

# 9,9-Diarylfuorene-Based Poly(alkyl aryl ether)s: Synthesis and Property

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Polyethers possessing 9,9-diarylfuorene moieties in the main chain (F-PEs **3**) were synthesized in 85–99% yields by the polycondensation of 9,9-bis(hydroxyaryl)fluorenes with alkyl ditosylates in the presence of cesium carbonate. Molecular weight of the F-PEs was dependent on the structure of the ditosylate **1**; cyclohexyl-1,4-dimethylene (**1a**), 1,2-ethylene (**1b**), 1,3-trimethylene (**1c**), and 1,6-hexamethylene (**1d**). Higher molecular weight F-PEs ( $M_n$  32000–60000,  $M_w$  74000–160000) was obtained when longer alkyl chain ditosylates (**1a** and **1d**) were used. The F-PEs showed good solubility toward various organic solvents such as toluene and high 5% weight loss temperature ( $T_{d5}$ : 424–447 °C). The glass transition temperature of F-PEs ( $T_g$ ) was ranging from 147 to 220 °C. No melting point ( $T_m$ ) was observed. F-PEs showed high water-resistance. The transmittance of F-PEs in film state (thickness: 21–32  $\mu\text{m}$ ) reached over 90% in the visible region. The F-PEs exhibited high refractive indices in a range of 1.62–1.66 at 590 nm in addition to sufficiently low birefringence values, probably due to the *cardo* structure of the fluorene moiety placed in the main chain. The structural dependence of dispersing ability to fullerene  $C_{60}$  was investigated.

KEY WORDS: *Cardo* Structure / Polyether / Refractive Index / Birefringence / Solubility / Thermal Stability / Processability /

9,9-Diarylfuorene-based polymers attract much attention due to the unique characteristics originated from the “*cardo*” structure as characterized often by the high refractive index and low birefringence.<sup>1–9</sup> Such optical property is caused by the presence of many aromatic rings in the 9,9-diarylfuorene moiety which occupy the different planes to disturb the interchromophore packing, effectively decreasing the optical anisotropy. Meanwhile, such polymers also display excellent filler-dispersing ability<sup>10–12</sup> in addition to their high thermal stability,<sup>13–16</sup> high solubility,<sup>17–19</sup> and so on.<sup>20–25</sup> We have recently reported the special  $\pi$ – $\pi$  interaction of the 9,9-diarylfuorene moiety in the matrix polymers toward  $\pi$ -face of the carbon fillers.<sup>26</sup> Although many polymers possessing 9,9-diarylfuorene moieties in the main chain have been developed to date,<sup>1–30</sup> there is no study on polyethers. Polyethers are an important class of high performance engineering thermoplastics with a favorable combination of physical, mechanical, and chemical properties, other than processability,<sup>31–41</sup> and are easily synthesized usually by the polycondensation of diols and ditopic electrophiles. Polyethers with good optical and physical properties can be obtained,<sup>42,43</sup> if saturated alkyl group is introduced into the polymer main chain in addition to 9,9-diarylfuorene moiety, because the alkyl group often shows no optical anisotropy.

Herein, we wish to disclose the synthesis and property of poly(alkyl aryl ether)s (F-PEs) containing 9,9-diarylfuorene moiety in the main chain, with emphasis on the effect of alkyl chain on the polymer property such as thermal property, water-resistance, and optical property.

## EXPERIMENTAL

### Materials and Methods

9,9-Bis(4-hydroxyphenyl)fluorene (**2a**) and 9,9-bis(4-hydroxy-3-methylphenyl)fluorene (**2b**) (provided by Osaka Gas Co., Ltd.) were used after drying *in vacuo* at 100 °C for 5 h. All solvents used in this work were dried over freshly activated molecular sieves 4A. Other commercially available materials were used without further purification.

<sup>1</sup>H NMR (400 MHz) spectra were recorded on a JEOL AL-400 spectrometer using  $\text{CDCl}_3$  as the solvent and tetramethylsilane as the internal standard. Molecular weight and its distribution were measured by a gel permeation chromatography (GPC) on a JASCO Gulliver system equipped with two consecutive liner polystyrene gel columns (TOSOH TSKgel G2000HXL and GMHXL) at 30 °C, eluted with  $\text{CHCl}_3$  at a flow rate of 0.85 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  $\text{N}_2$  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 5 °C/min under  $\text{N}_2$  atmosphere (flow rate of 50 mL/min) to determine glass transition temperature  $T_g$ . Transmittance and filler dispersing ability of polymer films were evaluated by a UV-visible spectrophotometer (UV-550, JASCO) with the scanning range from 220 nm to 800 nm. The X-ray diffraction

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(XRD) profiles of the F-PE films were measured by a X-ray diffractometer (Miniflex/CW/S, Rigaku Co.), which was performed by the reflect method among  $2\theta$  range of 5–60° with an interval 0.02. Refractive index of polymers was measured with a spectroscopic ellipsometer (Mass-102, Five Lab.). Birefringence of the films was evaluated by taking the picture of the film placed between two cross axes polarizing films. Retardations were measured by an automatic birefringence analyzer (KOBRA-CCD, Oji Scientific Instruments) under the parallel-Nicols (590 nm).

