

Phase Transition Behaviors in Liquid Crystalline Poly(fumarate)s of Different Mesogen Density

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Poly(fumarate)s possess rigid main-chain moieties originating from the steric hindrance of densely packed side-chains. Besides such rigid characteristics, one of the most important features of poly(fumarate)s is the capability to vary the number and nature of side-chain functionality especially when mesogenic groups are anchored. Fumarate monomers carrying two mesogenic groups (abb. Bis-F) can be polymerized to afford the polymethylenes with the doubled mesogen density as compared to the ordinary α -olefin polymers, leading to a facile appearance of liquid crystal phase. Polymerization of fumarate monomers carrying an isopropyl and a mesogenic group (abb. Mono-F) similarly provides the corresponding rigid polymethylenes with the same mesogen density as α -olefin polymers. Copolymerization of Bis-F and Mono-F yields the polymethylenes with the intermediate mesogen density. In this paper, the phase transition behaviors of a series of novel poly(fumarate)s with different cyanobiphenyl mesogen density were studied. Although poly(Bis-F) exhibited the smectic phase, copoly(Bis/Mono-F) showed the nematic phase and poly(Mono-F) did not display any liquid crystalline phases. Moreover, the liquid crystalline temperature range was very wide for poly(Bis-F). These results clearly suggest that higher mesogen density is more advantageous for realization of well-ordered liquid crystalline phases, such as smectic phase, in side-chain liquid crystalline polymers.

Keywords: Poly(fumarate), Side-chain liquid crystalline polymer, Mesogen density, Rigid main-chain

Introduction

Liquid-crystalline polymers have attracted much attention in recent years because of their fundamental scientific interest and potential applications as optoelectronic materials. A number of side-chain liquid crystalline polymers (SCLCPs) with various polymer backbones, such as polysiloxane, polyacrylate, polymethacrylate, and poly(vinyl ether), have been synthesized.¹⁻⁴ The liquid crystallinity can be affected by the polymer backbone, spacer length, molecular weights, and the polydispersity.⁵⁻⁶ In contrast to mesogen structures introduced into side-chains, however, the influence of the mesogen density on the phase transition behaviors has not been studied extensively. This is partly because the mesogen density could not be varied or controlled over a wide range when the polymer backbones so far reported for SCLCPs were chosen.⁷⁻⁸

We have been continuing the project on functional poly(fumarate)s prepared by radical polymerization of fumarate monomers.⁹ The resulting polymers possess a rigid backbone originating from the bulky and dense side-chains. Recently, we expanded the poly(fumarate)s to SCLCPs, since the effect of the polymer backbone in SCLCPs has not extensively been studied for well-defined polymers. Besides the rigidity of the polymer backbone, one of the most important features of poly(fumarate)s is the capability of the high side-chain density especially when liquid crystallinity is expected. Introduction of a mesogenic group into every methylene unit of the polymer backbone doubles the mesogen density as compared to the α -olefin polymers.¹⁰⁻¹¹

