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ORIGINAL ARTICLE

Synthesis and properties of pendant fluorene moiety-tethered aliphatic polycarbonates

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A series of novel fluorene moiety-containing polycarbonates was synthesized by the anionic ring-opening polymerization of six-membered spirocyclic carbonates possessing 9,9-fluorene groups at the 5,5-position. The polymers could be considered cardo-type polymers because they had 9,9-fluorene groups as a loop-shaped side chain. Interestingly, the fluorene pendant polycarbonates were obtained in sufficiently high molecular weights and in good yields, although the monomers were structurally closely related to the 5,5-diphenyl-substituted cyclic carbonate that exhibited very low polymerizability. Furthermore, the polymerizations of substituted fluorene-based six-membered spirocyclic carbonates were investigated. All of the obtained polymers showed favorable properties, including good solubility, amorphous natures, favorable thermal stabilities, remarkably low birefringence values and high refractive indices despite consisting only of C, H and O atoms. The good potentiality in the application to optical materials was shown here.
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INTRODUCTION

Polymers containing 9,9-diarylfluorene moieties in the main chain, the so-called 'cardo polymers', have attracted considerable attention in a variety of fields because of their high performance and good optical properties, including high refractive index, low birefringence and high transparency. Furthermore, some of them have good processability because of their appropriate glass transition and high decomposition temperatures, as well as good solubility in organic solvents.[1,2] We have long studied the synthesis and properties of many cardo polymers having 9,9-diarylfluorene moieties[3–16] and recently reported the preparation of cardo-like polymers[17–21] that have 9,9′-spirobifluorene moieties as the main chain units. Most cardo polymers hitherto studied have been aromatic, whereas aliphatic cardo polymers, 'cardo carbochain polymers' as defined by Korshak,[1] are also interesting because of their expected moderate properties based on their flexible main chains, although only a few reports dealing with fluorene-containing polymers or oligomers have been reported so far, to the best of our knowledge.[22–27] Nakano et al.[25–27] reported the preparation of polydibenzofulvenes with interesting properties directed toward possible applications in optical materials. Among the cardo carbochain polymers, polycarbonates seem of particular interest because of their excellent properties such as high transparency and thermal stability as well as biodegradability. We have synthesized a few aliphatic polycarbonates with 9,9′-spirobifluorene moieties as one of the cardo-like aliphatic polymers via polycondensation.[19] Meanwhile, ring-opening polymerization (ROP) of six- or seven-membered cyclic carbonate[28–30] is one of the typical synthetic entries for polycarbonates without any by-product formation. However, two bulky substituents at the five-position of six-membered cyclic carbonate, such as phenyl groups, mostly diminish its polymerizability because of the equilibrium polymerization, as reported by Endo et al.[31,32] Polycarbonates derived by ROP have an additional merit from another point of view: Takata and Endo reported the volume expansion during the ROP of cyclic carbonates[33–36] and their sulfur analogs,[37] suggesting the possible control of their internal stress and optical distortion in actual use. Furthermore, ROP can be carried out by versatile methods such as cationic,[36,38,39] anionic,[31,40] coordination-insertion[41–43] and enzyme-catalyzed[44–46] polymerizations. We have studied the anionic ROP of six-membered cyclic carbonates, substituted spiro[fluorene-9,5′-[1,3]-dioxan]-2′-ones and have obtained corresponding aliphatic polycarbonates with fluorene groups as a new class of cardo carbochain polymers with interesting properties.[47] Recently, Hedrick's report on a copolymer involving a fluorene-tethered polycarbonate as a copolymer unit has prompted us to report our results on the synthesis and properties of aliphatic polycarbonates having substituted and unsubstituted fluorene moieties in the main chain.[48] Herein, we describe the synthesis of the aliphatic polycarbonates by anionic ROP of fluorene-containing six-membered spirocyclic carbonate monomers. The properties of the resulting polymers and the volume change during the polymerization are also discussed.

EXPERIMENTAL PROCEDURE

Materials and methods

Monomers **3-7** were prepared from 2,7-, or 3,6-dibromofluorene via Suzuki-Miyaura coupling reaction, hydroxymethylation and cyclization to spirocyclic carbonates according to typical methods (see supporting information). The other materials were commercially available and were used without further purification. The polymerization was conducted under an argon atmosphere in

dry tetrahydrofuran (THF) or *N,N*-dimethylformamide (DMF). THF was dried over sodium and distilled under a nitrogen atmosphere before use. DMF was dried over CaH$_2$ and distilled under reduced pressure.

