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Diphenolic 9,9-Diarylfluorene Trimers and Derivatives Possessing Flexible Alkylene Chain Spacers: Synthesis of the Monomers, Their Polymerization, and Properties of the Resulting Polymers

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ABSTRACT: 9,9-Diarylfluorene-based monomers capable of controlling the thermal properties of the corresponding polymers were synthesized. The monomers possess flexible alkylene chains linking 9,9-diarylfluorene units with diphenol, dialcohol, and diamine terminal units. All of these terminal units were synthesized from a common trimeric *tert*-alcohol-functionalized intermediate. Polycarbonates consisting of the 9,9-diarylfluorene trimer structure in the main chains were synthesized by interfacial polycondensation with triphosgene. The polymerizability of the diphenolic trimer was sufficiently high to afford a polycarbonate with a high molecular weight (M_w 334 000). The thermal properties (T_g and T_d) of the polymers were easily controlled by adjusting the feed ratio of the 9,9-diarylfluorene trimer to 9,9-bis(4-hydroxyphenyl)fluorene. The resulting highly transparent polymers showed high refractive indices and low birefringence values originating from the cardo structure.

Introduction

9,9-Diarylfluorene-based polymers are intriguing materials for optical use: they combine transparency with high refractive index and low birefringence.[1] Their optical properties can be attributed to the cardo structure of 9,9-diarylfluorene, in which each aromatic ring occupies different planes to disturb the one-directional folding and eliminate the optical anisotropy. In addition, such polymers exhibit other characteristic properties, including fine dispersing ability for inorganic fillers,[2] good solubility in organic solvents,[3] high thermal stability,[4] and so on.[5,6] Whereas various 9,9-diarylfluorene-containing polymers with excellent properties have been reported, polymers with finely tuned properties are strongly desired in actual use. The most straightforward way to attain such polymers with desired properties, for example, favorable thermal properties, is to modify the polymer main chain structure through the monomer structure change or the copolymerization with suitable comonomer. In fact, we previously attempted to synthesize a polycarbonate with lowered T_g by the copolymerization of 9,9-bis(4-hydroxyphenyl)fluorene (BPF, **1**) with 9,9-bis(4-(2-hydroxyethoxy)phenyl)fluorene (BPEF, **2**) as an alkylene-chain-containing related comonomer. However, we got any copolymers by neither direct polycondensation with carbonyl sources such as diphenylcarbonate nor interfacial polycondensation with triphosgene. The reason why no copolymer was formed is clear because their hydroxy groups are essentially different in reactivity from each other: one is phenolic, and the other is alcoholic. Focusing on the development of monomer designing to settle such problems, we thought of exploiting an oligomer of a 9,9-diarylfluorene-based cardo monomer connected by flexible alkylene segments (R group, Figure 1) for controlling thermal properties without sacrificing their inherent properties and polymerizability. Herein, we describe a new concept for the modification of the cardo structure based on C_2 symmetric trimerization of the 9,9-diarylfluorene structure. The polycarbonates are synthesized by polymerization of the new monomer.

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Experimental Section

General. ^{1}H spectra were recorded on a JEOL AL-400 NMR spectrometer (400 MHz) in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on the JEOL AL-400 NMR spectrometer operating at 100 MHz. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. Molecular weight and molecular-weight distribution were estimated by gel permeation chromatography using a JASCO HSS-1500 system equipped with consecutive TOSOH TSK-gel GMHXL and G5000HXL eluted with $CHCl_3$ at a flow rate of 1.0 mL/min calibrated by polystyrene standards. The decomposition temperature was obtained using a Shimadzu TGA-50 instrument at a heating rate of 10 °C/min. DSC was performed on a Shimadzu DSC-60 instrument at a heating rate of 10 °C/min under N_2 atmosphere at a flow rate of 50 mL/min. The glass-transition temperature was taken as the temperature in the middle of the thermal transition from the second heating scan. UV−vis spectra were recorded on a JASCO V-550 UV/vis spectrophotometer. Refractive indices and retardations of polymers were measured using a Kalnew precision refractometer (KPR-30, Shimadzu). The elementary analyses and FAB HRMS spectra were obtained at National University Corporation Tokyo Institute of Technology Center for Advanced Materials Analysis on request.