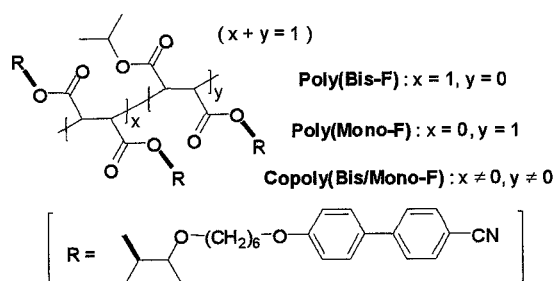
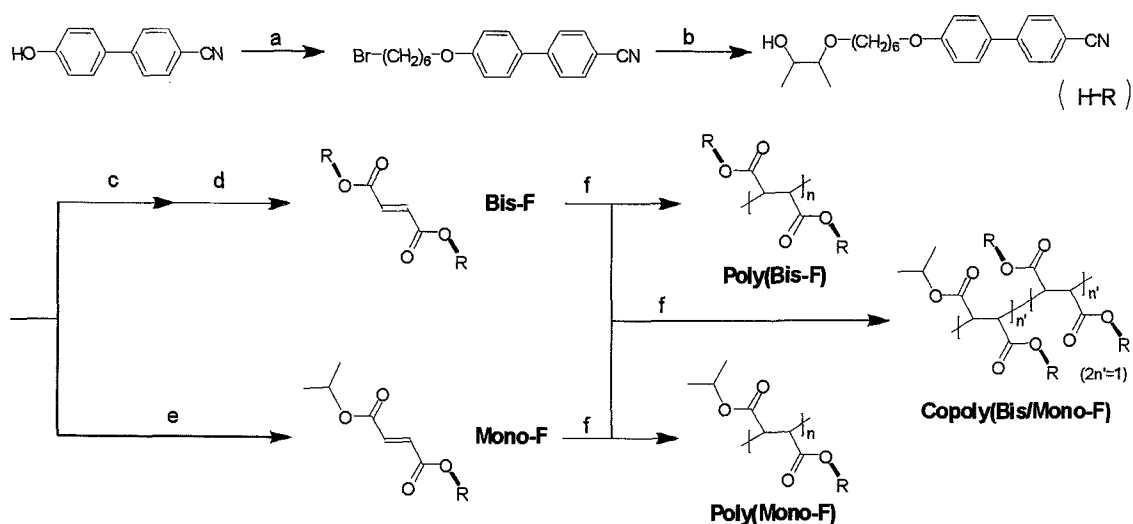


Figure 1. Chemical structures of liquid crystalline poly(fumarate)s.

In this paper, we report the phase transition behaviors of novel poly(fumarate)s bearing cyanobiphenyl mesogenic groups (see Figure 1). An increase in the mesogen density results in the formation of enantiotropic liquid crystal phases in a relatively wide temperature range.

Experimental Section

General. All NMR spectra were recorded on a JEOL Alpha300 with tetramethylsilane as an internal standard. Gel permeation chromatography was measured on a TOSOH TSKgel GMH-M using chloroform as an eluent after calibration with standard polystyrenes. The liquid crystalline textures were observed with an Olympus BX-50 polarized optical microscope (POM) equipped with a hot stage. Differential scanning calorimetry (DSC) measurements were carried out on a Rigaku Thermo plus DSC8230 at a scanning rate of 20 °C min⁻¹.



Scheme 1. Synthesis of side-chain liquid-crystalline poly(fumarate)s by radical (co)polymerization. (a) 1,6-dibromo hexane, K_2CO_3 , KI, acetone. (b) NaH, 2,3-butanediol, $BnEt_3NCl$, THF. (c) maleic anhydride, *p*-TsOH, C_6H_6 , 80 °C, 12 h. (d) morpholine, C_6H_6 , 80 °C, 4 h. (e) fumaric acid monoisopropyl ester, *p*-TsOH, C_6H_6 , 80 °C, 12 h. (f) benzoyl peroxide, 80 °C, 7 days.

Wide-angle X-ray scattering measurements were performed on a Rigaku RINT2100 diffractometer equipped with a heating stage with Cu K α radiation.

Materials. All reagents were purchased from Wako, Tokyo Kasei, and Aldrich and were used without further purification. Solvents were purified by distillation under nitrogen after drying over suitable drying agents. 4'-(6-Bromohexyloxy)-4-cyanobiphenyl¹² and fumaric acid monoisopropyl ester¹³ were prepared according to the literature procedures.

