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## Liquid Crystals

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### Thermotropic semi-rigid copoly(imide-carbonate)s composed of 3,4,3',4'-*p*-terphenyltetracarboxdi-imide and 3,4,3',4'-biphenyltetracarboxdi-imide rings

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## Preliminary communication

# Thermotropic semi-rigid copoly(imide-carbonate)s composed of 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide and 3,4,3',4'-biphenyltetracarboxdi-imide rings

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New semi-rigid copoly(imide-carbonate)s composed of 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide and 3,4,3',4'-biphenyltetracarboxdi-imide units and neighbouring homologous penta- and hexa-methylene spacer chains were prepared by melt polycondensation; the relationships between polymer structure and liquid crystalline (LC) properties are discussed. Differential scanning calorimetry measurements, polarizing microscope observations, miscibility tests and variable temperature X-ray analyses suggest that the 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide-rich copolymers form thermotropic LC nematic and smectic phases, but the 3,4,3',4'-biphenyltetracarboxdi-imide-rich copolymers are amorphous and have no LC melts. Therefore, the presence of 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide units confers good mesogenic properties

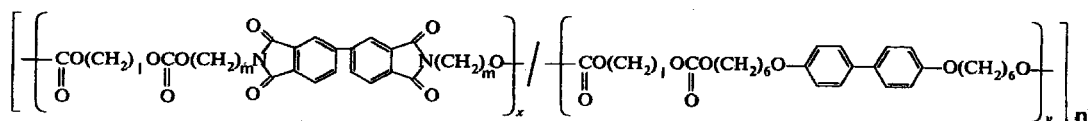
It is known that there are two groups of aromatic imide units which act as mesogens in thermotropic liquid crystalline (LC) polyimides: these are asymmetric and symmetric imide units [1–26]. Kricheldorf *et al.* very actively researched in areas concerning the syntheses, the LC characteristics and the layer structures of various polymers composed of imide units [2–10]. We have continued this interest by systematically investigating the relationships between polymer structure and LC properties for aromatic–aliphatic polyimides composed of symmetric aromatic di-imide units such as 3,4,3',4'-biphenyltetracarboxdi-imide and 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide rings and aliphatic spacers linked to the imide rings in the backbones [15–26]. It has been proposed that the total lengths of the aliphatic spacers (*m*) next to the imide rings and the aliphatic chains (*l*) of the interconnecting linkages and the distance of the linkage groups from the imide rings are important for the control of the orientation of the imide rings and the polymer chains [19] (scheme 1).

Our previous paper [26] reported that the aliphatic chains next to the imide rings play an important role in the LC formation by semi-rigid homopoly(imide-carbonate)s made up (scheme 2) of aromatic di-imide

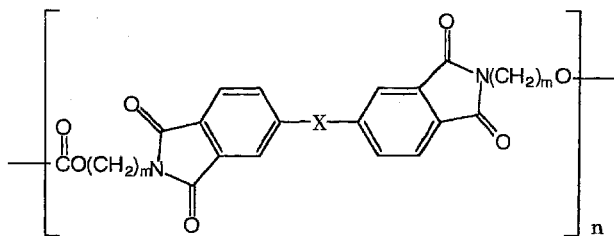
units, aliphatic segments (*m*) neighbouring the imide rings and an interconnecting carbonate linkage in the polymer backbones, which have no aliphatic segments (*l*) between the carbonate linkages. Of these, the homo-(imide-carbonate) having the 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide unit and a hexamethylene chain next to the imide rings formed a smectic phase and the homopolymer composed of 3,4,3',4'-biphenyltetracarboxdi-imide unit and a hexamethylene segment formed a nematic phase, despite the absence of individual biphenyl mesogenic units in the backbones, but the stabilities of the LC phases were lower than for the analogous semi-rigid poly(imide-carbonate) [17, 25] shown in scheme 1.

The purpose of this work was to prepare novel semi-rigid copoly(imide-carbonate)s **4b–i** characterized by symmetric aromatic di-imide rings (3,4,3',4'-biphenyltetracarboxdi-imide and 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide), aliphatic (penta- and hexa-methylene) chains next to the imide rings and the carbonate linkage in the backbones (scheme 3); and to investigate the effect of the polymer compositions, the di-imide structures and the aliphatic spacers (odd and even chains) next to the imide rings on the LC properties. These copolymers might have more stable LC phases than the corresponding homopolymers [17, 25] even although we do not have individual conventional mesogenic units in the backbones.