Dichloromethane was dried over freshly activated 4A molecular sieves (MS 4A). 9,9-Bis(4-hydroxyphenyl)fluorene (BPF, **1**) and 9,9-bis(4-(2-hydroxyethoxy)phenyl)fluorene (BPEF, **2**) were provided by Osaka Gas and were used without further

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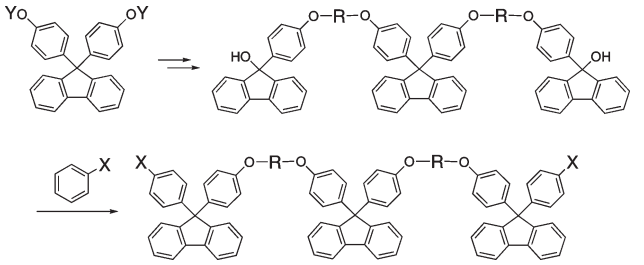


Figure 1. Synthetic strategy of 9,9-diarylfluorene trimer.

purification. Other chemicals were of reagent grade and were used without further purification.

Synthesis of Bistosylate 3. TsCl (28.7 g, 150.5 mmol) was added to a solution of BPEF **2** (30.0 g, 68.4 mmol) and Et_3N (22.9 mL, 164 mmol) in THF (150 mL) at 0 °C. The mixture was warmed to room temperature and stirred. To this mixture, additional TsCl (7.83 g, 90.3 mmol) and Et_3N (28.6 mL, 205 mmol) were added incrementally over a 5 day period. The reaction was quenched by the addition of sat. aq $NaHCO_3$. The products were extracted repeatedly with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. SiO_2 (200 g) was added to the crude materials diluted with hexane−$CHCl_3$ (1:1, 300 mL) at 0 °C. The mixture was warmed to room temperature, stirred for 1 h, filtered, and concentrated in vacuo to yield the bistosylate **3** (47.7 g, 93%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.78 (d, J = 8.3 Hz, 4H, ArH), 7.75 (d, J = 7.5 Hz, 2H, ArH), 7.37−7.31 (m, 4H, ArH), 7.31−7.23 (m, 6H, ArH), 7.05 (d, J = 8.7 Hz, 4H, ArH), 6.61 (d, J = 8.7 Hz, 4H, ArH), 4.34−4.29 (m, 4H, CH_2), 4.10−4.05 (m, 4H, CH_2), 2.39 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ): 156.7, 151.4, 144.9, 139.8, 138.7, 132.7, 129.8, 129.0, 127.9, 127.7, 127.4, 125.9, 120.1, 114.1, 68.1, 65.3, 64.0, 21.5. IR (KBr) ν: 3449, 3063, 3039, 2955, 2925, 2871, 1508, 1358, 1249, 1176, 1021, 931, 817, 749, 663, 577, 554. HRMS (FAB): $[M]^+$ calcd for $C_{43}H_{38}O_8S_2$, 746.2008; found, 746.2002.

Synthesis of Bis(4-bromophenyl) Derivative 4. K_2CO_3 (45.3 g, 0.327 mol) was added to a solution of bistosylate **3** (81.5 g, 0.109 mol) and 4-bromophenol (39.7 g, 0.229 mol) in DMF (300 mL) at room temperature. The resulting mixture was warmed to 80 °C and stirred overnight. The reaction was performed at room temperature and quenched by the addition of sat. aq $NaHCO_3$. The products were extracted with CH_2Cl_2, and the combined organic layer was washed with H_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude materials were washed with Et_2O to afford white solids, which were isolated by filtration to yield product **4** (72.3 g, 89%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.75 (d, J = 7.5 Hz, 2H, ArH), 7.39−7.32 (m, 8H, ArH), 7.29−7.23 (m, 2H, ArH), 7.12 (d, J = 8.7 Hz, 4H, ArH), 6.80 (d, J = 9.0 Hz, 4H, ArH), 6.79 (d, J = 8.7 Hz, 4H, ArH), 4.24 (s, 8H, OCH_2CH_2O). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ): 157.6, 157.2, 151.6, 139.9, 138.6, 132.2, 129.2, 127.7, 127.4, 125.9, 120.1, 116.4, 114.2, 113.2, 66.6, 66.2, 64.1. IR (KBr) ν: 3060, 3038, 2937, 2874, 1608, 1578, 1508, 1487, 1454, 1287, 1240, 1182, 1065, 945, 822, 750, 653, 508. HRMS (FAB): $[M]^+$ calcd for $C_{41}H_{32}Br_2O_4$, 746.0667; found, 746.0672.