**Typical Experimental Procedure for the Synthesis of Ditosylate (1d).** To a mixture of 1,6-hexanediol (50.1 g, 0.424 mol) and pyridine (107 mL, 1.32 mol) in  $\text{CH}_2\text{Cl}_2$  (180 mL) was added portionwise *p*-toluenesulfonyl chloride (177 g, 0.928 mol) at –15 °C. The mixture was warmed to 0 °C and stirred for 24 h. The mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and washed with 10% aq. HCl and 10% aq. NaCl. The organic layer was dried over  $\text{MgSO}_4$ , filtrated, and concentrated *in vacuo*. The solid material formed was recrystallized from MeOH to give 1,6-hexamethylene ditosylate (**1d**, 167 g, 93%) as white solids; m.p. 69.5–71.5 °C (lit. 70.0–71.5 °C).<sup>44</sup>

**Typical Experimental Procedure for the Polycondensation of 9,9-Bis(4-hydroxyphenyl)fluorene (2a) and 1,6-Hexamethylene Ditosylate (1d).** To a mixture of 9,9-bis(4-hydroxyphenyl)fluorene (**2a**, 3.50 g, 10.0 mmol), 1,6-hexamethylene ditosylate (**1d**, 4.26 g, 10.0 mmol) in mesitylene–DMSO (10 mL, 7:3 (v/v)) was added  $\text{Cs}_2\text{CO}_3$  (10.6 g, 32.5 mmol) at room temperature. The mixture was warmed to 150 °C and stirred for 3 h under an argon atmosphere. The resulting mixture was cooled to room temperature and diluted with toluene (100 mL) to precipitate inorganic materials, which were filtered off. The filtrate was washed with water, and then poured into MeOH. The precipitates formed were collected by filtration, and the solid product was dried *in vacuo* at room temperature for 1 d. To the product dissolved in  $\text{CHCl}_3$  (200 mL) was added activated charcoal (6.0 g). The mixture was stirred at room temperature overnight and filtrated. The filtrate was poured into MeOH to give F-PE **3d** (3.66 g, 85%) as a white solid;  $M_n$  60000,  $M_w$  160000, *MWD* 2.7;  $T_g$  147 °C,  $T_{d5}$  444 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.72 (d, 2H,  $J = 7.4$  Hz), 7.35 (d, 2H,  $J = 7.4$  Hz), 7.31 (t, 2H,  $J = 7.4$  Hz), 7.22 (t, 2H,  $J = 7.4$  Hz), 7.08 (d, 4H,  $J = 8.6$  Hz), 6.70 (d, 4H,  $J = 8.6$  Hz), 3.85 (t, 4H,  $J = 6.4$  Hz), 1.72 (br, 4H), 1.45 (br, 4H) ppm; IR (neat) 3035, 2938, 2863, 1607, 1507, 1472, 1447, 1245, 1178, 1013, 823, 747  $\text{cm}^{-1}$ ; Elemental Analysis Calcd: C, 86.06%; H, 6.52%; Found: C, 85.84%; H, 6.23%.

**F-PE 3a.** White solid (91%, *cis:trans* = 18:82);  $M_n$  32000,  $M_w$  74000, *MWD* 2.3;  $T_g$  220 °C,  $T_{d5}$  441 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.73 (d, 2H,  $J = 7.4$  Hz), 7.36 (d, 2H,  $J = 7.4$  Hz), 7.32 (t, 2H,  $J = 7.4$  Hz), 7.23 (t, 2H,  $J = 7.4$  Hz), 7.08 (d, 4H,  $J = 8.6$  Hz), 6.70 (d, 4H,  $J = 8.6$  Hz), 3.76 (d, 0.7H,  $J = 6.3$  Hz), 3.67 (d, 3.3H,  $J = 6.3$  Hz), 2.0–1.8 (m, 3.7H), 1.71 (br, 1.7H), 1.6–1.4 (m, 1.3H), 1.1–0.9 (m, 3.3H) ppm; IR (neat) 3035, 2918, 2854, 1606, 1507, 1466, 1447, 1244, 1177, 1031, 822, 746  $\text{cm}^{-1}$ ; Elemental Analysis Calcd: C, 86.43%; H, 6.59%; Found: C, 86.47%; H, 6.40%.

