Thermotropic Liquid Crystalline Semirigid Polycarbonates Based on Diphenyl Ether and Benzophenone Units

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ABSTRACT: Semirigid polycarbonates composed of nonconventional flexible rodlike units like diphenyl ether or benzophenone having bent linkages in the central parts between the benzene rings were prepared by melt polycondensation of 6,6′-(4,4′-oxy- or -carbonyldiphenylenedioxy)dihexanol with various alkylene diphenyl dicarbonates (n = 2–6, 8–10, and 12). The resulting polymers had high inherent viscosities and very good solubilities in organic solvents such as chloroform and tetrahydrofuran. Flexible films were cast from the chloroform solutions. The structures of the polymers were characterized by FTIR and ^{13}C NMR spectroscopy measuements and elemental analyses. The thermotropic liquid crystalline (LC) properties were examined by differential scanning calorimetry (DSC), polarizing microscopy, and powder X-ray analyses at various temperatures. These measurements demonstrated that the polycarbonates containing the diphenyl ether with alkylene chains of n = 4–10 and the ones consisting of the benzophenone unit having spacers of n = 6 and 8 could form nematic LC or birefringent melts. The others had no LC melts. The glass transition temperatures were below room temperature and tended to decrease with increasing alkylene spacer length. It was suggested that the diphenyls were responsible for the formation of the LC phases in the main-chain type semirigid polymers in spite of having kinked linkages and lowered the transition temperatures. The mesogenic character of the diphenyl ether was superior to that of the benzophenone unit.

Introduction

In general, main-chain type semirigid polymers composed of conventional rigid rodlike mesogens such as biphenyl, stilbene, and azobenzene show thermotropic liquid crystalline (LC) properties.[1] Flexible rodlike diphenyl moieties such as diphenyl ether, benzophenone, and diphenylmethane have nonconjugated and kinked linkages in the central parts between the benzene rings, so incorporation of them into polymer backbones disturbs the linearity of the polymer chains and formation of the LC phases.[2,3] Kricheldorf et al. investigated the influence of bond angles in the central parts of the diphenyls on the LC stability of aromatic polyesters and found that wider bond angles (>120°) are responsible for formation of stable mesophases in main-chain polymers.[4] It appears that diphenyls with bent linkages can act as mesogens in certain cases.

On the other hand, Percec et al. produced a series of semirigid LC polyethers with flexible rodlike diphenylethanes as nonconventional mesogens, which show LC melts based on conformational isomerism.[5,6] We previously reported that polyamides made up of flexible rodlike diphenyl units (3,4′- or 4,4′-diphenyl ethers and 4,4′-diphenylmethane) and aliphatic spacers in the main chains can form LC phases.[7] In addition, it was discovered that semirigid polyurethanes containing only a naphthalene ring as the rigid rodlike moiety in the repeating unit, in spite of the low aspect ratio, can have nematic LC mesophases.[8] This might be due to the excluded volume effect and attractive interaction. Jähnig[9] and Ohtsuki[10] theoretically predicted the potential of nematic phase formation due to intra- and intermolecular interaction in flexible rodlike polymers. These facts suggest that the conformation of the polymer backbone should affect the LC formation in semirigid main-chain polymers consisting of nonconventional and flexible rodlike units such as diphenyl ether and benzophenone.

The purpose of this work is to prepare semirigid polycarbonates built up of diphenyl ether (**5**) or benzophenone (**6**) and flexible spacers with various alkylene lengths (n = 2–6, 8–10, and 12) (Scheme 1) and to examine the thermotropic LC properties. Polycarbonates **5** and **6** were prepared from dioxydihexanols of diphenyls **3a** and **3b** and various alkylene diphenyl dicarbonates **4** according to our methods.[11–16]

Results and Discussion

Preparation of Monomers 3 and Polycarbonates 5 and 6. Monomers **3a** and **3b** for preparation of polymers **5** and **6** were derived in yields of 55–65% by the Williamson reaction of 4,4′-dihydroxydiphenyl ether or 4,4′-dihydroxybenzophenone (**1**) and 6-chloro-1-hexanol (**2**) in *N*,*N*-dimethylformamide (DMF) in the presence of potassium carbonate according to our methods for dioxydihexanols of naphthalene[8] or biphenyl.[11,12] They were characterized by their FTIR and ^{13}C NMR spectra and elemental analyses, whose data are presented in the Experimental Section.

Our previous articles described that the melt polycondensation of the dioxy dialcohols of the biphenyl or aromatic diimides with the alkylene diphenyl dicarbonates afforded high molecular weight semirigid homo- and copolycarbonates[11,12] or poly(imide–carbonate)s[15,16] without using phosgene, which showed thermotropic LC properties. This technique can be applied to develop LC polyurethanes[8,13] and poly(urethane–carbonate)s[14] of the biphenyl or the naphthalene rings and the alkylene diphenyl dicarbamates instead of diisocyanates and the dicarbonates. In the present work, polymers containing diphenyls having bent linkages in the central parts (**5** and **6**) were produced according to our published methods[11–16] (Scheme 1).

