H), 7.84 (s, 2H, Ph–H), 7.73 (d, J = 8.2 Hz, 2H, Ph–H), 7.71 (d, J = 8.2 Hz, 2H, Ph–H), 7.35 (s, 4H, Ph–H), 7.28 (dd, J = 8.2, 8.2 Hz, 2H, Ph–H), 7.11 (m, 4H, Ph–H), 7.03 (dd, J = 8.2, 8.2 Hz, 2H, Ph–H), 6.67 (m, 4H, Ph–H), 6.45 (s, 2H, Ph–H) ppm. ¹³C NMR (100 MHz, CDCl₃, 293 K, δ): 164.7, 150.6, 149.6, 148.9, 148.3, 147.9, 147.1, 140.8, 140.4, 139.2, 130.6, 129.3, 128.6, 128.2, 128.0, 127.8, 125.7, 124.1, 121.6, 121.2, 121.1, 120.5, 120.1, 119.9, 117.4, 65.8, 65.6 ppm. IR (KBr) ν_{\max} : 3063 (w, C–H), 1734 (s, C=O), 1609 (m, C=C), 1450 (m, C=C), 1207 (s, C–O), 1058 (m, CO–O) cm^{–1}. UV (THF) λ_{\max} , nm (ϵ): 299 (36300).

3. Results and discussion

3.1. Polymer synthesis

Racemic 2,2'-dihydroxy-9,9'-spirobifluorene (**1**) as a diphenolic monomer was prepared according to the literature [43–45]. Aromatic bis(acyl chloride)s **2a–2e** were prepared from commercially available carboxylic acids and thionyl chloride. Synthesis of SBF skeleton-containing acid chloride **2f** was carried out according to the literature [43,44]. Since we previously used optically active 2,2'-dihydroxy-9,9'-spirobifluorene (*R*)-**1** (99% *ee*) for the preparation of helical **PEs** [42], we first examined (*R*)-**1** as the monomer for the preparation of **PE** (Scheme 1). In spite of our considerable efforts to obtain high molecular weight **PE**, the polycondensation of (*R*)-**1** with **2a** in diphenyl ester (230 °C) yielded the corresponding **PE 3a'** with relatively low molecular weight (M_w 11,200) along with the formation of cyclic oligomers as byproducts (Table 1, Entry 1). This result probably comes from the highly regular structure of **3a'**,

Table 5
Optical property of **PE 3**.

Polymer	Refractive index ^a	Birefringence ^a	Abbe's number $\nu_D^{a,b}$
3a	1.676	0.0009	17
3b	1.703	0.0012	16
3c	1.676	0.0009	21
3d	1.684	0.0021	14
3e	1.677	0.0003	20
3f	– ^c	– ^c	– ^c
DAF-type PE ^d	1.658	– ^e	20

^a Measured using a Kalnew Precision Refractometer with a 587.6 nm line laser. The sample films were prepared by casting an NMP solution of polymer in followed by heating at 200 °C to arrange to 700 μ m thickness.^b Abbe's number $\nu_D = (n_D - 1)/(n_F - n_C)$; (n_D 587.6 nm, n_F 486.1 nm, n_C 656.3 nm).^c No self-standing film was obtained.^d The **PE** was obtained by polycondensation reaction of 9,9-(4-hydroxyphenyl) fluorene with **2d** (M_w 51,000 M_w/M_n 2.1) [20].^e Not reported.

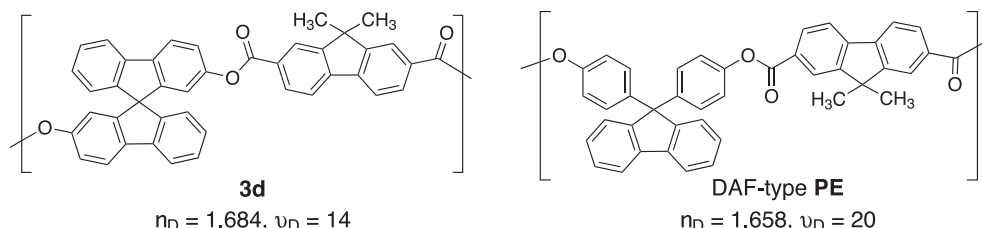


Fig. 4. Chemical Structures of **3d** and DAF-type PE.

which originating from optically active (*R*)-**1** skeleton, would not only enable the easy back-biting to form the cyclic oligomers but also be inactivated the end-groups of the propagating polymer by the steric hinderance. Therefore, we envisioned that the random copolymerization exploiting the racemic **1** could overcome such problem to yield the higher molecular weight **PEs**. Actually, the polycondensation of racemic **1** with not only **2a** but also other bis (acyl chloride)s **2b–f** under the same conditions afforded the SBF-containing **PEs 3** in relatively high yields (Table 1, Entries 2–7). Neither base nor special additive was added to the polymerization systems. The molecular weight of **3a–e** except for **3f**, estimated by SEC on the basis of polystyrene standards, was sufficiently high (M_w 41,600–22,300) to easily prepare the corresponding self-standing films by casting from CHCl_3 or THF solution. On the other hand, the molecular weight of **3f** was not so high (M_w 13,400), probably due to the steric hindrance between the two SBF monomers.