Synthesis. 4'-(6-(2-Hydroxy-1-methylpropoxy)hexyloxy)-4-cyanobiphenyl (1). Sodium hydride, 60% in paraffin, (0.54 g, 0.023 mol) was added to 30 ml of THF under a nitrogen flow. To this solution, 2,3-butanediol (raceme mixture, 5.42 g, 60.2 mmol) in 5 ml of THF and benzyltriethylammonium chloride (4.99 g, 21.9 mmol) were slowly added at room temperature. Stirring was continued for 30 min until the solution color became lime-yellow, and then 4'-(6-bromohexyloxy)-4-cyanobiphenyl (5.01 g, 14.0 mmol) was added dropwise. After stirring for 24 h, THF was removed under reduced pressure, and 150 ml of chloroform and 150 ml of water were added. After filtration the solution was evaporated to dryness. The purification by silica gel column chromatography eluted with chloroform/methanol = 20/1 followed by recycling HPLC afforded a white gum (3.49 g, 67%). ¹H-NMR, δ (ppm, $CDCl_3$, 300 MHz): 1.08–1.15 (m, 6 H), 1.41–1.54 (m, 4 H), 1.57–1.87 (m, 4 H), 2.12–2.81 (s, 1 H), 3.08–3.86 (m, 4 H), 4.00 (t, $J = 6$ Hz, 2 H), 6.98 (d, $J = 9$ Hz, 2 H), 7.52 (d, $J = 9$ Hz, 2 H), 7.65 ppm (m, 4 H); IR (liquid film): $\nu = 3497, 2985, 2941, 2868, 2226, 1600, 1496, 1474, 1294, 1250, 1180, 1126, 1104, 1088, 1028, 1006, 826, 798, 734, 532$ cm^{-1} .

Fumarate monomer carrying two mesogenic groups (Bis-F). Maleic anhydride (2.13 g, 21.7 mmol), **1** (3.98 g, 10.8 mmol) and *p*-toluenesulfonic acid (0.21 g, 1.1 mmol) in benzene (50 ml) were heated under reflux for 12 h using a Dean-Stark water separator. Chloroform was added and the solution was washed with saturated

aqueous $NaHCO_3$, water, and brine and then dried over sodium sulfate. After filtration the solution was evaporated to dryness. To this crude product, benzene (100 ml) and morpholine (2.32 ml, 22.6 mmol) were added. After the mixture was heated under reflux for 4 h, the solution was cooled to room temperature and poured into chloroform. The chloroform layer was washed and dried as described above. Filtration, evaporation, and purification as the same manner described in the preparation of **1** afforded a white gum (2.78 g, 70%). ¹H-NMR, δ (ppm, $CDCl_3$, 300 MHz): 1.16 (d, $J = 6$ Hz, 6 H), 1.26 (d, $J = 6$ Hz, 6 H), 1.38–1.53 (m, 8 H), 1.56–1.84 (m, 8 H), 3.40–3.56 (m, 6 H), 3.99 (t, $J = 7$ Hz, 4 H), 5.04 (m, 2 H), 6.87 (s, 2 H), 6.98 (d, $J = 9$ Hz, 4 H), 7.52 (d, $J = 9$ Hz, 4 H), 7.65 ppm (m, 8 H); IR (liquid film): $\nu = 2982, 2937, 2862, 2226, 1721, 1604, 1521, 1493, 1474, 1291, 1253, 1177, 1070, 1000, 820, 753, 662, 561, 532$ cm^{-1} .

Fumarate monomer carrying single mesogenic group (Mono-F). Fumaric acid monoisopropyl ester (1.02 g, 6.43 mmol), **1** (1.55 g, 4.22 mmol) and *p*-toluenesulfonic acid (0.15 g, 0.87 mmol) in benzene (50 ml) were heated under reflux for 12 h using a Dean-Stark water separator. Chloroform was added and the solution was washed with saturated aqueous $NaHCO_3$, water, and brine and then dried over sodium sulfate. Filtration, evaporation and purification as the same manner described in the preparation of **1** afforded a white gum (1.34 g, 63%). ¹H-NMR, δ (ppm, $CDCl_3$, 300 MHz): 1.16 (d, $J = 6$ Hz, 3 H), 1.25–1.29 (m, 9 H), 1.38–1.53 (m, 4 H), 1.56–1.84 (m, 4 H), 3.40–3.56 (m, 3 H), 4.00 (t, $J = 7$ Hz, 2 H), 5.04 (m, 2 H), 6.87 (s, 2 H), 6.98 (d, $J = 9$ Hz, 2 H), 7.52 (d, $J = 9$ Hz, 2 H), 7.65 ppm (m, 4 H); IR (liquid film): $\nu = 2980, 2938, 2864, 2224, 1717, 1643, 1601, 1577, 1523, 1496, 1469, 1376, 1294, 1256, 1178, 1159, 1105, 981, 825, 659, 562, 531$ cm^{-1} .