Characterization

The melting points were measured on a SMP3 melting point apparatus (Stuart Scientific, Staffordshire, UK). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL-400 NMR spectrometer (JEOL, Tokyo, Japan) operating at 400 and 100 MHz, respectively, in CDCl$_3$ or dimethyl sulfoxide-d_6 and with tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer (JASCO, Tokyo, Japan). The molecular weights (M_n and M_w) and polydispersity (M_w/M_n) of the polymers were measured using size exclusion chromatography at 30 °C with DMF (10 mM LiBr, 0.85 ml min^{-1}) on a JASCO HSS-1500 system equipped with consecutive linear polystyrene gel columns (TOHSO TSK gel G2000HXL and GMHXL) and were calculated based on a polystyrene calibration. High-resolution mass spectra FAB were obtained with a JEOL JMS-700 at the Center for Advanced Materials Analysis, Tokyo Institute of Technology, Tokyo, Japan. Thermogravimetric analyses were carried out with a Shimadzu TGA-50 (heating rate of 10 °C min^{-1}) under the use of nitrogen. Differential scanning calorimetry was performed using a Shimadzu DSC-60 instrument under nitrogen (heating rate of 10 °C min^{-1}). The refractive indices and retardations of **poly 2** were measured using a Kalnew precision refractometer (KPR-30, Shimadzu, Kyoto, Japan).

Synthesis of 9,9-bis(hydroxymethyl)fluorene 1. Fluorene (30.0 g, 180 mmol) and paraformaldehyde (43.3 g, 1.44 mol) were dissolved in a mixed solvent of dimethyl sulfoxide (180 ml) and MeOH (10 ml), and the mixture was degassed. NaOMe (5.0 M in MeOH, 145 ml, 722 mmol) was added to the mixture from a dropping funnel at 0 °C under an argon atmosphere, and then the resulting mixture was stirred at 0 °C for 1 h. The reaction mixture was acidified with concentrated HCl, diluted with water (200 ml), and extracted with ethyl acetate (100 ml × 3). The combined organic layer was washed with water, dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure. The residual product was purified by recrystallization from toluene to give 9,9-bis(hydroxymethyl)fluorene **1** (24.6 g, 112 mmol, 62%) as a white needle, mp. 146.0–146.9 °C (Lit.^{50} mp. 145.5–146.5 °C); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.77 (d, $J=$ 7.6 Hz, 4H), 7.61 (d, $J=$ 7.5 Hz, 2H), 7.42 (t, $J=$ 7.5 Hz, 2H), 7.33 (t, $J=$ 7.5 Hz, 2H), 4.00 (s, 4H), 2.19 (t, 2H) p.p.m.; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ 145.75, 140.97, 128.13, 127.13, 124.49, 120.26, 66.81, 57.31 p.p.m.; IR (KBr) ν 3313(br), 2973, 2941, 2872, 1476, 1447, 1376, 1066, 1041, 1024, 994, 761, 755, 559 cm^{-1}.

Synthesis of spiro[fluorene-9,5′-[1,3]-dioxan]-2′-one 2. Ethyl chloroformate (9.9 ml, 103 mmol) was added to a solution of **1** (11.6 g, 51.4 mmol) in dry THF (130 ml). Triethylamine (14.3 ml, 103 mmol) was slowly added dropwise into the mixture at 0 °C. After stirring for 30 min at 0 °C, the mixture was warmed up to room temperature and stirred for an additional 2 h. The precipitates formed were removed by filtration, and the filtrate was washed with aq. NH$_4$Cl, dried over MgSO$_4$, filtered and concentrated. The residual product was purified by recrystallization from toluene to give **2** (8.02 g, 56.7 mmol, 55%) as a white solid mp. 156.5 °C (decomp.); ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.81 (d, $J=$ 8.0 Hz, 2H), 7.53–7.49 (m, 4H), 7.39 (t, $J=$ 7.5 Hz, 2H), 4.59 (s, 4H) p.p.m.; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ 148.20, 142.45, 140.56, 129.36, 128.14, 124.01, 120.70, 74.87, 46.70 p.p.m.; IR (KBr) ν 3048, 2994, 2972, 2902, 1930, 1762, 1479, 1458, 1406, 1258, 1196, 1162, 1138, 1108, 760, 734, 622, 591, 574 cm^{-1}; high-resolution mass spectra (FAB) *m/z* Calcd for C$_{16}$H$_{12}$O$_3$ [M]$^+$= 252.0786, found 252.0790.