Monomers **3** were polymerized with the dicarbonates having the various alkylene lengths (n = 2–6, 8–10, and 12) (**4**) to yield the expected semirigid polycarbonates (**5** and **6**) by the melt polycondensation under the reaction conditions presented in the Experimental Section.[11,16] The polycondensation proceeded soon and the desired polymers (**5** and **6**) were readily obtained. The synthetic results for the polymers containing the diphenyl ether unit (**5**) and

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Scheme 1

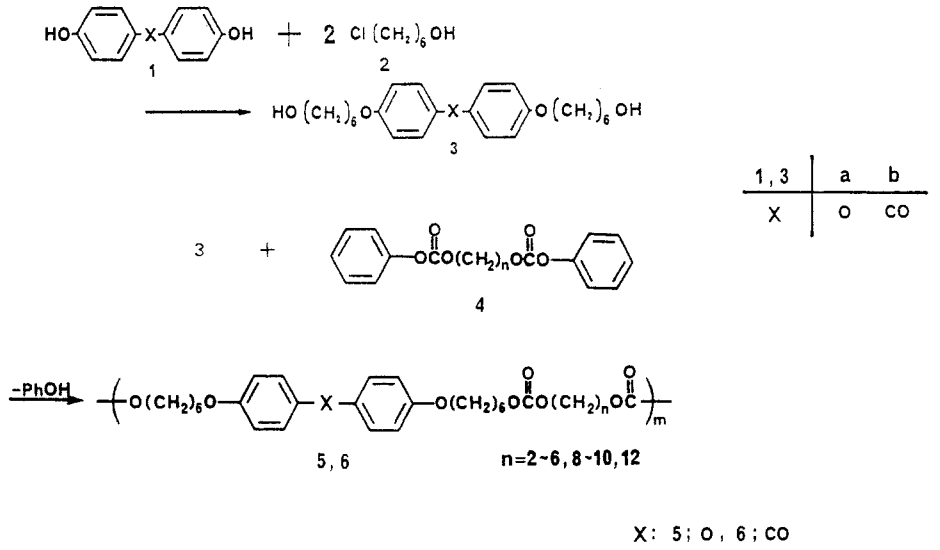

Table 1. Synthetic and Phase Transition Data for Polycarbonates 5[a]

polymer	n	yield (%)	η_{inh}[b] (dL/g)	T_g (°C)	T_c (°C)	T_m (°C)	T_i (°C)	ΔH_i (J/mol)	ΔT (°C)
5a	2	71	0.88[c]	−4	60	91			
5b	3	77	1.08	−6	71	90			
5c[d]	4	96	1.10	−8	54	77	100	55.3	23
5d[d]	5	91	1.19[e]	−11	54	71	95	67.0	24
5e[d]	6	93	1.05	−13	46	72	90	57.4	18
5f[d]	8	94	1.08	−17	43	69	87	54.1	18
5g[d]	9	93	0.97	−20		57	72	135	15
5h[d]	10	66	1.16	−22		65	86	264	21
5i	12	67	1.03	−22	−7.8, 52	68			

[a] T_g = glass transition temperature; T_c = crystallization temperature; T_m = melting temperature; T_i = isotropization temperature; ΔH_i = enthalpy for isotropization; $\Delta T = T_i - T_m$. [b] Inherent viscosity measured at a concentration of 0.2 g/dL in chloroform at 30 °C. [c] Number-average molecular weight estimated by gel-permeation chromatography is 34 000 (using chloroform as a solvent and polystyrene as a standard). [d] Phase transition data after annealing before the second heating scans. [e] Number-average molecular weight: 64 400.

Table 2. Synthetic and Phase Transition Data for Polycarbonates 6[a]

polymer	n	yield (%)	η_{inh}[b] (dL/g)	T_g (°C)	T_c (°C)	T_m (°C)	T_i (°C)	ΔH_i (J/mol)	ΔT (°C)
6a	2	57	0.70[c]	15	100	116			
6b	3	65	0.83	16	98	116			
6c	4	93	0.92	2.1		48			
6d	5	82	0.90	−0.2		48			
6e[d]	6	90	1.26[e]	−0.3		41	59	70.2	18
6f[f]	8	88	0.74	−7.7	66	85[g]	140[g]	623[g]	55[g]
			0.54			46[h]	67[h]	518[h]	21[h]
6g	9	87	0.82	−6.0		43			
6h	10	84	0.79	−13	63	88			
6i	12	82	0.91	−8.0		50			