The structure of **3** was confirmed by the IR, ^1H NMR, and ^{13}C NMR spectra. The IR spectra of **3** showed the characteristic absorptions around 1740 and 1240 cm^{-1} of the stretching vibrations of C=O and C–O bonds and the absorption from the aromatic rings at 1600–1400 cm^{-1} . The ^1H NMR spectra of **3** were well consistent with their structures. A typical ^1H NMR spectrum is depicted in Fig. 2 (**3a**). All proton signals were completely assignable as shown in Fig. 2, while these signals were sharp throughout the spectrum, clearly indicating the structural uniformity of **3a** as expected from the **PE** structure.

3.2. Thermal property

Thermal stability of **3** was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are summarized in Table 2.

All **PEs 3** had good thermal stability with an onset of degradation temperature consistently higher than 410 °C and the 5% decomposition temperature (T_{d5}) in a range of 443–511 °C under nitrogen and 416–517 °C in air. **PEs** without alkyl substituents (**3a–c** and **3f**) were specially stable to show T_{d5} over 500 °C in nitrogen and over 480 °C in air, while **PEs** with alkyl substituents (**3d** and **3e**) showed thermal property depending on the length of the alkylene chain, suggesting the occurrence of the initial decomposition at the alkyl substituent. Most **PEs** exhibited the high T_g (331–352 °C), except for **3e** possessing the long alkylene chains as the side chain groups (177 °C), indicating the large T_g decrease due to the flexible alkylene side chains.

3.3. Solubility

Table 3 shows the solubility of **3** in ordinary organic solvents. All **PEs 3** exhibited good solubility in many solvents such as CHCl_3 , CH_2Cl_2 , and THF at room temperature, but **3** was insoluble in MeOH and hexane. Polymer **3e** with long alkylene chains was soluble even in acetone and toluene. The excellent solubility of **3** is probably

originated from the twisted SBF structure which prevented the strong intra/intermolecular interactions of the polymer chains.

3.4. Optical property

The colorless, flexible, transparent, and strong thin films were obtained from all **PEs** by casting from CHCl_3 or THF solution. Fig. 3 illustrates the UV–vis spectra of a few **PEs** in film state in the wavelength region ranging from 200 to 900 nm. All **PEs 3** had high transparency in the visible region where the transmittance at ca. 410 nm was over 90% in each case. The cut off wavelength was about 350 nm for **3d** and **3f**, 360 nm for **3c**, and 370 nm for **3a**, **3b**, and **3e** (Table 4). The very high transparency of **PEs 3** comes mainly from the amorphous nature owing to the SBF structure in the main chain.

Table 5 summarizes the typical optical properties of **PEs 3** along with those of a DAF-containing polymer for comparison. As expected, the refractive indices of **3** were sufficiently high 1.68–1.70 at a typical wavelength of 587.6 nm, being higher than those of a few commercial high performance polymers such as polycarbonate (PC: 1.585) used in the optical field [47–51]. Moreover, comparing the refractive indices of **3d** (1.684) with DAF-type **PE** (1.658) (Fig. 4) having the same spacer structure as **3d** [20], it turned out that **3d** had much higher refractive index than that of DAF-type **PE**. The high refractive index of **3** was undoubtedly attributable to the structures of the polynuclear aromatic polymers including the SBF unit.

As shown in Table 5, the degree of birefringence of **3** was quite low in any case. Each of **3** displayed approximately zero retardation to the visible light with the wavelength of 587.6 nm in undrawn state. The sufficiently low birefringence of **3** would result mainly from the effect of the SBF structure in the main chain. Because the two fluorene planes of the SBF moiety are crossed each other at ca. 90° angle and are not folded in one direction, the optical anisotropy of **3** completely disappears.

Abbe's numbers of **3** (14–21) were lower than that of DAF-type **PE**. This is also dependent on the incorporation ratio of the fluorene skeleton in the polymer [52].

4. Conclusion

The SBF moiety-containing aromatic polyesters (**PEs 3**) were synthesized in high yields by the polycondensation of 2,2'-dihydroxy-9,9'-spirobifluorene **1** with several aromatic bis(acyl chloride)s. The T_g s of **PEs 3** appeared in a range from 177 to 352 °C depending on the structures, while the decomposition temperatures of the **PEs 3** were sufficiently high (over 410 °C). The **PEs 3** showed high solubility to give the strong cast films with high transparency, and exhibited high refractive indices along with quite low degree of birefringence, revealing a promising applicability to high performance optical materials. Thus, the excellent effect of the SBF moiety incorporated into polymer main chain on the optical property is again emphasized in this work.

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Appendix. Supplementary information

Supplementary information associated with this article can be found in the on-line version, at [doi:10.1016/j.polymer.2010.08.032](https://doi.org/10.1016/j.polymer.2010.08.032).

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