Typical polymerization procedure

All glass vessels used were heated *in vacuo* before use, filled with dry argon and handled under an argon atmosphere. To a suspension of cyclic carbonates in dry THF in a dried Schlenk tube equipped with a magnetic stir bar, initiator was added at a set temperature to start the polymerization. The reaction was quenched with the addition of phosphoric acid (10 vol% methanol solution, 2 ml) to the reaction mixture, and the mixture was purified by reprecipitation from methanol (100 ml) to give the corresponding polycarbonates as the precipitates.

Polymerization of 2. Monomer **2** (0.500 g, 1.98 mmol) was suspended in THF (2.0 ml), and 0.020 mmol of initiator was added (Run 1: *t*-BuOK (1.0 M in THF, 20 μl), Run 2-3: *n*-BuLi (2.6 M in hexane, 7.7 μl), Run 4: *s*-BuLi (1.02 M in hexane, 20 μl)). After reprecipitation from methanol, **poly 2** was obtained as a white solid. ^{1}H NMR (400 MHz, CDCl$_3$, 328 K) δ 7.65 (d, $J=$ 7.6 Hz, 2H), 7.45 (d, $J=$ 7.6 Hz, 2H), 7.31 (t, $J=$ 7.4 Hz, 2H), 7.19 (t, $J=$ 7.6 Hz, 2H), 4.32 (s, 4H) p.p.m.; ^{13}C NMR (100 MHz, CDCl$_3$, 328 K) δ 154.49, 143.87, 140.88, 128.71, 127.55, 125.18, 120.31, 69.15, 53.41 p.p.m.; IR (KBr) ν 3436, 3064, 2952, 2895, 1751, 1449, 1338, 1231, 968, 735 cm^{-1}; T_g: 129 °C, T_{d5}: 303 °C.

Polymerization of spiro[2,7-diphenylfluorene-9,5′-[1,3]-dioxan]-2′-one 3. Monomer **3** (0.100 g, 0.247 mmol) was suspended in dry DMF (0.25 ml), and *s*-BuLi (1.1 M in hexane, 21 μl, 23 μmol) was added at −20 °C. The procedure was carried out in the same manner as that of **poly 2**. However, polymers and oligomers were obtained, and the monomer was recovered.

Polymerization of spiro[2,7-bis(p-fluorophenyl)fluorene-9,5′-[1,3]-dioxan]-2′-one 4. Monomer **4** (0.100 g, 0.247 mmol) was suspended in dry DMF (0.25 ml), and *s*-BuLi (1.1 M in hexane, 21 μl, 23 μmol) was added at −20 °C. The procedure was carried out in the same manner as that of **poly 2**. However, polymers and oligomers were not obtained, and the monomer **4** was recovered.

Polymerization of spiro[3,6-diphenylfluorene-9,5′-[1,3]-dioxan]-2′-one 5. Monomer **5** (0.150 g, 0.494 mmol) was suspended in dry DMF (0.35 ml), and *t*-BuOK (5.5 mg, 49 μmol) or *s*-BuLi (0.75 M in cyclohexane, 53 μl, 49 μmol) was added at −20 or 0 °C. The procedure was carried out in the same manner as that of **poly 2** to give **poly 5** (entry 5: 0.126 g, entry 6: 0.102 g) as a white solid insoluble in methanol. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.97–7.78 (m, 2H), 7.65–7.20 (m, 14H), 4.29 (s, 4H) p.p.m.; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ 154.64, 143.05, 141.94, 141.19, 140.88, 128.93, 127.60, 127.39, 126.92, 125.55, 119.04, 69.11, 52.67 p.p.m.; IR (NaCl) ν 3056, 3031, 2954, 2893, 1753, 1478, 1401, 1243, 967, 909, 836, 766, 733, 697 cm^{-1}; T_g: 156 °C, T_{d5}: 287 °C.