**F-PE 3b.** White solid (94%);  $M_n$  6100,  $M_w$  13000, *MWD* 2.1;  $T_g$  200 °C,  $T_{d5}$  439 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.71 (d, 2H,  $J = 7.4$  Hz), 7.4–7.3 (m, 4H), 7.22 (t, 2H,  $J = 7.4$  Hz), 7.07 (d, 4H,  $J = 8.6$  Hz), 6.72 (d, 4H,  $J = 8.6$  Hz), 4.2–4.1 (m, 4H) ppm; IR (neat) 3035, 2927, 2875, 1606, 1506, 1447, 1241, 1178, 1069, 939, 823, 745  $\text{cm}^{-1}$ ; Elemental Analysis Calcd: C, 86.14%; H, 5.36%; Found: C, 85.96%; H, 5.33%.

**F-PE 3c.** White solid (97%);  $M_n$  6800,  $M_w$  19000, *MWD* 2.9;  $T_g$  185 °C,  $T_{d5}$  447 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.71 (d, 2H,  $J = 7.4$  Hz), 7.4–7.3 (m, 4H), 7.21 (t, 2H,  $J = 7.4$  Hz), 7.06 (d, 4H,  $J = 8.8$  Hz), 6.69 (d, 4H,  $J = 8.8$  Hz), 4.00 (t, 4H,  $J = 5.6$  Hz), 2.12 (quintet, 2H,  $J = 5.6$  Hz) ppm; IR (neat) 3035, 2933, 2876, 1606, 1507, 1471, 1447, 1243, 1178, 1060, 823, 745  $\text{cm}^{-1}$ ; Elemental Analysis Calcd: C, 86.13%; H, 5.68%; Found: C, 86.04%; H, 5.61%.

**F-PE 3e.** White solid (99%);  $M_n$  32000,  $M_w$  110000, *MWD* 3.3;  $T_g$  208 °C,  $T_{d5}$  424 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.72 (d, 2H,  $J = 7.4$  Hz), 7.37 (d, 2H,  $J = 7.4$  Hz), 7.31 (t, 2H,  $J = 7.4$  Hz), 7.23 (t, 2H,  $J = 7.4$  Hz), 7.0–6.9 (m, 4H), 6.59 (d, 2H,  $J = 8.5$  Hz), 3.77 (d, 0.7H,  $J = 6.8$  Hz), 3.69 (d, 3.3H,  $J = 5.7$  Hz), 2.09 (s, 6H), 1.8–2.0 (m, 3.7H), 1.75 (br, 1.7H), 1.7–1.5 (m, 1.3H), 1.2–1.0 (m, 3.3H) ppm; IR (neat) 3019, 2919, 2854, 1605, 1500, 1465, 1447, 1249, 1131, 1031, 806, 742  $\text{cm}^{-1}$ ; Elemental Analysis Calcd: C, 86.38%; H, 7.04%; Found: C, 86.10%; H, 6.97%.

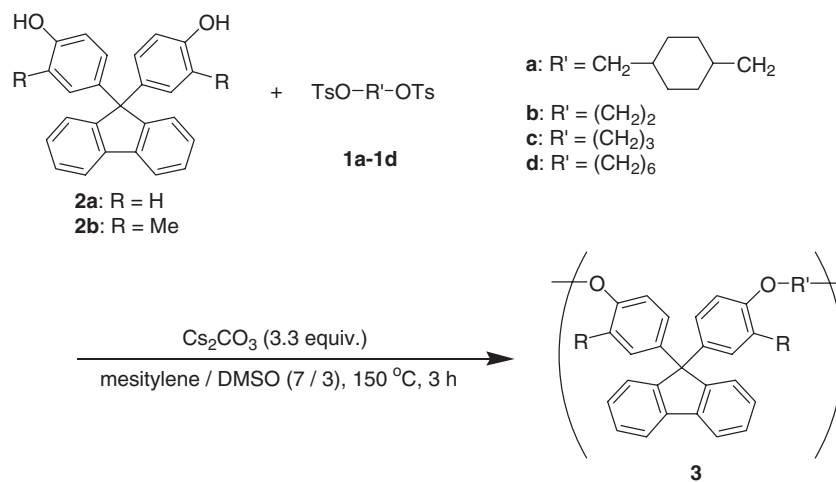
## Film Preparation

Polymer films of the F-PEs for the evaluation of refractive index and retardation were prepared by a heat-press method (200–260 °C) using the corresponding polymers which were dried *in vacuo* at 80 °C. The films for the evaluation of transmittance and XRD profiles were prepared by casting from the toluene solutions of the corresponding polymers at room temperature.