Polymerization of Bis-F [Poly(Bis-F)]. 10 mol% BPO was added to Bis-F (0.48 g, 0.59 mmol). The mixture was degassed in vacuo, sealed, and heated in a thermostated bath at 80°C. After 10 days, the reaction

was terminated by addition of methanol. The polymer was purified by recycling HPLC, affording a white gum (100 mg). Number-average molecular weight (M_n): 6200, weight-average molecular weight (M_w): 7500. $^1\text{H-NMR}$, δ (ppm, CDCl_3 , 300 MHz): 1.09-1.65 (m, 20 H), 2.76-3.80 (m, 6 H), 4.68-4.92 (m, 1 H), 6.80 (m, 2 H), 7.37-7.48 ppm (m, 6 H).

Polymerization of Mono-F [Poly(Mono-F)]. 1.0 mol% BPO was added to Mono-F (0.53 g, 10 mmol). As the same manner described above, the mixture was polymerized in a degassed sealed vessel at 80°C for 10 days. Purification by recycling HPLC afforded a white gum (30 mg). M_n : 19700, M_w : 28600. $^1\text{H-NMR}$, δ (ppm, CDCl_3 , 300 MHz): 1.17-1.69 (m, 20 H), 2.96-3.41 (m, 5 H), 3.86 (m, 2H), 4.59-4.85 (m, 2 H), 6.85 (m, 2 H), 7.40-7.56 ppm (m, 6 H).

Copolymerization of Bis-F and Mono-F [Copoly-(Bis/Mono-F)]. 5.0 mol% BPO was added to an equimolar mixture of Bis-F (0.562 g, 0.690 mmol) and Mono-F (0.350g, 0.690 mmol). As the same manner described above, the mixture was polymerized in a degassed sealed vessel at 80°C for 10 days. Purification by recycling HPLC afforded a white gum (45 mg). M_n : 15700, M_w : 18800. $^1\text{H-NMR}$, δ (ppm, CDCl_3 , 300 MHz): 1.13-1.67 (m, 16.3 H), 2.98-3.37 (m, 4 H), 3.81 (m, 2H), 4.59-4.89 (m, 1.35 H), 6.81 (m, 2 H), 7.37-7.50 ppm (m, 6 H).

Results and Discussion

The two monomers, Bis-F and Mono-F, prepared via etherification¹⁴ and esterification¹⁵⁻¹⁶ processes, were polymerized by the conventional radical initiation using BPO to furnish the corresponding three polymers, i.e., poly(Bis-F), poly(Mono-F), and copoly(Bis/Mono-F). The polymer structures were confirmed by ^1H NMR spectra. The mesogen density or the composition of copoly(Bis/Mono-F) was calculated from the methine signal ratio of [main-chain >CH- (4.8 ppm) / side-chain branching >CH- (6.8 ppm)] to be $x=0.47$ (definition of x , see Fig. 1). Because the monomer feed ratio of Bis-F and Mono-F was 1:1, these monomers exhibited almost the same polymerizability. Thus, the mesogen density of copoly(Bis/Mono-F) was estimated to be about 75% of poly(Bis-F). As a result, poly(fumarate)s with different mesogen densities, i.e., 100% [poly(Bis-F)], 75% [copoly(Bis/Mono-F)], and 50% [poly(Mono-F)], were prepared.