Synthesis of Bis(*tert*-alcohol) Derivative 5. BuLi (1.6 M in hexane, 52.6 mL, 84.2 mmol) was added dropwise to a solution of bis(4-bromophenol) **4** (30.0 g, 40.1 mol) in THF (300 mL) at −78 °C over 40 min. After stirring for 1 h at the same temperature, a solution of fluorenone (15.1 g, 84.2 mmol) in THF (150 mL) was added dropwise to the mixture over a 1.5 h period. The resulting mixture was warmed to room temperature overnight and quenched by the addition of sat. aq NH_4Cl; the products were extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel ($CHCl_3$−Et_2O 20:1) to yield product **5** (31.1 g, 82%) as a fluffy pale-yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.73 (d, J = 7.4 Hz, 2H, ArH), 7.66 (d, J = 7.6 Hz, 4H, ArH), 7.21−7.38 (m, 22H, ArH), 7.09 (d, J = 8.8 Hz, 4H, ArH), 6.81 (d, J = 8.8 Hz, 4H, ArH), 6.76 (d, J = 8.8 Hz, 4H, ArH), 4.22 (s, 8H, OCH_2CH_2O), 2.40 (s, 2H, OH). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ): 157.7, 157.2, 151.6, 150.4, 139.8, 139.3, 138.4, 135.6, 129.1, 128.9, 128.3, 127.6, 127.3, 126.5, 125.9, 124.6, 120.1, 120.0, 114.21, 114.15, 83.2, 66.2, 64.1. IR (KBr) ν: 3449, 3060, 3037, 2927, 2879, 1606, 1507, 1448, 1241, 1178, 1033, 918, 826, 769, 749, 734, 641. HRMS (FAB) $[M]^+$ calcd for $C_{67}H_{50}O_6$, 950.3607; found, 950.3622.

General Procedure for Incorporating Aromatics. Synthesis of 9,9-Diarylfluorene-trimer 6. $BF_3 \cdot OEt_2$ (3.50 mL, 28.4 mmol) was added to a solution of bistritylalcohol **5** (9.00 g, 9.46 mmol) and phenol (2.14 g, 22.7 mmol) in CH_2Cl_2 (90 mL) at 0 °C. The mixture was stirred for 1.5 h at the same temperature and quenched by the addition of H_2O. The products were repeatedly extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude materials were purified by column chromatography on silica gel ($CHCl_3$−Et_2O 10:1) to afford the corresponding 9,9-diarylfluorene-trimer **6** (10.1 g, 97%) as a fluffy white powder. (See Scheme 1.) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, δ): 7.74 (d, J = 7.5 Hz, 6H, ArH), 7.38−7.30 (m, 12H, ArH), 7.28−7.21 (m, 6H, ArH), 7.09 (d, J = 8.8 Hz, 4H, ArH), 7.08 (d, J = 8.8 Hz, 4H, ArH), 7.05 (d, J = 8.7 Hz, 4H, ArH), 6.75 (d, J = 8.8 Hz, 4H, ArH), 6.74 (d, J = 8.8 Hz, 4H, ArH), 6.66 (d, J = 8.7 Hz, 4H, ArH), 4.70 (s, 2H, OH), 4.20 (s, 8H, OCH_2CH_2O). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K, δ): 157.09, 157.07, 154.2, 151.62, 151.58, 139.8, 138.5, 138.4, 138.0, 136.7, 129.2, 129.1, 127.6, 127.3, 125.9, 120.1, 115.0, 114.2, 66.2, 64.0. IR (KBr) ν: 3422, 3060, 3034, 2927, 2875, 1607, 1507, 1447, 1241, 1176, 1068, 916, 824, 746, 730, 629, 588, 524. HRMS (FAB): $[M+Na]^+$ calcd for $C_{79}H_{50}O_6$, 1125.4131; found, 1125.4142.