Polymerization of spiro[3,6-bis(p-fluorophenyl)fluorene-9,5′-[1,3]-dioxan]-2′-one 6. Monomer **6** (0.150 g, 0.341 mmol) was suspended in dry DMF (0.34 ml), and *t*-BuOK (3.8 mg, 34 μmol, entry 7) or *s*-BuLi (0.75 M in cyclohexane, 46 μl, 34 μmol, entry 8 & 9) was added at −20 or 0 °C. The procedure was carried out in the same manner as that of **poly 2** to give **poly 6** (entry 7: 0.123 g, entry 8: 0.117 g) as a white solid insoluble in methanol. In entry 9, the polymer could not be isolated from the mixture with oligomers. ^{1}H NMR (400 MHz, dimethyl sulfoxide-d_6, 373 K) δ 8.03 (br, 2H), 7.48 (br, 4H), 7.36–7.20 (m, 4H), 7.00 (br, 4H), 4.21 (s, 4H) p.p.m.; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ 162.69 (d, $J=$ 247 Hz), 154.50, 142.95, 141.18, 141.07, 136.83, 128.84, 126.75, 125.40, 118.91, 115.84 (d, $J=$ 21 Hz), 69.05, 52.65 p.p.m.; IR (NaCl) ν 3038, 2948, 1747, 1600, 1513, 1485, 1383, 1223, 1159, 963, 912, 843, 820, 774, 730, 622, 525 cm^{-1}; T_g: 185 °C, T_{d5}: 272 °C.

Polymerization of spiro[3,6-bis(p-methoxyphenyl)fluorene-9,5′-[1,3]-dioxan]-2′-one 7. Monomer **7** (0.150 g, 0.323 mmol) was suspended in dry DMF (0.43 ml), and *t*-BuOK (3.6 mg, 32 μmol) was added at −20 or 0 °C. The procedure was carried out in the same manner as that of **poly 2** to give **poly 7** (entry 10: 48 mg, entry 11: 60 mg) as a white solid insoluble in methanol. ^{1}H NMR (400 MHz, CDCl$_3$, 333 K) δ 7.90–7.72 (m, 2H), 7.61–7.40 (m, 8H), 6.96–6.78 (m, 4H), 4.31 (br, 4H), 3.80 (br, 6H) p.p.m.; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ 159.24, 154.55, 143.64, 142.39, 141.04, 133.34, 128.26, 126.32, 125.37, 118.52, 114.21, 68.96, 55.29, 52.53 p.p.m.; IR (NaCl) ν 3029, 2998, 2954, 2934, 2899, 2832, 1751, 1608, 1518, 1486, 1245, 1179, 1038, 822 cm^{-1}; T_g: 119 °C, T_{d5}: 270 °C.