[a] T_g = glass transition temperature; T_c = crystallization temperature; T_m = melting temperature; T_i = isotropization temperature; ΔH_i = enthalpy for isotropization; $\Delta T = T_i - T_m$. [b] Inherent viscosity measured at a concentration of 0.2 g/dL in chloroform at 30 °C. [c] Number-average molecular weight (M_n) estimated by gel-permeation chromatography is 22 000 (using chloroform as a solvent and polystyrene as a standard). [d] Phase transition data after annealing. [e] M_n = 72 500. [f] Phase transition data after annealing. [g] Data on the first heating scan. [h] Data on the second heating scan.

the benzophenone unit (**6**) are given in Tables 1 and 2, respectively, which indicate that the resultant polycarbonates (**5** and **6**) have high inherent viscosities of 0.70–1.26 dL/g in chloroform at a concentration of 0.2 g/dL at 30 °C. The yields of the polymers containing the diphenyl ether unit (**5**) are low in ones with the short (n = 2 and 3) (**5a** and **5b**) and the long alkylene units (n = 10 and 12) (**5h** and **5i**), but the others are obtained quantitatively. In the polymers containing the benzophenone unit (**6**) the polymers with alkylene lengths of n = 4–12 (**6c–i**) are prepared in yields of 82–93% and the yields for ones with n = 2 and 3 (**6a** and **6b**) are 57–65%. The reason the yields are low in the polymers with the shorter alkylene units (**5a**, **5b**, **6a**, and **6b**) is that they become considerably viscous immediately with the proceeding of polycondensation and the mixtures could not be stirred. Polymers **5** and **6** are readily soluble in chloroform, dichloroacetic acid (DCAA), and tetrahydrofuran (THF) at room temperature and in DMF on heating as well as the previously-reported polycarbonates[11-12] but insoluble in methanol. Flexible films were cast from the chloroform solutions of polymers **5** and **6**. Polymers **5h** and **5i** have very good solubilities in chloroform, used for reprecipitation, so it was not easy to isolate them in high yields.

The assigned structures of polymers **5** and **6** were confirmed by their FTIR and ^{13}C NMR spectra and elemental analyses. Typical ^{13}C NMR spectra for Polymer **5e** and polymer **6f** in $CHCl_3$-*d* are illustrated in Figures 1 and 2, respectively. The FTIR spectra of polymers **5** and **6** show characteristic absorption bands based on carbonate C=O at 1740–1744 cm^{-1} in addition to bands for the ether linkage at around 1270 cm^{-1} in polymers **5** or for C=O of benzophenone at 1645 cm^{-1} in polymers **6**. The ^{13}C NMR spectra for polymers **5** and **6** display the carbon signals for carbonate C=O at 151.5–155.4 ppm together with those for the diphenyls and the alkylene chains or for benzophenone C=O at 194.8 ppm. The elemental analysis data were in agreement with the calculated values.

Mesogenic Properties of Polycarbonates 5 and 6. Polycarbonates **5** and **6** were subjected to differential scanning calorimetry (DSC) measurements with a heating and a cooling rate of 10 °C/min under a nitrogen atmosphere and powder X-ray analyses at various temperatures to evaluate the thermotropic LC properties, because flexible rodlike polymers **5** and **6** with bent linkages are predicted to form a thermotropic LC phase. Peak maxima or shoulders and steps in the DSC curves were taken as phase transition temperatures. The mesophases were observed with a polarizing microscope equipped with a hot stage.