## RESULTS AND DISCUSSION

### Synthesis and Structure of F-PEs

We first examined the polycondensation of 9,9-bis(4-hydroxyphenyl)fluorene (**2a**, BPF) as the *cardo* monomers and ditosylate **1a** (*cis:trans* = 18:82) for the preparation of F-PEs (Scheme 1). The polycondensation of **2a** with **1a** in the presence of  $\text{Cs}_2\text{CO}_3$  was conducted in a few solvents capable of solubilizing **1a**, **2a**, and **3a** in some extents. The results are summarized in Table I. It turned out that the mixed solvent of mesitylene:DMSO (7:3 (v/v)) was a suitable solvent which gave the corresponding polyether **3a** with  $M_n$  32000 and  $M_w$  74000 (entry 3). The polycondensation in DMSO alone resulted in the lowering of the molecular weight probably due to the low solubility of **3a** (entry 1), while that in mesitylene was also unfruitful owing to the low solubility of  $\text{Cs}_2\text{CO}_3$  (entry 6). In addition, the prolonged reaction time caused the coloration of the resulting polymer due mostly to the oxidation of the phenol moieties (entry 4). The polycondensations of **2** with a few ditosylates **1** were examined in the mixed


**Table I.** Effect of solvent on the synthesis of F-PE **3a**<sup>a</sup>

Entry	Mesitylene/DMSO Ratio	Time/h	Yield <sup>b</sup> /%	$M_n^c$	$M_w^c$	$MWD^c$
1	0:10 (DMSO only)	3	85	4500	28000	6.3
2	5:5	3	77	22000	73000	3.4
3	7:3	3	91	32000	74000	2.3
4	7:3	6	90	26000	62000	2.4
5	9:1	3	87	31000	80000	2.6
6	10:0 (Mesitylene only)	3	77	6100	13000	2.1

<sup>a</sup>A mixture of **2a** (10.0 mmol) and **1a** (10.0 mmol) was heated in the presence of  $\text{Cs}_2\text{CO}_3$  (32.5 mmol) in a solvent (10 mL) at 150 °C under an argon atmosphere. <sup>b</sup>Yield of MeOH-insoluble part. <sup>c</sup>Estimated by GPC using polystyrene standards (eluent:  $\text{CHCl}_3$ ).

**Table II.** Synthesis of F-PEs **3** from **2** and **1**<sup>a</sup>

Entry	<b>2</b>	<b>1</b>	F-PE	Yield <sup>b</sup> /%	$M_n^c$	$M_w^c$	$MWD^c$
1	R = H	R' = $\text{CH}_2$ -- $\text{CH}_2$	<b>3a</b>	91	32000	74000	2.3
2	R = H	R' = $(\text{CH}_2)_2$	<b>3b</b>	94	6100	13000	2.1
3	R = H	R' = $(\text{CH}_2)_3$	<b>3c</b>	97	6800	19000	2.9
4	R = H	R' = $(\text{CH}_2)_6$	<b>3d</b>	85	60000	160000	2.7
5	R = Me	R' = $\text{CH}_2$ -- $\text{CH}_2$	<b>3e</b>	99	32000	110000	3.3

<sup>a</sup>A mixture of **2** (10.0 mmol) and **1** (10.0 mmol) was heated in the presence of  $\text{Cs}_2\text{CO}_3$  (32.5 mmol) in a mixed solvent (10 mL; mesitylene/DMSO; 7/3 (v/v)) at 150 °C for 3 h under an argon atmosphere. <sup>b</sup>Yield of MeOH-insoluble part. <sup>c</sup>Estimated by GPC using polystyrene standards (eluent:  $\text{CHCl}_3$ ).

solvent system (Table II). The molecular weight of **3a** ( $M_n$  32000,  $M_w$  74000), **3d** ( $M_n$  60000,  $M_w$  160000), and **3e** ( $M_n$  32000,  $M_w$  110000) were higher than those of **3b** ( $M_n$  6100,  $M_w$  13000) and **3c** ( $M_n$  6800,  $M_w$  19000). This is probably owing to the low reactivity originated from the steric hindrance on the nucleophilic displacement between the monomers, as suggested by the MM2 calculation. There seems no effect of the methyl substituents at the *ortho* position of the phenolic nucleophile.