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Scheme 1.



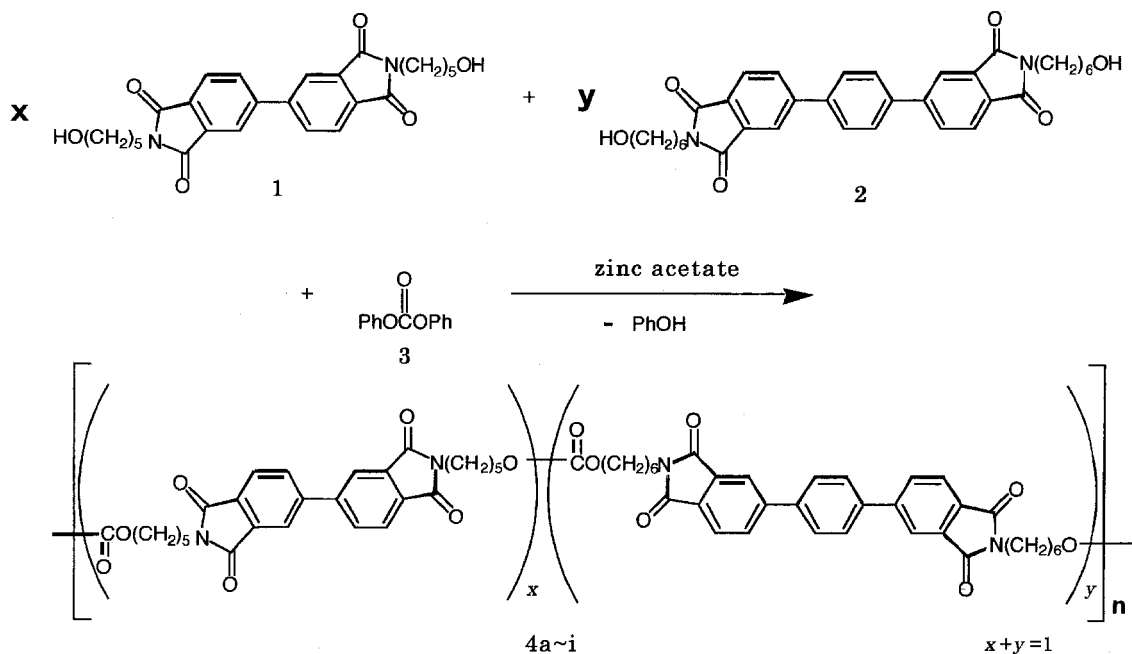
Scheme 2.

The novel semi-rigid copoly(imide-carbonate)s **4b-i**, were synthesized by melt polycondensation of a mixture of *N,N'*-bis(6-hydroxyhexyl)-3,4,3',4'-*p*-terphenyltetracarboxdi-imide **2** [24] and *N,N'*-bis(5-hydroxyhexyl)-3,4,3',4'-biphenyltetracarboxdi-imide **1** [17] in defined mole ratios ( $x:y = 0.9:0.1-0.1:0.9$ ), together with diphenyl carbonate **3** in the presence of zinc acetate, as previously reported [26] (scheme 3). The polycondensation proceeded smoothly and readily gave the desired copolymers **4b-i** in yields of 81–97%, with number average molecular masses ( $\bar{M}_n$ ) and molecular mass distributions ( $\bar{M}_w/\bar{M}_n$ ) of 9 300–26 000 and 2.23–3.47, respectively (table 1). The copolymers **4b-i** were soluble in chloroform, dichloro-

acetic acid (DCAA) and trifluoroacetic acid (TFAA), like the previously reported, analogous homopoly(imide-carbonate)s [26].