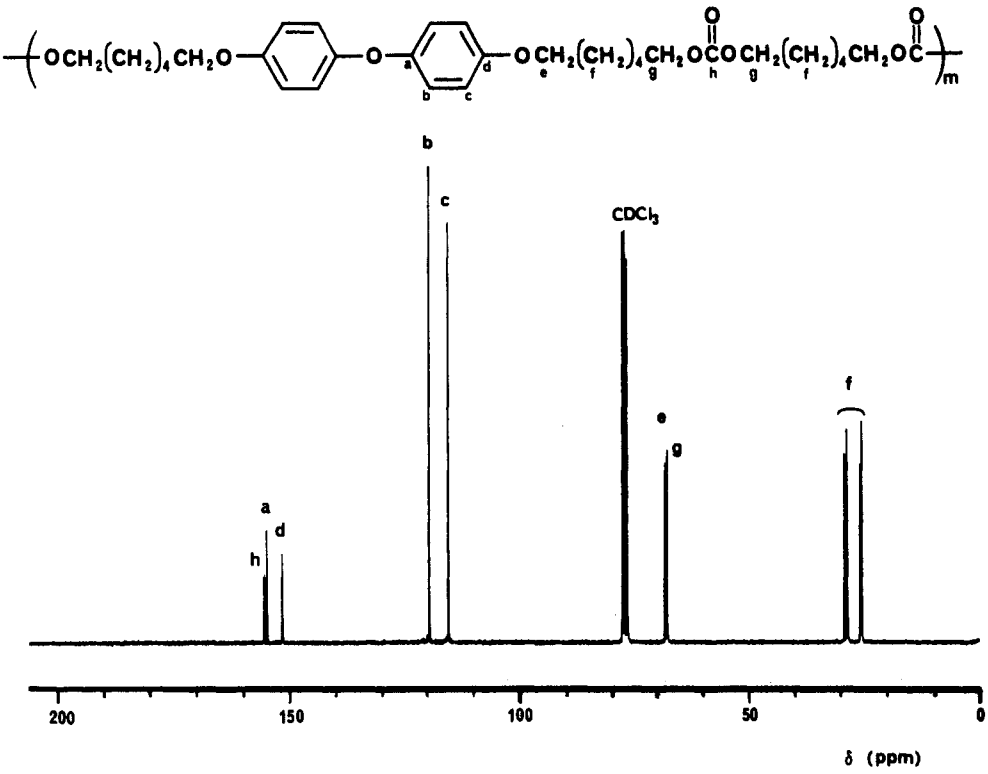

Figure 1. ^{13}C NMR spectrum for polycarbonate **5e** in $CHCl_3$-*d*.

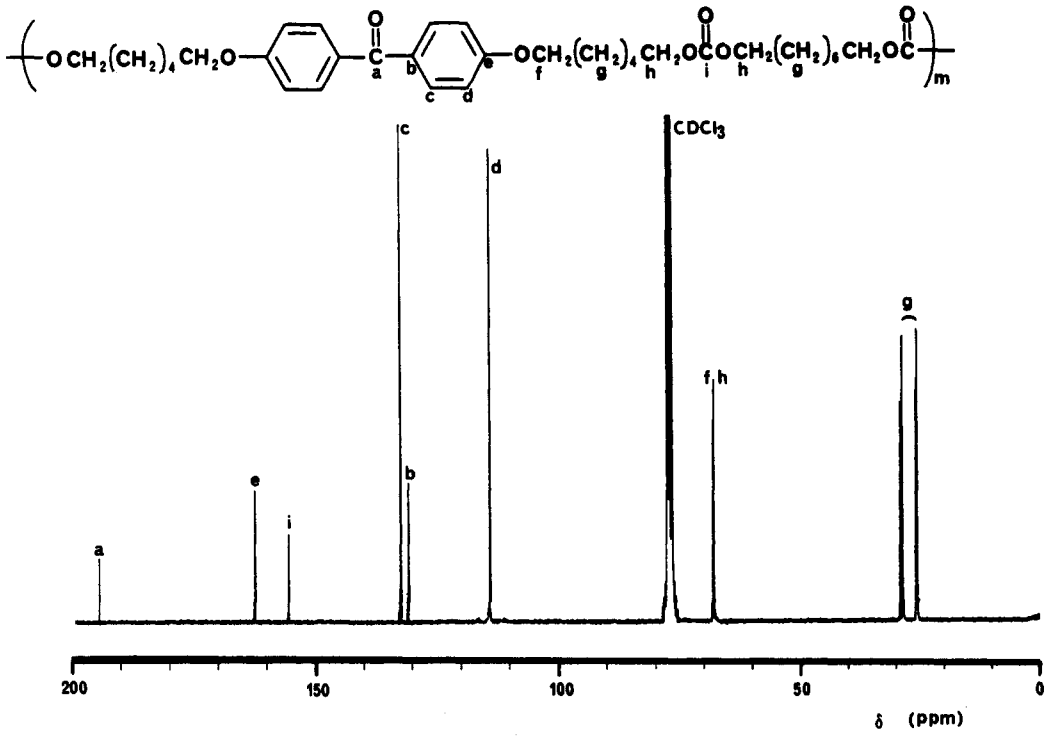

Figure 2. ^{13}C NMR spectrum for polycarbonate **6f** in $CHCl_3$-*d*.

On the second heating scans the DSC curves of the polymers containing the diphenyl ether unit (**5**) show that the polymers with the shorter (n = 2 and 3) or longer alkylene spacers (n = 12) (**5a**, **5b**, and **5i**) possess endotherms based on melting transitions (T_m) at 90–91 and 68 °C and exotherms due to crystallization (T_c) at −7.8 and +52–71 °C in addition to glass transition steps (T_g) at −4 to −6 and −22 °C, but the others (**5c–h**) display no endotherms except for the T_g steps (−8 to −22 °C). The texture observation by the polarizing microscope suggests that unfortunately polycarbonates **5a**, **5b**, and **5i** have no LC melts at the T_ms. Polymers **5c–h** display turbid melts at room temperature on cooling from the isotropic states. This means that the cooling rate of 10 °C/min is sufficient to suppress the crystallization of polymers **5c–h**. Thus polymers **5c–h** were kept at room temperature above the T_gs for 24 h after the first cooling runs and then the second heating scans were performed. In the DSC curves of polymers **5** on heating after annealing in Figure 3, sharp endothermal peaks at 31–41 °C, broad endotherms due to the T_m at 57–77 °C, and isotropizations (T_i) at 72–100 °C together with exotherms of T_c at 43–54 °C appeared. As we would expect, polymers **5c–h** form well-defined thermotropic LC phases (thread textures) in the corresponding