Figure 1 shows <sup>1</sup>H NMR spectra of F-PEs **3**. All aromatic signals of **3** appeared sharply in any case, which suggested high degree of polymerization and low degree of disorderliness in polymer structure as recognized from the polymerization type. In the spectrum of **3a**, the signals based on the structural

isomerism around the cyclohexyl group appeared separately (**g**: methylene of  $\text{ArOCH}_2$ - (*cis*), **h**: methylene of  $\text{ArOCH}_2$ - (*trans*), **i**: CH (*cis*), **j**: Cy-eq-H (*trans*), **k**: CH (*trans*), **l**: Cy-eq-H (*cis*), **m**: Cy-ax-H (*cis*), **n**: Cy-ax-H (*trans*)). The *cis:trans* ratio in **3a** reflected the *cis:trans* ratio of **1a**, suggesting that the reactivity of the two diastereomers **1a** was almost same in the polymerization. The same thing was observed in F-PE **3e**. IR spectral data also supported the polyether structure; a strong broad absorption at 1300–1200  $\text{cm}^{-1}$  and a medium broad absorption at 1100–1000  $\text{cm}^{-1}$  for alkyl aryl ether linkage.<sup>53</sup>

### Solubility

Solubility of **3** toward organic solvents was evaluated and the results are shown in Table III. All polymers were highly

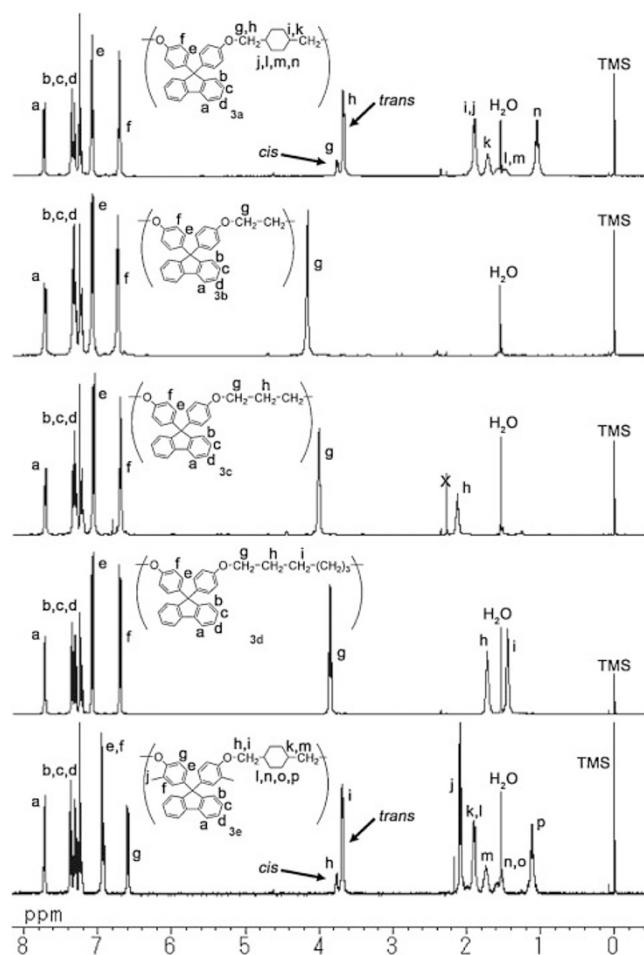


Figure 1.  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ , 298 K) of F-PEs **3**.

Table III. Solubility behavior of F-PEs **3** to organic solvents<sup>a</sup>

F-PE	$\text{CHCl}_3$	THF	toluene	acetone	MeCN	MeOH	hexane
<b>3a</b>	+	+	+	-	-	-	-
<b>3b</b>	+	+	+	-	-	-	-
<b>3c</b>	+	+	+	-	-	-	-
<b>3d</b>	+	+	+	-	-	-	-
<b>3e</b>	+	+	+	-	-	-	-

<sup>a</sup>F-PE (100 mg) was added in a solvent (1 mL) and stirred at room temperature: +, soluble; -, insoluble.

soluble in typical organic solvents such as toluene,  $\text{CHCl}_3$ , and THF. The high solubility of **3** presumably comes from the 9,9-diarylf luorene moieties as the “cardo” in the main chain, like other polymers.<sup>17–19</sup>

### Thermal Property

Thermal property of **3** was evaluated by TGA and DSC under nitrogen atmosphere (Figures 2 and 3). The 5% weight loss temperature ( $T_{d5}$ ) of **3** was high enough; 441 °C (**3a**), 439 °C (**3b**), 447 °C (**3c**), 444 °C (**3d**), and 424 °C (**3e**). There was no clear difference in  $T_{d5}$  of **3** with different alkyl chains. No melting point ( $T_m$ ) was observed in any case, being clearly consistent with the amorphous nature of the F-PEs.  $T_g$  of the F-

PEs undoubtedly depended on the structure of the alkyl chain: 220 °C (**3a**), 200 °C (**3b**), 185 °C (**3c**), 147 °C (**3d**), and 208 °C (**3e**). This result suggests the easy control of  $T_g$  of the F-PE.