Phase transition behaviors of poly(Mono-F), copoly(Bis/Mono-F), and poly(Bis-F) were characterized by DSC and POM measurements. All three poly(fumarate)s showed glass transition temperatures. The DSC trace of poly(Bis-F) and copoly(Bis/Mono-F) clearly displayed the presence of a liquid crystalline phase, whereas poly(Mono-F) showed the direct "glass/ isotropic liquid" change without any mesophases (Fig. 2). These liquid crystal phases of poly(Bis-F) and copoly(Bis/Mono-F) were observed upon both heating and cooling cycles, indicating the enantiotropic liquid crystal nature. The clearing point corresponding to the mesophase/isotropic transition was drastically elevated from 26.2 to 140.7 °C by polymerization of Bis-F to poly(Bis-F). On the other hand, the shift of "glass/liquid crystal" transition temperature by the polymerization was less significant (from -2.4 to 23.0 °C). Therefore, in

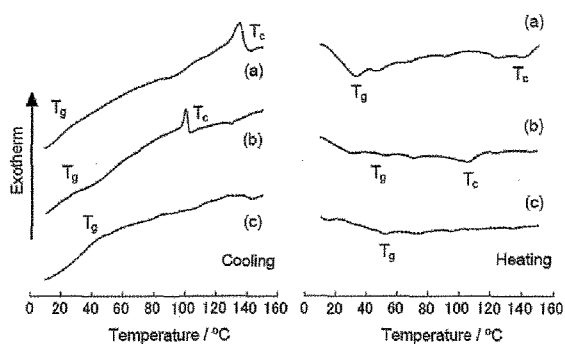


Figure 2. DSC thermograms of the first cooling (left) and the second heating (right) cycles of the polymers at 10 °C min⁻¹. (a) poly(Bis-F), (b) copoly(Bis/Mono-F), (c) poly(Mono-F).

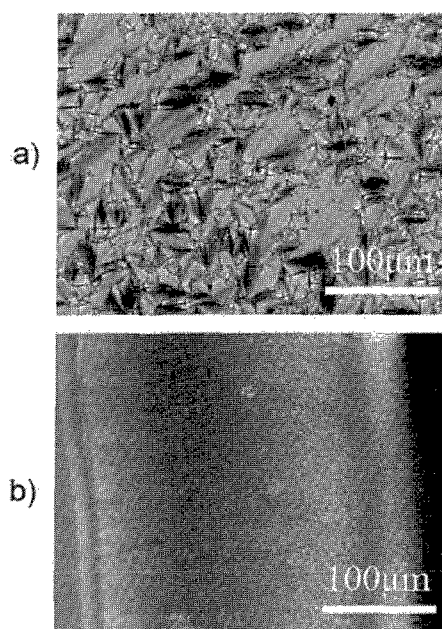


Figure 3. Polarized optical microscopy images of (a) poly(Bis-F) and (b) copoly(Bis/Mono-F) at 20 °C.

total, the liquid crystal temperature range was expanded upon polymerization. Similar expansion of the liquid crystal temperature range was observed for copoly-(Bis/Mono-F). The clearing point was elevated from 3.3 to 106.9 °C by polymerization of the equimolar mixture of Bis/Mono-F to copoly(Bis/Mono-F). Again the shift of "glass/liquid crystal" transition temperature was less significant (from -12.5 to 25.3 °C). As for Mono-F, merely the T_g elevation from -27.6 to 34.0 °C by polymerization to poly(Mono-F) was noticed.

The POM observation supported the DSC results. The POM image of poly(Bis-F), measured at 20 °C upon cooling, exhibited fan-shaped textures, revealing the smectic phase. Under the same conditions, the POM image of copoly(Bis/Mono-F) exhibited sand-like textures characteristic of the nematic phase that has no layered structures. As mentioned above, poly(Mono-F) did not show any specific textures over the temperature range measured.