RESULTS AND DISCUSSION

Synthesis and polymerization of cyclic carbonate 2

Polymerization of the fluorene-tethering monomer (spiro[fluorene-9,5′-[1,3]-dioxan]-2′-one, **2**) was studied in detail. Monomer **2** was synthesized by a two-step reaction starting from fluorene (Scheme 1). 9,9-Bis(hydroxymethyl)fluorene, **1**, was prepared by the hydroxymethylation of fluorene with paraformaldehyde and NaOMe.^{49}
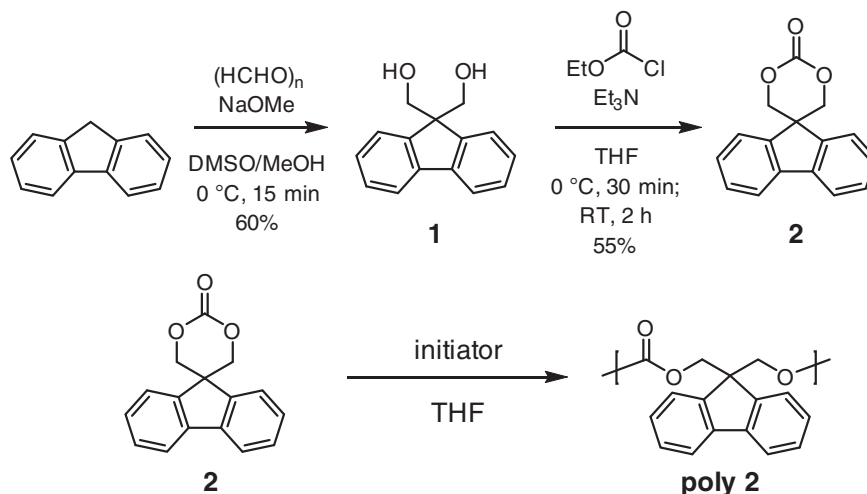
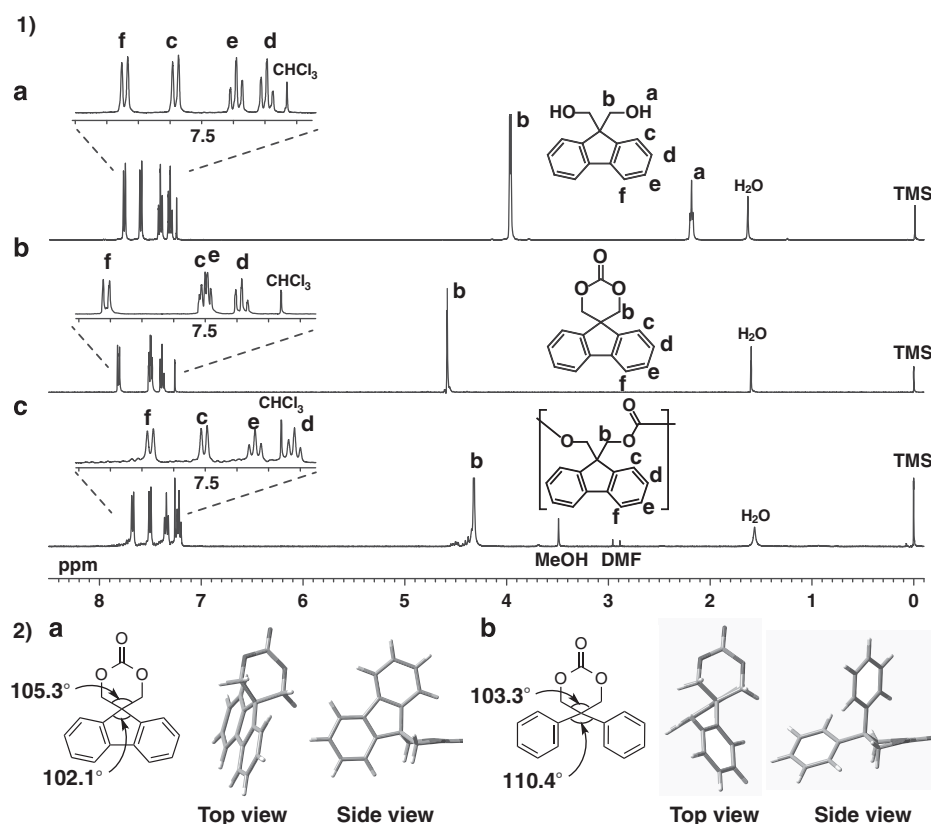Scheme 1 Synthesis and polymerization of 2.

Figure 1 (1) ^{1}H NMR spectra of (a) 1, (b) 2 and (c) poly 2 (400 MHz, CDCl$_3$). (2) Calculated structures of (a) cyclic carbonate 2 and (b) 5,5-diphenyl-1,3-dioxan-2-one calculated at the B3LYP/6-31G(d.p) level. A full color version of this figure is available at *Polymer Journal* online.

Subsequent cyclization of 1 was achieved by the reaction with ethyl chloroformate according to our previously reported procedure,[36] providing the corresponding cyclic carbonate 2 in 55% yield. The cyclization of 1 to 2 was confirmed by the reasonable ^{1}H NMR spectral change. The large downfield shift of the methylene signal (H$_b$) from 4.00 to 4.59 p.p.m. was indicative of the electron-withdrawing effect of the carbonate skeleton and the ring current effect of the fluorene moiety. Furthermore, the 1,8-protons (H$_c$) of fluorene were shifted upfield by the cyclization (Figure 1(1)-a and -b). The stretching

vibration signal of the carbonate carbonyl bond was observed at 1762 cm^{-1} in the IR spectrum, which was consistent with the typical cyclic carbonate value.

Anionic ROP of 2 was carried out in THF with a few appropriate initiators (Scheme 1 and Table 1).

First, *t*-BuOK was used in accordance with the literature procedure[31] at 0 °C. The initial heterogeneous solution of 2 in THF at 0 °C became homogeneous, indicating the initiation of the polymerization by *t*-BuOK. The time-molecular weight (M_n) relationship

by size exclusion chromatography supported the formation of polymer (Table 1, Run 1). However, the M_n and dispersity hardly changed even when the reaction time was prolonged up to 120 min. These results indicated the good polymerizability of **2** along with the negligible backbiting reaction under the conditions, which was enough to give the high molecular weight of the polymer. The resultant polymer was purified by reprecipitation with methanol to give **poly 2** in 84% yield. The chemical structure of **poly 2** was fully characterized by the spectral data. A characteristic $C=O$ stretching vibration was clearly observed at 1751 cm^{-1} in the IR spectrum, which was consistent with that of linear carbonate. In the ^{1}H NMR spectrum, signals assignable to the methylene moiety (H_b) was shifted upfield from 4.59 to 4.32 p.p.m.