### Water-Resistance

Water-resistance of the F-PEs **3a** and **3d** was evaluated using the films. The films were prepared by casting from the toluene solution of them. The film of a polyester possessing 9,9-diarylf luorene moiety with main chain<sup>5</sup> was used for comparison. These films were heated in water at 80 °C for 8 h. The results were shown in Figure 4. The clear polyester film remarkably became clouded along with its deformation. In contrast to it, the films of F-PEs showed no change in its film shape and transparency. These films were subjected to the measurements of the molecular weight and thermal stability. However, no decrease in molecular weight and weight of the films was observed in all polymers. The results seem to suggest that the heating in water caused the crystallization of the polyester. Thus, the F-PEs were proved to have good water-resistant property.

### Transparency

Colorless transparent thin films of the F-PEs were readily prepared by casting from the toluene solution (thickness: 21–32  $\mu\text{m}$ ). The transparency of **3d** film was demonstrated in Figure 5 as an example. The transmittance of the films increased from *ca.* 320 nm, and reached over *ca.* 90% at 400 nm in any polymers. In addition, it gradually increased with increase of wavelength in the visible light region (Figure 6). The X-ray diffraction (XRD) analyses of the F-PE cast-films showed only a broad signal in any case, strongly supporting the amorphous nature corresponding to the high transparency of the F-PEs (Figure 7). The amorphous nature certainly comes from the *cardo* structure of the 9,9-diarylf luorene moiety, which is consistent with the largely decreased interchromophore interaction in or within the polymer chain.

### Refractive Index

Refractive indices of the F-PEs were measured using their thin films which were obtained by a heat-press method at 200–260 °C. The results are summarized in Table IV. The refractive indices were sufficiently high in all five polymers despite their polymer structures consisting only of C, H, and O atoms: 1.62 (**3a**), 1.66 (**3b**), 1.65 (**3c**), 1.63 (**3d**), and 1.62 (**3e**) at a typical wavelength of 590 nm. The high refractive index values of the F-PEs are probably attributable to the high content of the aromatic rings of the 9,9-diarylf luorene moieties with main chain. The slightly low refractive index of **3a**, **3d**, and **3e** compared to **3b** and **3c** would be caused by the reduction of the polymer density, which might come from the rigid alkyl chain. In addition, *ortho*-methyl group of **3e** afforded no distinct effect on the refractive index.

### Birefringence

Birefringence of F-PEs **3a** and **3d** was evaluated by taking the picture of their polymer films placed between two cross

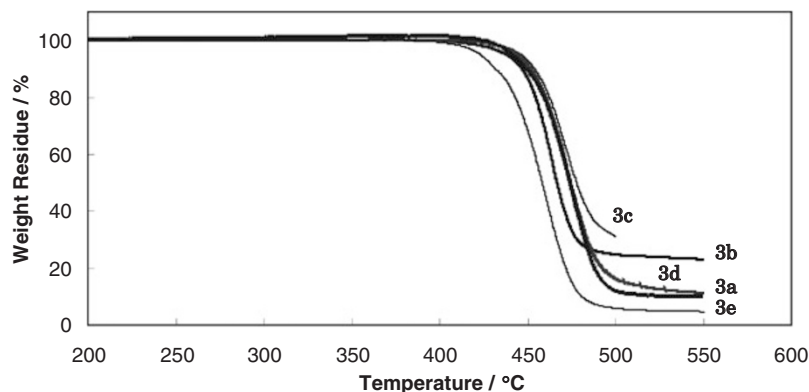


Figure 2. TGA profiles of the F-PEs, measured at a heating rate 10°C/min in N<sub>2</sub> atmosphere.

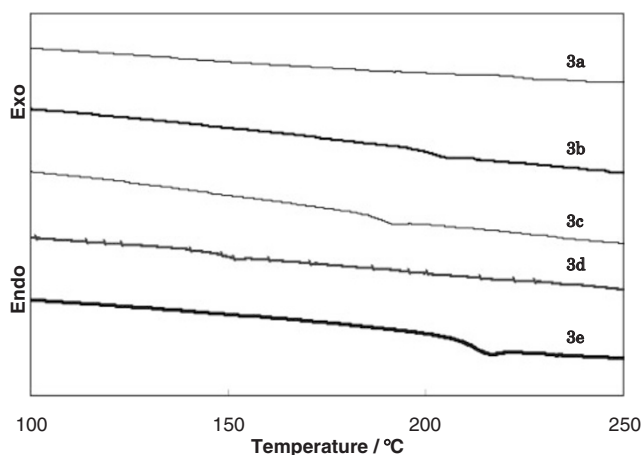


Figure 3. DSC profiles of the F-PEs, measured at a heating rate 5°C/min in N<sub>2</sub> atmosphere.