Flexible or brittle films were cast from chloroform solutions of the copolymers **4b-i**. Figure 1 shows a typical  $^{13}\text{C}$  NMR spectrum for copolymer **4g**, in which signals for the imide C=O at 168.2 ppm (3,4,3',4'-*p*-terphenyltetracarboxdi-imide) and 167.7 ppm (3,4,3',4'-biphenyltetracarboxdi-imide), the carbonate C=O at 154.9 ppm, aromatic carbons at 121.6–146.2 ppm, C(O)OCH<sub>2</sub> at 67.7 ppm, NCH<sub>2</sub> at 38.0 ppm and aliphatic chains at 23.1–30.3 ppm are recorded. The other copolymers showed analogous  $^{13}\text{C}$  NMR spectra. The FTIR spectra of the copolymers **4b-i** display characteristic absorption bands of imide C=O around 1770–1710  $\text{cm}^{-1}$  and carbonate C=O at 1740  $\text{cm}^{-1}$ , in addition to CH stretching at 2860–3030  $\text{cm}^{-1}$  and C–O–C at 1260  $\text{cm}^{-1}$ . Elemental analysis results for the copolymers **4b-i** were in agreement with the calculated values. These data support the formation of the expected copolymers **4b-i**.

The thermal and mesogenic properties of the copolymers **4b-i** were examined by differential scanning calorimetry (DSC), polarizing microscopy, miscibility tests and



Scheme 3.

Table 1. Synthetic results for polymers **4a-j**.

Polymer	<i>x</i>	<i>y</i>	Yield/%	$\bar{M}_n^a$	$\bar{M}_w/\bar{M}_n^b$	Solubility <sup>c</sup>	
						CHCl <sub>3</sub>	MeOH
<b>4a<sup>d</sup></b>	1.0	0	92	$1.78 \times 10^4$	2.46	+	-
<b>4b</b>	0.9	0.1	89	$1.63 \times 10^4$	2.32	+	-
<b>4c</b>	0.8	0.2	92	$1.52 \times 10^4$	2.42	+	-
<b>4d</b>	0.7	0.3	91	$1.85 \times 10^4$	2.28	+	-
<b>4e</b>	0.6	0.4	84	$1.23 \times 10^4$	2.23	+	-
<b>4f</b>	0.5	0.5	97	$2.60 \times 10^4$	2.50	+	-
<b>4g</b>	0.4	0.6	90	$1.93 \times 10^4$	2.75	+	-
<b>4h</b>	0.2	0.8	85	$1.11 \times 10^4$	2.52	+	-
<b>4i</b>	0.1	0.9	81	$0.93 \times 10^4$	3.47	+	-
<b>4j<sup>d</sup></b>	0	1.0	83	$1.05 \times 10^4$	2.74	+	-

<sup>a</sup>  $\bar{M}_n$ : number average molecular mass estimated by size exclusion chromatography using chloroform as solvent and polystyrene as standard.

<sup>b</sup>  $\bar{M}_w/\bar{M}_n$ : molecular mass distribution.

<sup>c</sup> + soluble at room temperature; - insoluble.

<sup>d</sup> See [26].