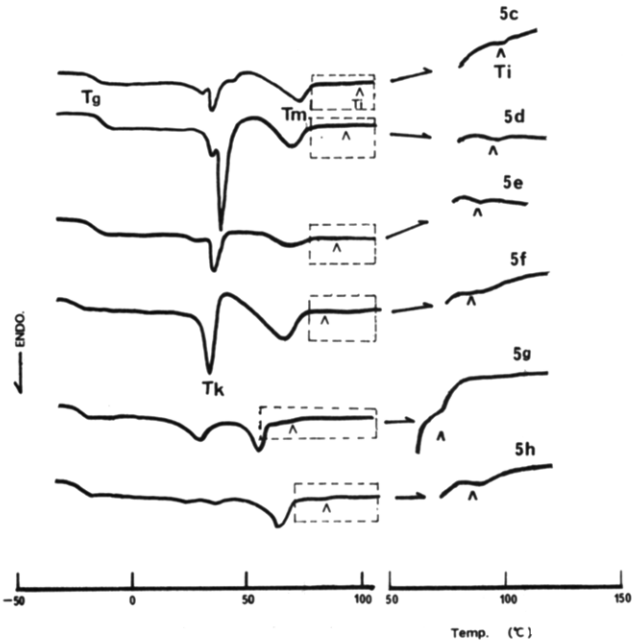

Figure 3. DSC curves for polymers 5c–h after annealing for 24 h at room temperature before the second heating.

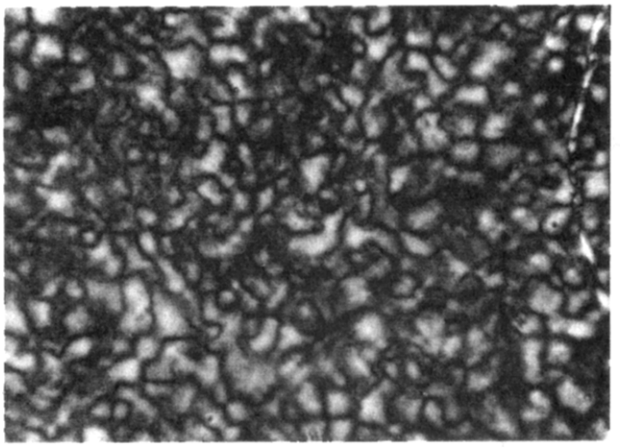

Figure 4. Polarizing microphotograph for polymer **5e** at 75 °C on heating after annealing (original magnification ×400; the photograph has been reduced to 70% of its original size for publication purposes).

temperature ranges of the T_m and the T_i after annealing, although they are made up of the flexible rodlike nonconventional diphenyl ether and the alkylene chains. A typical polarizing microphotograph for polymer **5e** at 75 °C after annealing is presented in Figure 4. The phase transition temperatures are listed in Table 1. These data describe that the phase transition temperatures (T_m, T_i, and T_g) are lower than those for the already-reported analogous semirigid LC polycarbonates composed of alkylene chains[11,17] and have a tendency to decrease with increasing alkylene spacer lengths without showing odd–even fluctuations as well as the analogues. The transition enthalpies of the isotropization temperatures (ΔH_i) in polymers **5c–h** are 54.1–264 J/mol. Polymers **5g** and **5h** with longer alkylene spacers have higher ΔH_is than those consisting of shorter spacers (**5c–f**). These values coincide with ones for the nematic-to-isotropic transition in thermotropic LC compounds.[18] The LC temperature ranges (ΔT) in polymers **5c–h** are 15–24 °C. The T_gs for all of the polymers **5** are below 0 °C (−4° to −22 °C).

To check the LC mesophases for polymers **5c–h**, powder X-ray diffraction measurements at various temperatures were carried out. X-ray diffraction patterns for polymer

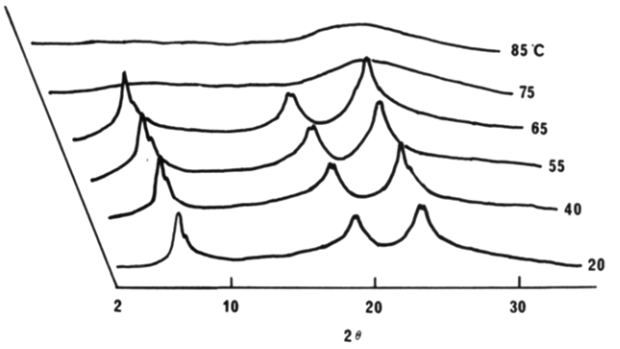

Figure 5. Powder X-ray patterns for polymer **5e** at various temperatures.