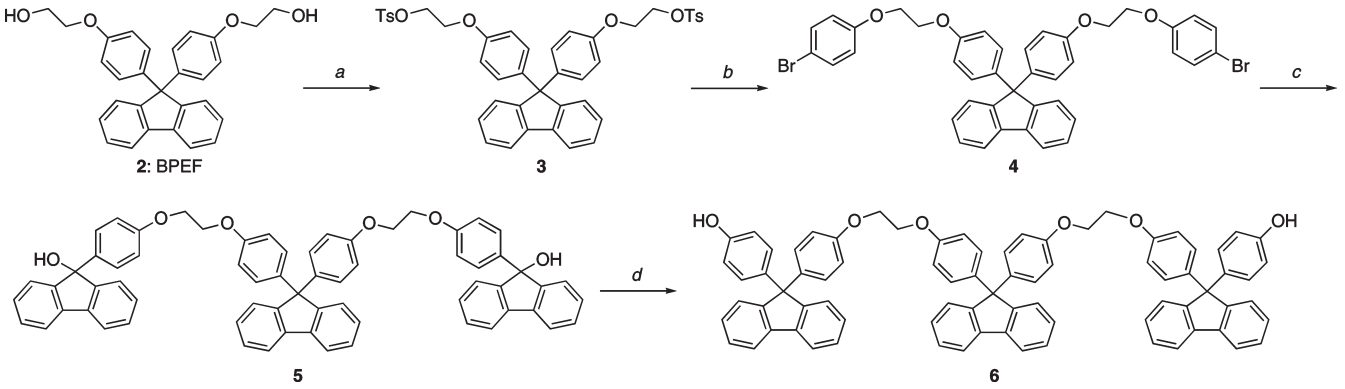
General Procedure for the Synthesis of Polycarbonate Poly-12 Using Triphosgene.[7] A solution of NaOH (65.3 mg, 1.63 mmol) in H_2O (5 mL) was cooled by a mixture of crushed ice and NaCl. To this solution, a solution of **6** (300 mg, 0.272 mmol) in CH_2Cl_2 (3 mL) was added dropwise, and then a solution of triphosgene (54.1 mg, 0.182 mmol) in CH_2Cl_2 (2 mL) was added. A catalytic amount of Et_3N (3.8 μL, 0.027 mmol) was added to the water phase, and the resulting mixture was stirred vigorously for 15 min. Later, the resulting mixture was warmed to room temperature and stirred for 45 min. It was then diluted with CH_2Cl_2 (10 mL) and H_2O (50 mL), and the two phases were separated. The aqueous phase was extracted with CH_2Cl_2 (30 mL × 2). The combined organic layers were washed with H_2O (50 mL × 2), dried over $MgSO_4$, filtered, and concentrated in vacuo to 50 mL. The crude product was precipitated by the addition to MeOH (200 mL) to yield a white solid, which was collected by filtration to afford the polycarbonate in a quantitative yield. The polymer was purified by gel permeation chromatography to afford **poly-12** (206.4 mg) as a white solid in 67% yield: M_w 334 000; M_n 165 000; M_w/M_n 2.0; T_g 221 °C; T_{d5} 435 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) 7.77−7.69 (m, 6H, ArH), 7.38−7.28 (m, 12H, ArH), 7.28−7.17 (m, 10H, ArH), 7.12−7.03 (m, 12H, ArH), 6.78−6.69 (m, 8H, ArH), 4.17 (s, 8H, OCH_2CH_2O). IR (film) ν: 3063, 3035, 3018, 2925, 2871, 1773, 1605, 1505, 1447, 1239, 1189, 1163, 1068, 1012, 915, 823, 745.

Film Preparation. Polymer films of the polycarbonates were prepared by a hot-press method (150 °C, 15 min) using the corresponding polymers plasticized by NMP for the evaluation of refractive index and retardation. The films for the evaluation of transmittance were prepared by a casting method using a chloroform solution of the corresponding polymers at room temperature.