because of the cancellation of the ring current effect of the fluorene moiety by the ring opening (Figure 1(1)-c and (2)-a,b). Other signals coincided with the structure of **poly 2** to rule out the partial elimination of carbon dioxide during the polymerization. To increase the polymer molecular weight, we used the polymerization at lower temperature with *t*-BuOK; however, the polymer yield significantly decreased to 25%. As monomer **2** was recovered in the methanol soluble part along with a small amount of oligomers, it was considered that the polymerization could not proceed sufficiently at $-20\,^\circ$C because of the low solubility of **2** and **poly 2**. Next, *n*-BuLi was used instead of *t*-BuOK as a homogeneous initiator (Run 2).[40] As expected, the polymerization of **2** proceeded quickly, whereas the prolongation of the reaction time led to a gradual decrease in the molecular weight, likely because of the emerging backbiting reaction to oligomers. When the reaction time was shortened to 5 min, a higher molecular weight **poly 2** was obtained in an excellent yield (Run 3). Furthermore, *s*-BuLi

Table 1 Optimization of the polymerization of 2[a]

Run	Initiator	$M_n/10^4$ (M_w/M_n)[b]				Yield[c] (%)
		5 Min	*10 Min*	*30 Min*	*120 Min*	
1	*t*-BuOK	—	—	1.45 (1.19)	1.43 (1.22)	84
2	*n*-BuLi	—	1.96 (1.63)	1.67 (1.47)	1.02 (1.39)	83
3	*n*-BuLi	1.45 (1.55)	—	—	—	86
4	*s*-BuLi	2.40 (1.53)	—	—	—	99

[a]Conditions: initiator 1 mol%, monomer: 1.0 M, temperature 0 °C.
[b]Estimated by size exclusion chromatography (SEC) based on polystyrene standards.
[c]Yield of poly 2 as the MeOH-insoluble part.

Table 3 Thermal properties of the polycarbonates

	Poly 2	*Poly 5*	*Poly 6*	*Poly 7*
T_g (°C)	129	156	185	119
T_{d5}(°C)	303	287	272	270

Glass-transition temperature (T_g) was obtained at a heating rate of 10 °C min^{-1} under nitrogen (50 ml min^{-1}). 5% Weight-decrease temperature (T_{d5}) was obtained at a heating rate of 10 °C min^{-1} under nitrogen (50 ml min^{-1}).

Table 2 Polymerization of the monomers 3-7[a]

3 **4** **5** **6** **7**
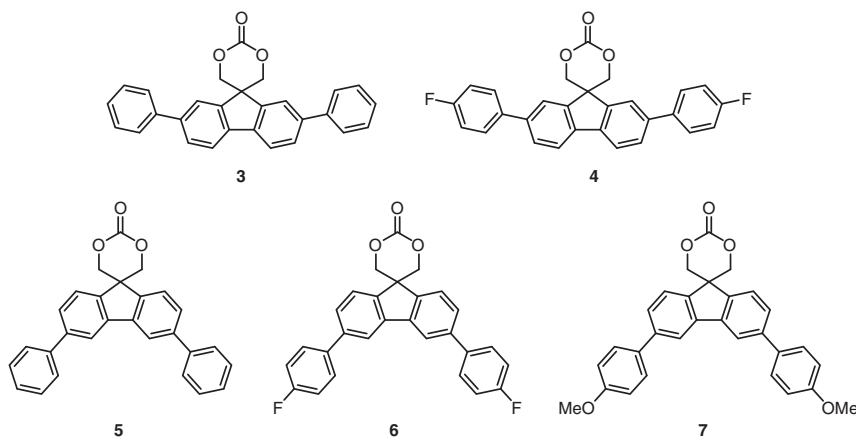
Entry	Monomer (M)	Initiator	Temp. (°C)	Yield[b] (%)	M_n[c]	M_w/M_n[c]
1	3 (1.00)	*s*-BuLi	−20	NP[d]	—	—
2	4 (1.00)	*t*-BuOK	−20	Trace	6300	1.14
3	4 (1.00)	*s*-BuLi	−20	Trace	6400	1.19
4	5 (0.75)	*t*-BuOK	0	Trace	5400	1.15
5	5 (0.75)	*s*-BuLi	−20	84	22 000	1.51
6	5 (0.75)	*s*-BuLi	0	68	7700	1.42
7	6 (0.75)	*t*-BuOK	−20	82	12 000	1.45
8	6 (0.75)	*s*-BuLi	−20	78	11 000	1.63
9	6 (1.00)	*s*-BuLi	0	—	5100	1.26
10	7 (1.00)	*t*-BuOK	−20	32	14 000	1.25
11	7 (1.00)	*t*-BuOK	0	40	14 600	1.37