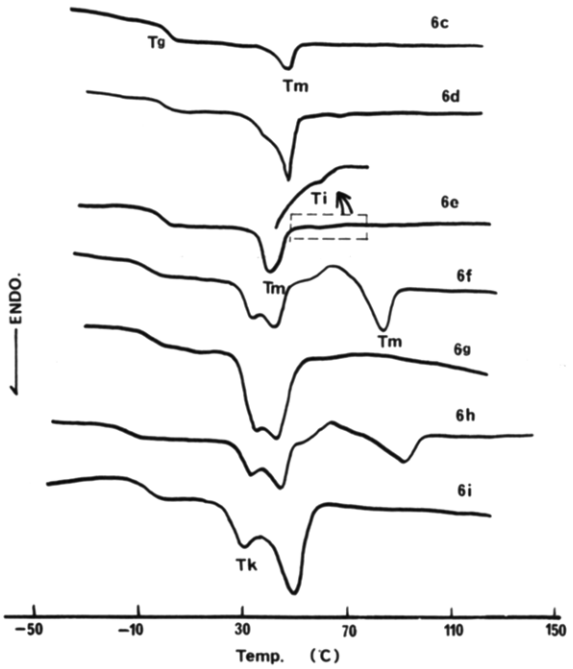

Figure 6. DSC curves for polymers 6c–i after annealing for 24 h at room temperature before the second heating.

5e are illustrated in Figure 5, which demonstrate that polymer **5e** shows reflections at $2\theta = 6.35°$ and at $2\theta = 18.8$ and 23.1° at room temperature. The former ($2\theta = 6.35°$) disappears and the latter (2θ = 18.8 and 23.1°) become broad in the range of the LC state (at 75 and 85 °C). These patterns indicate that polymer **5e** is a crystalline material, has a smectic-like ordered structure at room temperature, and forms a nematic melt. The other polymers (**5c**, **5d**, and **5f–h**) also possess the same LC melts.

On the other hand, in the polycarbonates containing the benzophenone unit (**6**), the DSC traces for the polymers with alkylene chains of n = 4–12 (**6c–i**) show only the T_g steps at 2.1 to −13 °C on the second heating as well as polycarbonates **5c–h** containing the diphenyl ether unit. The others (**6a** and **6b**) display one endotherm (T_m) at 116 °C and exotherms (T_c) at 98–100 °C in addition to T_g steps (15–16 °C). Polymers **6a** and **6b** show normal melting transitions. Thus polymers **6c–i** were annealed above the T_gs. The DSC curves of polymers **6c–i** after annealing at room temperature for 24 h (Figure 6) exhibit new endotherms or exotherms due to T_m and T_i or T_c. In polymers **6e** and **6f** the dark field of view brightens instantly when a light pressure or shear is applied to them between T_m and T_i in the optical texture observation with the polarizing microscope. In the DSC curve for polymer **6e** on the second heating run the endotherms coresponding to the T_m and the T_i transitions are detectable at 41 and 59 °C,

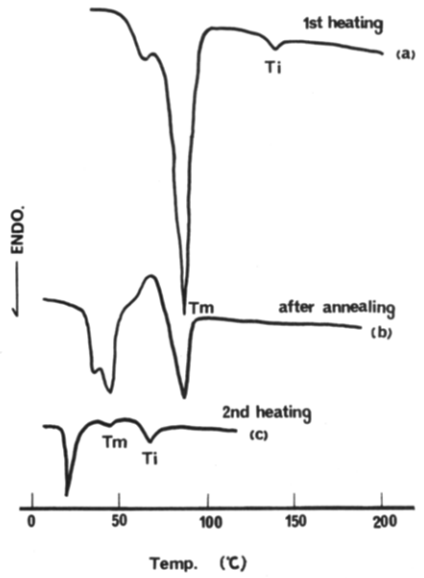

Figure 7. DSC curves for polymer **6f**: (a) data on the first heating run for polymer **6f** having an inherent viscosity of 0.74 dL/g (Table 2); (b) after annealing polymer **6f** having an inherent viscosity of 0.74 dL/g (Table 2); (c) curves of polymer **6f** with an inherent viscosity of 0.54 dL/g (Table 2).