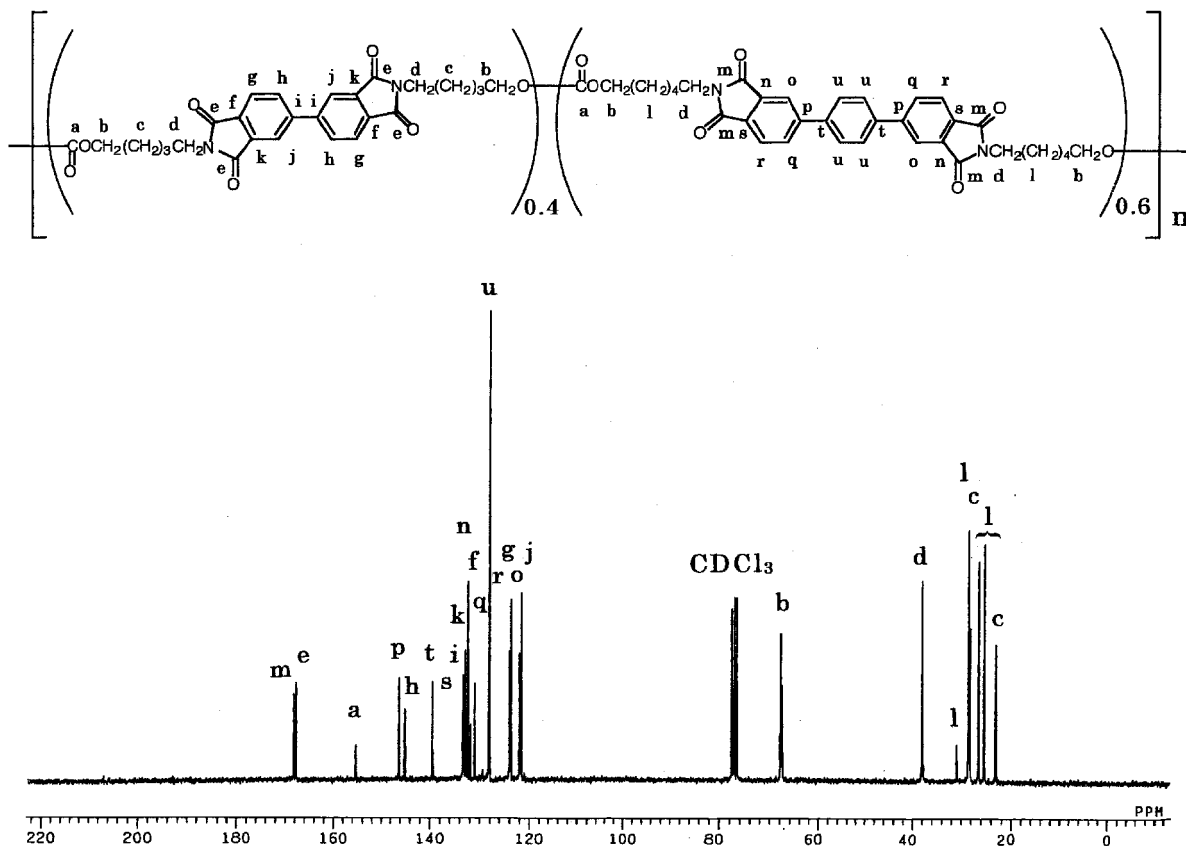


Figure 1. <sup>13</sup>C NMR spectrum of copolymer **4g** in CDCl<sub>3</sub>.

variable temperature X-ray analyses. The DSC curves of copolymer **4i** showed three endothermic peaks ( $T_1$  at 127°C,  $T_2$  at 175°C and  $T_3$  at 192°C) in addition to a glass transition step ( $T_g$ ) at 79°C on the first and the

second heating runs. On the first cooling, the corresponding exotherms were observable. In the DSC curves of copolymer **4h**, two endotherms were detected at 117°C ( $T_2$ ) and at 177°C ( $T_3$ ) on the first heating scan and on

the second heating after annealing at 80°C for 24 h; the corresponding exotherms for  $T_2$  and  $T_3$  were again observed on the first cooling run. The copolymers **4f** and **4g** showed two transitions ( $T_2$  and  $T_3$ ) on the first heating and cooling runs, but no peaks were found on the second heating scans even after annealing above the  $T_g$  steps. The polarizing microscope observations showed that the copolymers **4f–h** have nematic melts between  $T_2$  and  $T_3$ . The variable temperature X-ray diffraction results supported the formation of the nematic phase in the range between  $T_2$  and  $T_3$  in the copolymers **4f–h**, where no reflections at small angles and broad reflections around  $2\theta = 20\text{--}22^\circ$  were observed. This means that  $T_2$  and  $T_3$  are solid to nematic ( $T_N$ ) and nematic to isotropic ( $T_I$ ) transitions, respectively. In the variable-temperature X-ray diffraction patterns for the undrawn copolymer **4i**, reflections were detected with difficulty at small angles and around  $2\theta = 20\text{--}30^\circ$ .

In summary, the LC phases were recognized by polarizing microscopy observations, but miscibility tests using 2,5-bis(4-methoxyphenyl)-1,3,4-thiadiazole [27] were also used. These measurements suggested the emergence of a smectic phase between  $T_1$  (solid to smectic:  $T_S$ ) and  $T_2$  (smectic to nematic:  $T_N$ ) and a nematic phase between  $T_2$  ( $T_N$ ) and  $T_3$  ( $T_I$ ) in the copolymer **4i**. On the other hand, the DSC curves of copolymers **4b–d** showed only  $T_g$  steps at 76–84°C on the heating and the cooling scans.

The copolymer **4e** had a normal melting temperature at 124°C. The phase transition temperatures of the copolymers **4b–i** on the first heating scans are listed in table 2 together with the thermal data for the homopoly-(imide-carbonate)s **4a** and **4j** reported in our previous paper [26]. The relationships between the copolymer composition and the phase transition temperatures are illustrated in figure 2. The phase transition temperatures ( $T_g$ ,  $T_S$ ,  $T_N$  and  $T_I$ ) vary with compositions.