Results and Discussion

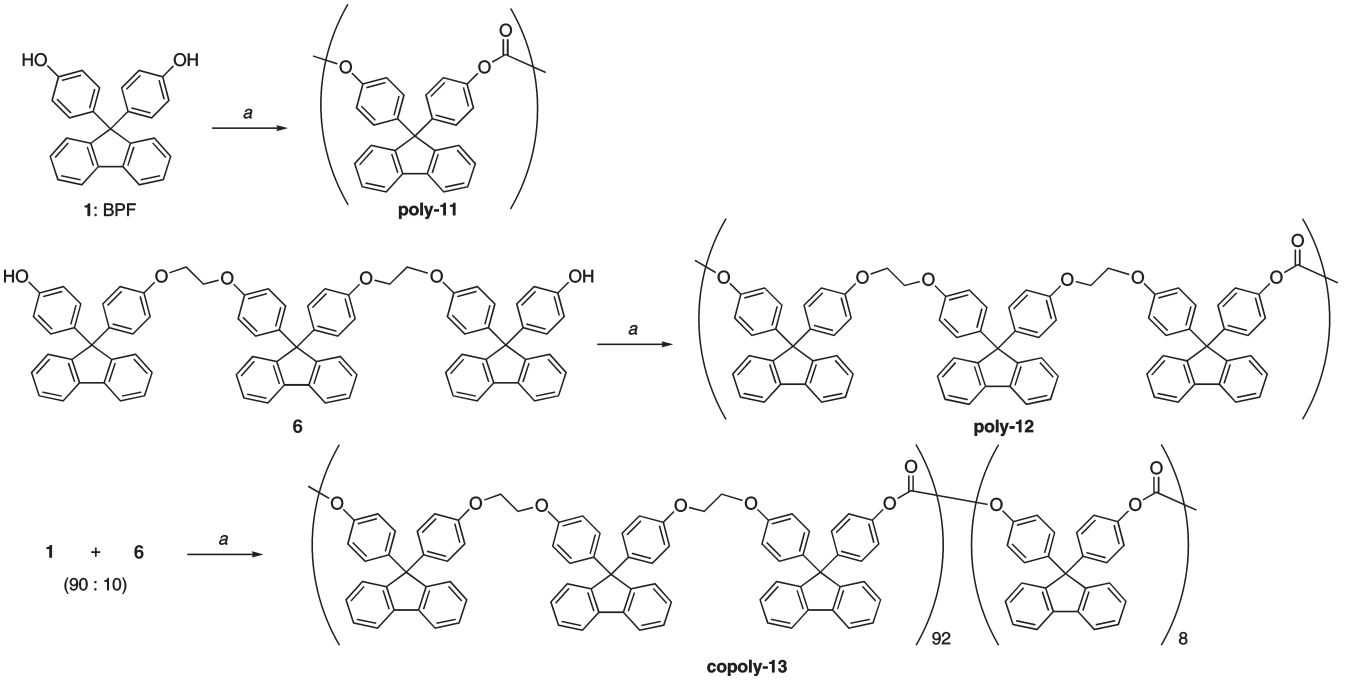
Monomer Synthesis. C_2 Symmetric 9,9-diarylfluorene trimerization started with commercially available 9,9-bis(4-(2-hydroxyethoxy)phenyl)fluorene **2** (BPEF) (Scheme 1).

Scheme 1. Synthesis of 9,9-Diarylfluorene-trimer 6[a]



[a] Reagents and conditions: (a) TsCl (2.8 equiv), Et_3N (7.8 equiv), CH_2Cl_2, RT, 5 d, 93%; (b) 4-bromophenol (2.2 equiv), Cs_2CO_3 (4.8 equiv), DMF, 80 °C, overnight, 89%; (c) BuLi (2.2 equiv), fluorenone (2.2 equiv), THF, −78 °C, overnight, 82%; (d) phenol (2.2 equiv), $BF_3 \cdot OEt_2$ (3.0 equiv), CH_2Cl_2, 0 °C, 1.5 h, 82%.

Scheme 2. Synthesis of 9,9-Diarylfluorene-Based Polycarbonates[a]



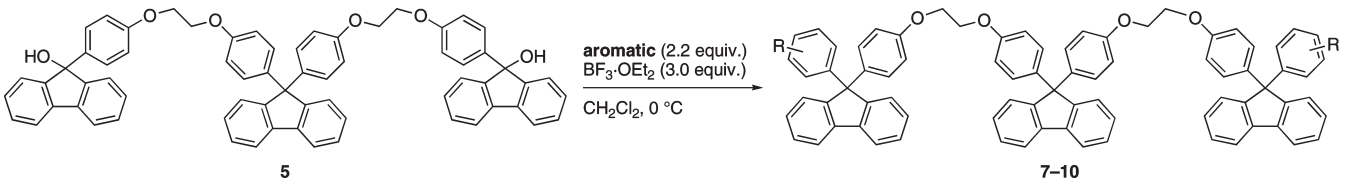
[a] Reagents and conditions: (a) triphosgene (0.67 equiv), NaOH (6.0 equiv), Et_3N (0.1 equiv), $CH_2Cl_2-H_2O$ (1:1), 0 °C, 15 min, then RT, 45 min.