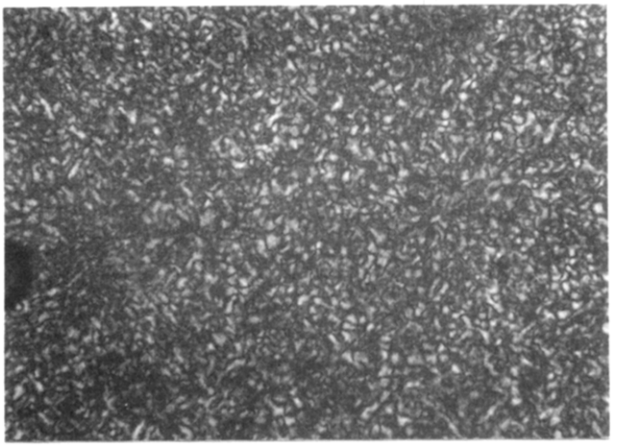

Figure 8. Polarizing microphotograph for polymer **6f** (η_{inh} = 0.54 dL/g in chloroform at 30 °C) at 65 °C on the second heating (original magnification ×400; the photograph has been reduced to 70% of its original size for publication purposes).

respectively. Polymer **6f** shows endothermal peaks based on T_m at 85 °C and T_i at 140 °C on the first heating run and only the T_g step at −7.7 °C on the second heating scan. As shown in Figures 6 and 7, the DSC curve for polymer **6f** after annealing displays an endothermal peak attributed to T_m at 85 °C without detecting an endotherm for the T_i transition (140 °C), but the polarizing microscope observation indicates that polymer **6f** has an obscure and birefringent melt between 85 and 140 °C. Interestingly, the polycarbonate **6f** in Table 2 having the lower inherent viscosity (0.54 dL/g in chloroform at 30 °C) forms a well-defined thread texture in the range 46–67 °C in the optical texture observation with the polarizing microscope as shown in Figure 8. The texture is retained at room temperature on cooling from the LC phase. The reflections at wide angles (at and around 2θ = 20–23°) observed at room temperature in the X-ray diffraction patterns disappear and broaden in the LC state, which proves formation of the nematic phase in the polymers with the benzophenone unit. This means that the molecular weights of polycarbonates **6** affect the LC formation ability. Unfortunately, no LC melts are detectable in the other polymers (**6c**, **6d**, and **6g–i**). The phase transition data for polycarbonates **6** are summarized in Table 2. The T_g values tend to decrease with increasing alkylene spacer length as well as the polycarbonates containing the diphenyl ether unit (**5**).

In conclusion, it was discovered that some flexible rodlike polycarbonates (**5** and **6**) composed of diphenyl units with appropriate lengths of alkylene chains (n = 4–10) can form birefringent or nematic LC melts in spite of incorporation of nonconventional mesogenic units having kinked linkages such as diphenyl ether or benzophenone in the backbones. It can be explained that the introduction of appropriate spacer lengths into the polycarbonate backbones contributes to the formation of LC states due to the excluded volume effect and the attractive interaction. This means that the traditional and rigid rodlike mesogens are not always necessary for the formation of LC phases in main-chain type semirigid polymers. It is also suggested that diphenyls having bond angles above 120° in the central parts between the benzene rings (diphenyl ether, 122–124°; benzophenone, 120.6°)[4] can play a role of mesogens and are responsible for the formation of LC phases in semirigid main-chain type polymers. The diphenyl ether unit has definitely superior mesogenic character to that of the benzophenone unit. Introduction of diphenyls with bent linkages has an effect on lowering the transition temperatures.

Experimental Section

Materials. 4,4′-Dihydroxydiphenyl ether (**1a**), 4,4′-dihydroxybenzophenone (**1b**), 6-chloro-1-hexanol (**2**), *N*,*N*-dimethylformamide (DMF), and potassium carbonate were purchased from Tokyo Kasei Co. Ltd. and used as received.

Monomer Synthesis. Alkylene Diphenyl Dicarbonates 4. These compounds were prepared from alkanediols and chlorophenyl carbonate in pyridine according to our previously-described methods.[11] The melting temperatures coincide with the previous data.

4g (n = 9): yield 66%; mp 39.5–40.5 °C; FTIR (KBr, cm^{-1}) 2926 and 2853 (CH), 1757 (C=O), 1258 (C–O–C).

6,6′-(4,4′-Oxydiphenylenedioxy)dihexanol (3a). Into a solution of **1a** (0.025 mol, 5.06 g) in 70 mL of DMF containing potassium carbonate (0.05 mol, 6.91 g) was added **2** (0.05 mol, 6.91 g). The reaction mixture was refluxed over 12 h and poured into an excess volume of water. The precipitated solid was washed with diluted hydrochloric acid and then thoroughly with water three times. The crude product was collected by filtration and dried at 40 °C. The compound was recrystallized twice from chloroform and dried at 40 °C for 1 day in vacuo. Yield 65%; mp 121–122 °C; FTIR (KBr, cm^{-1}) 3320 (OH), 2940 and 2865 (CH), 1242 (C–O–C); ^{13}C NMR ($CHCl_3$-d, 67.8 MHz) δ 115.4–154.8 (aromatic ring), 62.9 ($OHCH_2$), 25.6–32.7 (–$(CH_2)_4$–), 68.4 (–CH_2O–). Anal. Calcd for $C_{24}H_{34}O_5$ (402.6): C, 71.60; H, 8.53. Found: C, 71.60; H, 8.50.