Considering the fact that many α -olefin polymers with relatively low mesogen density such as a cyanobiphenyl

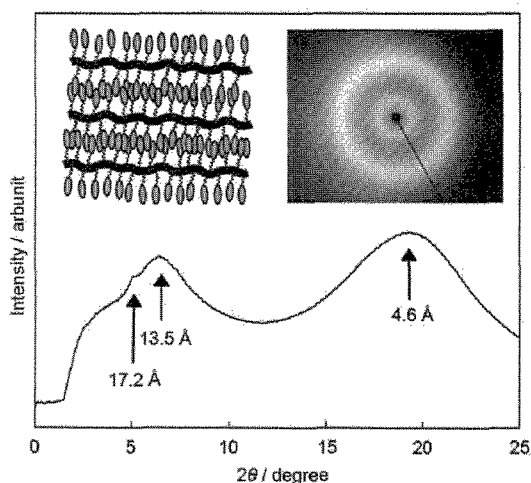


Figure 4. Wide-angle X-ray diffraction pattern of poly(Bis-F) at 60 °C and schematic illustration of the smectic layered structure.

group at every two main-chain carbons exhibit liquid crystal phase¹, the rigid poly(fumarate) backbone requires more mesogenic groups for use as SCLCPs.

The enthalpy of phase transition was estimated from the second heating cycles of the DSC profile in Figure 2 to be 2.06 and 1.43 kJ/mol for poly(Bis-F) and copoly(Bis/Mono-F), respectively. These values are specific to the smectic and nematic phases, respectively, and consistent with the POM images of poly(Bis-F) and copoly(Bis/Mono-F) as described above.

X-ray diffraction (XRD) pattern of poly(Bis-F) measured at 60 °C is shown in Figure 4. Three diffraction peaks were observed at $2\theta = 5.15^\circ$ ($d = 17.2$ Å), 6.55° (13.5 Å), and 19.45° (4.6 Å). The small angle peak corresponding to the d -spacing value of 17.2 Å provides evidence for the half length of smectic layers. In the small angle region, there was one more diffuse peak at $2\theta = 6.55^\circ$ overlapping the peak of the layer interval. The calculated value of 13.5 Å coincides with the diameter of the main-chain moiety including isopropyl or isopropylene groups. This characteristic peak is common to the present three poly(fumarate)s containing the same semi-rigid main-chain moiety.

The phase behaviors of three polymers were summarized in Figure 5. Although three polymers have the same main-chain and side-chain structures, they showed significantly different liquid crystallinity. Such difference was merely derived from the mesogen density variation. Although poly(Mono-F), of which mesogen density is equal to polyacrylate-type SCLCPs, formed no

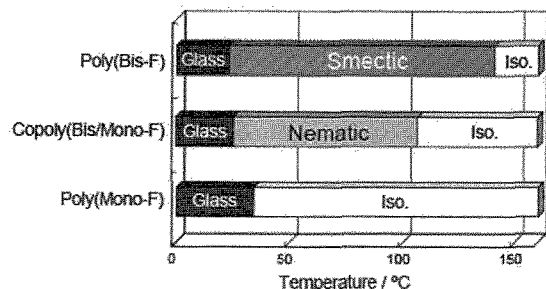


Figure 5. Phase transition map for poly(Bis-F), copoly(Bis/Mono-F), and poly(Mono-F).

mesophase, the increment of mesogen density to copoly(Bis/Mono-F) or poly(Bis-F) was revealed to recover mesophases. Especially, the full introduction of mesogenic groups into every main-chain carbon as represented by poly(Bis-F) enabled to form the smectic phase. The semi-rigid main-chain without forming entanglement seemed to be advantageous to realize a higher ordering mesophase.

Conclusions

The synthesis and thermal properties of side-chain liquid crystalline poly(fumarate)s with different mesogen density were studied. A significant influence of the mesogen density on their liquid crystal-forming properties was demonstrated. Poly(Bis-F) exhibited smectic phase, whereas poly(Mono-F) was non-mesomorphic. The nature of copoly(Bis/Mono-F) was in-between and it exhibited nematic phase. It is thought that high mesogen density is necessary to promote the formation of a smectic phase or the higher ordering of mesogenic groups.

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