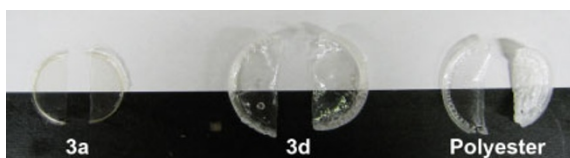


Figure 4. Pictures of the films of **3a**, **3d**, and a polyester possessing 9,9-diarylfuorene moiety before and after heating at 80°C for 8 h in water (left: before heating, right: after heating).

side products, and selections to those of some of the products of metal triflates. The results reported with metal triflic acid as catalyst, the results are similar to observing addition at the ortho positions and the results are controlled by the triflic acid often the reactions initiated with m

Figure 5. Transparent film of F-PE **3d** (film thickness: 520 μm) obtained by casting from the toluene solution at room temperature.

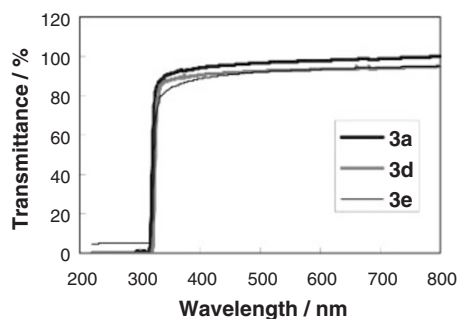


Figure 6. Transmittance of **3** in film state measured by a UV-vis spectrometer (film thickness: 21–32 μm).

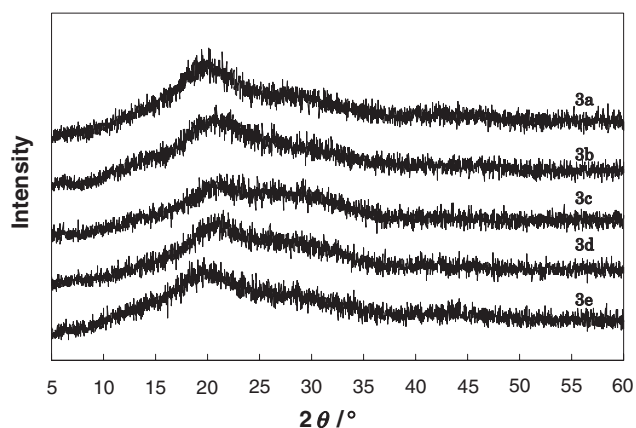


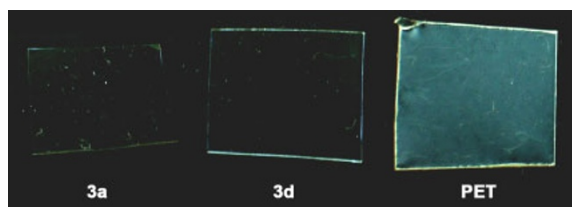
Figure 7. XRD pattern of F-PE films which casted by the toluene solution.

Table IV. Refractive index of F-PEs **3**<sup>a</sup>

F-PE	Refractive Index		
	485 nm	590 nm	655 nm
<b>3a</b>	1.64	1.62	1.61
<b>3b</b>	1.68	1.66	1.65
<b>3c</b>	1.67	1.65	1.64
<b>3d</b>	1.66	1.63	1.63
<b>3e</b>	—	1.62	—

<sup>a</sup>Refractive indices of polymer sample were measured by a spectroscopic ellipsometer.