[a]Solvent: *N,N*-dimethylformamide (DMF), initiator: 10 mol%, reaction time: 5 min.
[b]MeOH-insoluble part.
[c]Estimated by size exclusion chromatography (SEC) based on polystyrene standards.
[d]No polymerization occurred.

Table 4 Optical properties of poly 2

Wavelength (nm)	Refractive index	Birefringence value[a]	Abbe number
436	1.6567	0.0002	23.45
486	1.6397	0.0002	
546	1.6268	0.0002	
587	1.6206	0.0001	
656	1.6132	0.0001	

[a]Retardation was measured by a polarizing optical microscopy under the crossed Nicols (undrawn state).

was used because it is usually more effective than *n*-BuLi because of its lower association nature, which can lead to higher initiation efficiency.[50–54] Indeed, *s*-BuLi resulted in the formation of a higher molecular weight **poly 2** in an excellent yield (Run 4). In the time-conversion plot for the *s*-BuLi-initiated polymerization of **2** at −20 to 20 °C using ^{1}H NMR (Supplementary Figures S1–S5 (see Supplementary Information)), only the disappearance of **2** and the formation of the oligomers and **poly 2** were observed. At higher temperature, the signals attributable to the oligomers increased according to the decrease of **2**. Based on these results, the short reaction time and low temperature effectively afforded both sufficiently high yield and high molecular weight of **poly 2** by reducing the oligomerization via the backbiting reaction. Meanwhile, the fact that the monomer **2** showed good polymerizability in anionic ROP was interesting in the light of the low polymerizability of 5,5-diphenyl-1,3-dioxan-2-one, which had a similar structure to **2**, even when the difference in polymerization conditions was considered.[31,32] A plausible explanation for this significant difference would come from the higher ring strain of **2** because of the spirocyclic structure or the slower backbiting reaction than 5,5-diphenyl-1,3-dioxan-2-one. As the steric hindrance around the carbonate carbon as the reaction center seemed similar in these monomers, the internal angle of six-membered ring may have an important role in the polymerizability (**2**, 105.3°; 5,5-diphenyl-1,3-dioxane-2-one, 103.3°), as shown in their calculated structures (Figure 1(2)). In fact, the above NMR study indicated the absence of **2** in the equilibrium stage, which was clearly different from the case of 5,5-diphenyl-1,3-dioxan-2-one,[31,32] although the oligomer formation was confirmed (see Supplementary Information).

One of the most interesting properties of the ROP of cyclic carbonate results in the occurrence of volume expansion upon polymerization from monomer to polycarbonate,[33–36] although most monomers shrink in volume during polymerization. To evaluate the degree of volume expansion associated with the ROP of cyclic carbonate, the densities of **2** and **poly 2** were measured. The density of **2** and **poly 2** were 1.3667 and 1.3202 g cm^{−3}, respectively. These results revealed the certain volume expansion of 3.5%, which was consistent with values previously reported for similar ROPs of six-membered cyclic carbonates.[33–36]

Synthesis and polymerization of substituted derivatives of 2

The substituent effect on the fluorene moiety was examined using several additional monomers **3-7**, that is, 2,7- and 3,6-substituented derivatives of **2** (Table 2). These monomers were synthesized by the Suzuki-Miyaura coupling reactions of 2,7- or 3,6-dibromofluorenones and the corresponding arylboronic acids, followed by the reduction, hydroxymethylation and carbonate-cyclization via similar procedures mentioned above.[50] Subsequent anionic ROP of **3-7** (from −20 to 0 °C) was carried out in DMF because of their poor solubility. The

2,7-disubstituted monomers **3** and **4**, in particular, were hardly soluble even in DMF at 0 °C. Consequently, no polymer was obtained by this method, and only monomers and a trace amount polymer were recovered, as detected by size exclusion chromatography as a small peak (entries 2 and 3). The polymerization of **6** was carried out at 0 °C; however, **poly 6** had a low M_n, which was indicative of the occurrence of some depolymerization, a typical reverse polymerization in a backbiting manner (entry 9). In contrast, the polymerization of monomer **7** with *t*-BuOK successfully proceeded even at 0 °C (entries 10 and 11). As mentioned above, the polymerization of **2** rapidly reached equilibrium even at low temperature. The low polymerizability of **3** and **4** was likely due to not only the poor solubilities of the monomer and polymer but also the steric hindrance of the substituent around the cyclic carbonate moiety.