Treatment of BPEF **2** with tosylchloride in the presence of Et_3N afforded the bistosylate **3** in a high yield, followed by an S_N2 reaction with 4-bromophenol to yield the corresponding bromophenylether **4**. The crude material was pure enough to be used for the next reaction (i.e., did not required further purification, such as by column chromatography). The resulting compound was reacted with BuLi in THF to undergo a Br−lithium exchange. To this solution, fluorene was added to afford a bis(*tert*-alcohol) derivative **5** in 82% yield. Having the key compound **5** in hand, we investigated the introduction of various nucleophilic aromatics to **6** via Friedel−Crafts alkylation reaction. After considerable effort, the synthesis was achieved using $BF_3 \cdot OEt_2$ in CH_2Cl_2 in the presence of the aromatics to yield the 9,9-diarylfluorene trimers.[8] When a phenol was used as a nucleophilic aromatic, the corresponding diphenolic 9,9-diarylfluorene trimer **5** was obtained in 82% yield. The structure of **6** was determined by ^1H NMR, IR, and FAB HRMS spectra. The ^1H NMR spectrum of **6** is shown in Figure 2 and is discussed later in this study.

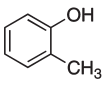
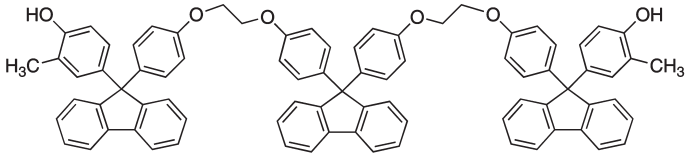
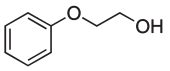
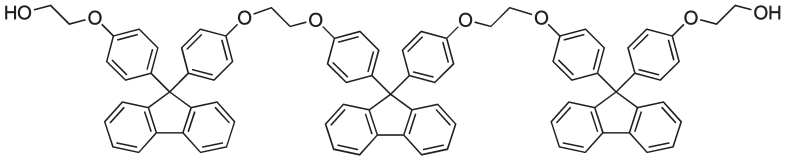
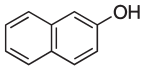
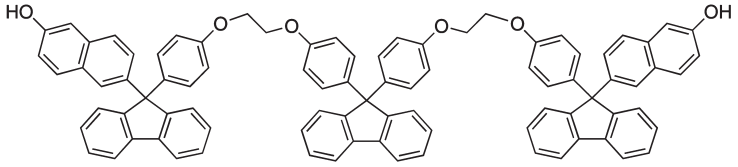
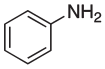
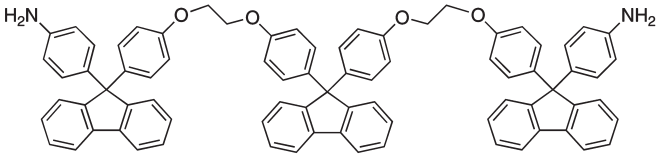
Table 1 summarizes the results of the synthesis of the 9,9-diarylfluorene trimers, which were prepared in a similar manner as **6**. Phenol derivatives such as *o*-cresol, phenoxyethanol, and 2-naphthol regioselectively reacted with **5** to afford the corresponding trimers **7**, **8**, and **9**, respectively, in high yield. The introduction of an aniline moiety was also successful, affording Bisamine-terminated trimer **10** in 20% yield. These results suggested the versatility and generality of the present functionalization method using the key intermediate **5**.[9]

Polymer Syntheses. Scheme 2 features the polymerization and copolymerization of 9,9-bis(4-hydroxyphenyl)fluorene (BPF) **1** and trimer **6** to polycarbonates using the known method of interfacial polycondensation.[7] Treatment of **1** with triphosgene (0.67 equiv) and NaOH (6.0 equiv) in $CH_2Cl_2-H_2O$ (1:1) in the presence of a catalytic amount of Et_3N (0 °C, 15 min, then RT, 45 min) afforded the corresponding polycarbonate **poly-11** in 92% yield. The molecular weight and molecular-weight distribution were estimated by SEC on the basis of PSt standards (M_w 32 000,

Table 1. Syntheses of 9,9-Diarylfluorene Trimers



5 7–10

entry	aromatics	time (h)	products (yield)
1		2	 **7** (99%)
2		2	 **8** (90%)
3		2.5	 **9** (74%)
4		2.5	 **10** (20%)