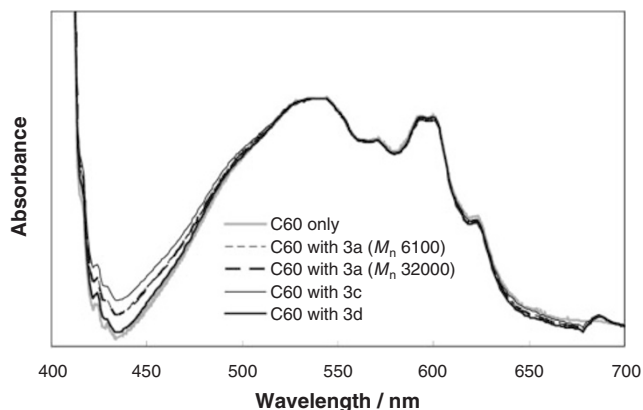


**Figure 8.** Birefringence of PET and F-PEs **3** under the cross-Nicols.

axes polarizing films (Figure 8). The polymer films were prepared by casting from the toluene solution. Polyethylene terephthalate (PET) film was used for comparison. The PET film had clear birefringence, as showed in Figure 8, while the films of **3a** and **3d** hardly showed the birefringence, in accordance with the reports on other polymers containing 9,9-diarylfuorenes.<sup>1–9</sup> Degree of retardation at 590 nm in **3d** (thickness: 250  $\mu\text{m}$ ) was less than 3.28 nm in undrawn state,<sup>53</sup> and the birefringence value was remarkably low (less than  $1.3 \times 10^{-5}$ ). In the drawn film of **3d** (drawn ratio is 2.0), the birefringence value was  $-8.9 \times 10^{-4}$ , and the stress optical coefficient was very low ( $-0.15 \text{ GPa}^{-1}$ ). Such low birefringence should be attributed to the optical anisotropy decreasing effect of the *cardo* structure of the 9,9-diarylfuorene moiety placed in the main chain as mentioned.<sup>1–9</sup> The fluorene moiety and the two phenyl groups at the C9-position occupy different planes and are crossed at the precise angle that renders the structure most stable. Placing the aromatic rings on the different planes might disturb their one-directional folding, and thereby the optical anisotropy of the F-PEs disappears.

#### Dispersing Ability for Fullerene C<sub>60</sub>

UV-vis spectrum of fullerene C<sub>60</sub> usually shows the characteristic broad absorption at 440–650 nm originated from the aggregation of C<sub>60</sub>.<sup>45–52</sup> The dispersing ability of the F-PEs was evaluated using C<sub>60</sub> as a model filler material. Namely, absorption change of F-PEs ( $3.00 \times 10^{-3} \text{ M}$  vs. unit structure) by the addition of C<sub>60</sub> (10 mL;  $3.00 \times 10^{-4} \text{ M}$ ) in CHCl<sub>3</sub> was observed as decrease of the absorption intensity at 440–650 nm region according to the Armaroli's report.<sup>52</sup> The spectral change is shown in Figure 9. The absorption intensity at 440 nm increased in all F-PEs, probably by the increasing interaction between the F-PEs and fullerene C<sub>60</sub>. The absorption intensity at 440 nm decreased in the following order of **3c**, **3a**, and **3d** which was in a good agreement with the order of alkyl chain length, *i.e.*, the length between oxygen–oxygen atoms in the main chain. The length was calculated by MM2 as **3c** (4.73 Å), **3a** (*cis*: 7.30 Å, *trans*: 7.57 Å), and **3d** (8.65 Å). It seems that the shorter the distance between the neighboring 9,9-diarylfuorene moieties in F-PE is, the more efficient the interaction between F-PE and C<sub>60</sub> becomes. Effect of molecular weight on the absorption intensity change was little observed in the case of **3a** (Figure 9), being in consistent with the sizes of two molecules F-PE and C<sub>60</sub>. It is readily concluded that the alkyl chain length affects the dispersing ability of the F-PEs toward C<sub>60</sub> as a carbon filler model.



**Figure 9.** UV-vis absorption spectral change of **3** by the addition of C<sub>60</sub> in CHCl<sub>3</sub> at 293 K.

## SUMMARY

This paper has disclosed the synthesis and property of poly(alkyl aryl ether)s (F-PEs **3**) derived from 9,9-bis(4-hydroxyaryl)fluorenes (**2**) with a few ditosylates (**1**). The F-PEs showed the relatively high decomposition temperature  $T_d$ , while the glass transition temperature  $T_g$  depended on the structure of the alkyl chain structure in the main chain. Furthermore, the F-PEs had good solubility, which seems to enhance their processability. The F-PEs showed high water-resistance. The transparent films of the F-PEs exhibited high refractive indices in a range of 1.62–1.66, whereas they showed much low birefringence. These characteristic optical properties of the F-PEs come mainly from the *cardo* structure of the 9,9-diarylfuorene skeleton as well as the alkyl chains in the main chain.<sup>1–9</sup> In addition, the carbon filler (C<sub>60</sub>) dispersing power of the F-PEs was confirmed and decreased with increase in length of the alkyl chain. Thus, the F-PEs can unambiguously be regarded as one of the potential polymer materials being used in a variety of fields including optical materials field.

*Electronic Supporting Information Available:* Figures S1, S2, S3, S4, S5 and S6. These materials are available *via* the Internet at <http://www.spsj.or.jp/c5/pj/pj.htm>

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53. Supporting Information.