6,6′-(4,4′-Carbonyldiphenylenedioxy)dihexanol (3b). This was synthesized from **1b** and **2** by the same method as the hexanol **3a**. Yield 55%; mp 142.5–143 °C; FTIR (KBr, cm^{-1}) 3310 (OH), 2940 and 2865 (CH), 1636 (C=O), 1252 (C–O–C); ^{13}C NMR ($CHCl_3$-d, 67.8 MHz) δ 199.4 (C=O), 113.9–162.4 (aromatic ring), 62.9 ($OHCH_2$), 25.5–32.7 (–$(CH_2)_4$–), 68.1 (–CH_2O–). Anal. Calcd for $C_{25}H_{34}O_5$ (414.6): C, 72.42; H, 8.28. Found: C, 72.41; H, 8.25.

Polymer Preparation. Polycarbonates 5. A typical procedure for **5e** is described. A mixture of diol **3a** (0.5 mmol, 0.201 g) and hexamethylene diphenyl dicarbonate (n = 6) (0.5 mmol, 0.179 g) was stirred at 180–185 °C for 2 h under nitrogen in the presence of zinc acetate (5 mg). Then the mixture was heated at 190–195 °C for 1 h at a pressure of 15 Torr and finally at 200–205 °C for 30 min under a reduced pressure of 2 Torr to remove byproduct. After the polycondensation, the product was dissolved in chloroform, and the solution was poured into cold methanol to reprecipitate polymer **5e**. The obtained product was collected by filtration and dried at 50 °C for 24 h in vacuo. Yield 93%; FTIR (film, cm^{-1}) 2940 and 2862 (CH), 1744 (carbonate C=O), 1589 (Ph), 1271 (C–O–C).

Anal. Calcd for $(C_{32}H_{44}O_9)_m$ (572.8)$_m$ (**5e**): C, 67.10; H, 7.76. Found: C, 66.43; H, 7.54.

Anal. Calcd for $(C_{30}H_{40}O_9)_m$ (544.7)$_m$ (**5c**): C, 66.15; H, 7.42. Found: C, 65.95; H, 7.82.

Anal. Calcd for $(C_{35}H_{50}O_9)_m$ (615.9)$_m$ (**5g**): C, 68.37; H, 8.21. Found: C, 68.16; H, 8.14.

Anal. Calcd for $(C_{38}H_{56}O_9)_m$ (656.9)$_m$ (**5i**): C, 69.47; H, 8.61. Found: C, 68.86; H, 9.62.

Polycarbonates 6. Diol **3b** (0.5 mmol, 0.207 g) was reacted with octamethylene diphenyl dicarbonate (n = 8) (0.5 mmol, 0.193 g) in the presence of zinc acetate (5 mg) at 170–175 °C for 2 h in nitrogen. Then at the same temperature the mixture was stirred for 1 h under a reduced pressure of 15 Torr and finally for 30 min at a pressure of 2 Torr to prevent cross-linking. After the reaction, the product was dissolved in chloroform and poured into methanol to reprecipitate polymer **6f**. The resulting polymer was filtered off and dried at 50 °C for 1 day under vacuum. Yield 88%; FTIR (film, cm^{-1}) 2940 and 2861 (CH), 1740 (carbonate C=O), 1645 (C=O), 1601 (Ph), 1267 (C–O–C).

Anal. Calcd for $(C_{35}H_{48}O_9)_m$ (612.8)$_m$ (**6f**): C, 68.59; H, 7.91. Found: C, 68.10; H, 8.04.

Anal. Calcd for $(C_{31}H_{40}O_9)_m$ (556.7)$_m$ (**6c**): C, 66.88; H, 7.26. Found: C, 66.48; H, 8.19.

Anal. Calcd for $(C_{37}H_{52}O_9)_m$ (640.9)$_m$ (**6h**): C, 69.34; H, 8.19. Found: C, 68.65; H, 8.08.

Anal. Calcd for $(C_{39}H_{56}O_9)_m$ (669.0)$_m$ (**6i**): C, 70.02; H, 8.46. Found: C, 68.43; H, 8.40.

Measurements. The FTIR spectra were obtained on a Jasco FT/IR 5300 spectrometer using KBr disks or film cast from chloroform solutions of the polymers. The ^{13}C NMR spectra were conducted on a JEOL LNM-GSX270N spectrometer in $CHCl_3$-d. The DSC curves were recorded with a Shimadzu DSC-50 calorimeter at a heating and a cooling rate of 10 °C/min in nitrogen. The optical texture observation was carried out with a polarizing microscope (Olympus Model POM) equipped with a hot stage (400-fold magnification). The powder X-ray diffraction patterns were measured with a Rigaku Denki RU-200 generator equipped with a PTC-10C temperature controller with Cu Kα irradiation. The viscosity measurements were undertaken at a concentration of 0.2 g/dL in chloroform at 30 °C using an Ostwald-type viscometer.

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