M_w/M_n 2.3). In the present polycondensation process, a prolonged reaction time or higher temperature resulted in a decrease in yield and lowering of the molecular weight, probably because of the cleavage of the labile diarylcarbonate linkage by hydrolysis. Given this knowledge, the polymerization of **6** was performed with a limited reaction time similar to that of **1** to afford the corresponding polycarbonate **poly-12** in quantitative yield. For a detailed evaluation of properties, the polymer was purified by gel permeation chromatography to afford **poly-12** in 67% yield (M_w 334 000, M_w/M_n 2.0). To evaluate the reactivity of **6** and the properties of the resultant polymer, the copolymerization reaction of **6** and **1** (feed ratio, **6**:**1** = 1:9) was also performed, and copolymer **copoly-13** (M_w 74 000, M_w/M_n 2.5) was obtained in 99% yield. Although the reason is not clear, trimer **6** seems to have sufficiently high reactivity under interfacial polycondensation conditions despite its higher molecular weight. It reacted especially well in homopolymerization, judging from the high molecular weight of the product (**poly-12**, M_w 334 000).

Structural Characterization. Figure 2 shows ^{1}H NMR spectra of monomers **1** and **6** and the three polycarbonates. In the ^{1}H NMR spectrum of **6** (b), the signals (c−f and c′−f′) originating from the fluorene skeleton were in good agreement with those of BPF **1** (C−F). The signals of the phenyl ether moieties (a, b, a′, and b′) were split into two couplets, which come from terminal phenol moieties and four phenyl ether moieties, strongly supporting the structural identification of trimer **6**. All aromatic signals of the polymers were sharp enough to confirm the formation of high-molecular-weight polymers with a low degree of disorder in the polymer structures. The signals (A and a″) of phenolic *ortho*-position protons of **1** and **6** shifted downfield from 6.7 to 7.2 ppm, indicating carbonate bond formation in **poly-11** and **poly-12**. The copolymer composition of **copoly-13** was (**6**:**1** = 8:92), as evaluated by the integral ratio of the ^{1}H NMR spectrum.

Thermal Properties. Thermal properties of the polycarbonates were determined by DSC and TGA (Table 2). The glass-transition temperature (T_g) of **poly-12** was observed at 221 °C, which was 32 °C lower than that of **poly-11** as a consequence of the presence of the flexible spacer. The slightly lowered T_g of **poly-13** (248 °C) was reasonable given the copolymer composition. The temperature at which decomposition occurred (T_{d5}) was 456 °C for **poly-11** and 404 °C for **poly-12**, indicating that the spacer chains reduced the thermal stability. Furthermore, the incorporation of comonomer **6** in the polycarbonate structure lowered both T_g and T_{d5} of **copoly-13**.

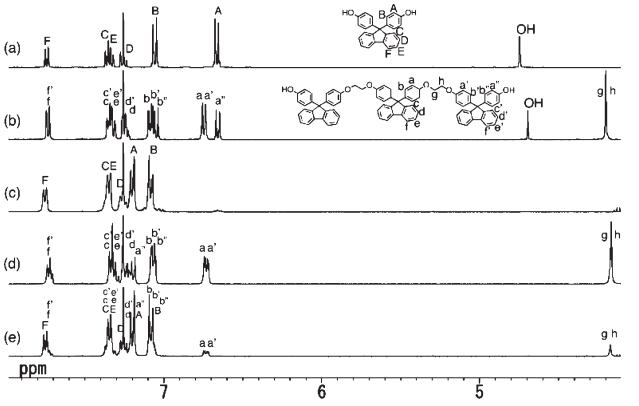


Figure 2. ^{1}H NMR spectra of monomers and polymers (400 MHz, $CDCl_3$, 298 K): (a) **1**, (b) **6**, (c) **poly-11**, (d) **poly-12**, and (e) **copoly-13**.

Table 2. Polymerization Results and Properties of the Polymers

polycarbonate	yield (%)	M_w[a]	M_w/M_n[a]	T_g (°C)[b]	T_{d5} (°C)[c]
poly-11	92	32 000	2.3	253	456
poly-12	67	334 000	2.0	221	435
copoly-13	99	74 000	2.5	248	447

[a] Estimated by SEC on the basis of polystyrene standards. [b] Glass-transition temperature was obtained at a heating rate of 10 °C/min under nitrogen (50 mL/min). [c] 5% decomposition temperature was obtained at a heating rate of 10 °C/min under nitrogen (50 mL/min).