Properties of polycarbonates

The polycarbonates (**poly 2, poly 5, poly 6** and **poly 7**) showed relatively good solubility in typical organic solvents such as chloroform, toluene, DMF and dimethyl sulfoxide (Supplementary Table S1; see Supplementary Information) The good solubility can be understood in terms of the pendant fluorene moieties placed perpendicular to the main chain, which can inhibit the aggregation of polymer chains in a manner similar to 9,9-diarylfluorene-based *cardo* polymers.[3–16] No diffraction peaks were observed by powder X-ray diffraction of the polymers, indicating their amorphous nature, which coincided with their observed good solubility (see Supplementary Information).

The thermal properties of the obtained polymers are summarized in Table 3. No melting points were confirmed, whereas the glass transition temperature (T_g) was observed. **Poly 2** showed its T_g at 129 °C, which was lower than those of aromatic polycarbonates with alkyl spacers[15,19] but higher than the previously reported poly(2,2-disubstituted trimethylene carbonate)s.[28,55] **Poly 6** had a T_g 185 °C, and the value was likely due to the rigid structure from the *p*-fluorophenyl group. The decomposition temperature (T_{d5}) was approximately 300 °C for all of the polymers.

With the exception of **poly 2**, the film-forming abilities of the polymers were poor, likely because of their low molecular weights and higher contents of bulky aromatic rings. Then, the optical property of **poly 2** in a film state was measured as a representative example. The thin film of **poly 2** was prepared by casting the *N*-methylpyrrolidone solution onto a glass substrate followed by heating at 150 °C to dry the film (the solubility of **poly 2** in ordinary low bp solvents was insufficient to prepare a clear cast film because of their high volatility. Therefore, we carried out the film preparation using high bp solvent such as NMP to which **poly 2** has high solubility). The transmittance of **poly 2** reached 90% at a wavelength of 380 nm and gradually increased with increasing wavelength over the visible light region. The high level of transparency observed for **poly 2** resulted from its amorphous nature and was consistent with the significantly reduced levels of interchromophore interactions between or within the polymer chains. The refractive indices and birefringence values for **poly 2** are summarized in Table 4. The refractive index at 587 nm was 1.620(6), which represented a high value for polymers consisting only of C, H and O atoms. The birefringence values of **poly 2** were also evaluated in the undrawn state. The degree of retardation of visible light was found to be 0.0001 at 587 nm. The remarkably low level of birefringence could also be attributed to the vertical arrangement of the fluorene side groups relative to the main chains. The Abbe number of **poly 2** was 23.45, which was low, as expected.

In summary, we have synthesized a series of novel fluorene-based cyclic carbonate monomers and obtained the corresponding *cardo*

polymers by the anionic ROP of six-membered spirocyclic carbonate monomers. The polymers possessed fluorene skeletons placed perpendicular to the main chain. Interestingly **2** had a sufficient polymerizability to provide **poly 2** with sufficiently high molecular weight in good yield, despite its structural similarity to the diphenyl-substituted cyclic carbonate with very low polymerizability. This result suggested that the connection of the two phenyl groups fairly enhanced the ROP of the six-membered cyclic carbonate. Volume expansion upon polymerization was confirmed with **2**, which was in accordance with our previous report. In addition to **2**, aromatic substituent-containing fluorene monomers were investigated their polymerizability. The 2,7-disubstituted fluorene monomers gave no polymers; however, the 3,6-disubstituted fluorene monomers afforded the corresponding polymers. All of the polymers obtained here exhibited good solubility in typical organic solvents, amorphous natures, favorable thermal stabilities, remarkably low birefringence values and high refractive indices. Thus, this study has demonstrated aliphatic polycarbonates having a fluorene moiety as *cardo* carbochain polymers with the characteristic optical property.

ACKNOWLEDGEMENTS

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