Solubility and Transparency. Although the three polymers mostly consist of aromatic units, they were highly soluble in typical organic solvents such as toluene, CH_2Cl_2, $CHCl_3$, and THF. The exceptionally high solubility comes from the cardo structure in the main chain. This cardo structure comprises 9,9-diarylfluorene units, as previously reported.[1i,j,n,o]

The transmittance of the films (**poly-12** and **copoly-13**) reached 90% over 360 nm and gradually increased over the visible light region with increasing wavelength (Figure 3). The high transparency of the films results from their amorphous nature and is consistent with the greatly reduced interchromophore interaction between or within the polymer chains.

Optical Properties. Thin films of the polycarbonates for the evaluation of refractive index and birefringence were prepared by a hot-press method (150 °C, 15 min) using the NMP solution. When the film of **poly-11** was cooled to room temperature, several cracks were observed despite the high molecular weight of the polymer, making it impossible to evaluate the retardation index. The poor film-forming capability is probably caused by the rigid polymer structure of **poly-11**, which possibly prevents the formation of entanglements of the polymer chains. In contrast, both **poly-12** and **copoly-13** with the flexible alkylene spacers allowed the formation of the corresponding colorless freestanding films with sufficient dimensional stability to evaluate the optical properties.

Table 3 summarizes the refractive index and birefringence values of the polycarbonates (**poly-11**, **poly-12**, and **copoly-13**). The refractive index value at a typical wavelength of 588 nm was quite high for polymers consisting only of C, H, and O atoms: 1.646 (**poly-11**), 1.653 (**poly-12**), and 1.645 (**copoly-13**). The present high refractive indices would be attributable not only to the polynuclear aromatic main chain, but also to the dense packing of the polymer chains permitted by the presence of the flexible alkylene segments and the cardo structure in the main chain. The birefringences of the polymers were evaluated using similar films in the undrawn state.

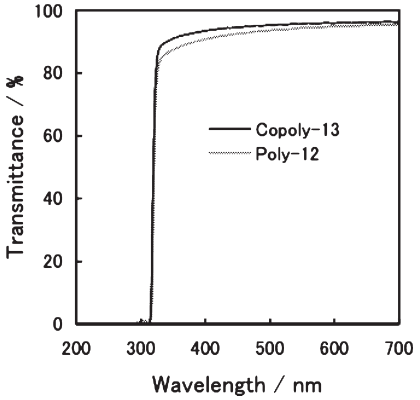


Figure 3. Transmittance of **poly-12** and **copoly-13** films measured by a UV−vis spectrometer (film thickness: 15 to 16 μm).

Table 3. Refractive Index and Birefringence Values of Polycarbonates

polycarbonate	refractive index (n)			$\Delta n_{p\text{-}s}$[a]
	486 nm	588 nm	656 nm	
poly-11	1.667	1.646	1.637	[b]
poly-12	1.674	1.653	1.645	0.0008
copoly-13	1.666	1.645	1.637	0.0009

[a] Retardation was measured by a polarizing optical microscopy under the crossed Nicols with a light wavelength of 588 nm. [b] Not determined.

The degree of retardation of visible light at 588 nm was 0.0008 (**poly-12**) and 0.0009 (**poly-13**) nm. The remarkably low birefringence must be also attributed to the cardo structure in the main chain that largely reduces the optical anisotropy.

Conclusions

This article has revealed the synthesis and polymerization of 9,9-diarylfluorene trimer-related monomers linked by flexible alkylene spacers. These monomers are capable of controlling the thermal properties of 9,9-diarylfluorene-based polymers while retaining their high reactivity in polymerization. The present synthetic protocol based on the C_2 symmetric trimerization through a bis(*tert*-alcohol) derivative **5** as the common intermediate was successful in the preparation of versatile monomers such as diphenol, diol, and diamine monomers. The diphenolic monomer possessing two flexible alkylene spacers was polymerized to the corresponding polycarbonate with a high molecular weight and low T_g in high yield. Copolymerization of the diphenolic monomer with BPF clearly decreased the glass-transition temperature of the corresponding copolycarbonate as compared with the fluorene homopolymer to an extent dependent on the feed ratio. The resulting transparent films exhibited remarkably high refractive indices in the range of 1.646 to 1.653 but showed low birefringence. The results obtained in this study demonstrate the usefulness of the flexible spacer-linked monomer as a highly reactive phenolic monomer. Meanwhile, the present new concept would allow us to access polymers with versatile properties by altering the spacer structure of the monomer.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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