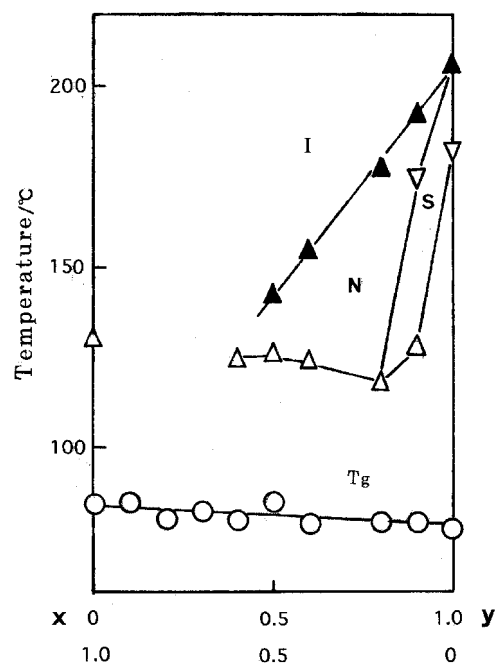


Figure 2. Relationship between polymer compositions and phase transition temperatures.

The  $T_1$  values of the copolymers **4f–i** increased and the nematic phase changed into the smectic phase with increasing concentration of the 3,4,3',4'-*p*-terphenyltetracarboxdi-imide unit. The LC temperature ranges ( $\Delta T$ ) were a maximum at the composition  $x:y = 0.1:0.9$ . The copolymers **4g–i** have more stable LC phases than the homopoly(imide-carbonate) **4j** composed of 3,4,3',4'-*p*-terphenyltetracarboxdi-imide rings.

From these data, it is found that the 3,4,3',4'-*p*-terphenyltetracarboxdi-imide-rich copolymers **4f–i** tend to form thermotropic nematic and smectic phases, but the 3,4,3',4'-*p*-terphenyltetracarboxdi-imide-poor

Table 2. Transition temperatures of polymers **4a–j**.

Polymer	$T_g/^\circ\text{C}^b$	$T_S/^\circ\text{C}^b$	$T_N/^\circ\text{C}^b$	$T_I/^\circ\text{C}^b$	$\Delta T/^\circ\text{C}^b$	Mesophase
<b>4a</b> <sup>d</sup>	84	—	130	—	—	—
<b>4b</b>	84	—	—	—	—	—
<b>4c</b>	80	—	—	—	—	—
<b>4d</b>	82	—	—	—	—	—
<b>4e</b>	79	—	124	—	—	—
<b>4f</b>	85	—	125	142	17	Nematic
<b>4g</b>	78	—	123	155	32	Nematic
<b>4h</b>	78	—	117(117) <sup>c</sup>	177	60(60) <sup>c</sup>	Nematic
<b>4i</b>	79	127(124) <sup>c</sup>	175	192	65(68) <sup>c</sup>	Smectic/nematic
<b>4j</b> <sup>d</sup>	77	182(186) <sup>c</sup>	—	206	24(20) <sup>c</sup>	Smectic

<sup>a</sup> Data observed on the first heating scans.

<sup>b</sup>  $T_g$ : glass transition temperature;  $T_S$ : solid to smectic;  $T_N$ : smectic to nematic or solid to nematic;  $T_I$ : nematic to isotropic transition.  $\Delta T = T_I - T_N$  or  $T_I - T_S$  temperature range of mesophase.

<sup>c</sup> Observed on the second heating scans.

<sup>d</sup> See [26].

(3,4,3',4'-biphenyltetracarboxdi-imide-rich) copolymers **4b–d** are amorphous and form no LC phases despite the presence of some 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide units [17, 19, 24–26] having better mesogenicity than the 3,4,3',4'-biphenyltetracarboxdi-imide units. This might be ascribed to the fact that in the 3,4,3',4'-biphenyltetracarboxdi-imide-rich copolymers **4b–d**, the lower mesogenic properties of the di-imide ring negatively contribute to the LC formation and the orientation of the 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide ring is depressed by the 3,4,3',4'-biphenyltetracarboxdi-imide ring and the pentamethylene chain. It is assumed that introduction of the pentamethylene chain (odd spacer) next to the imide ring in the polymer backbones is not responsible for the formation of LC phases in the semi-rigid copoly(imide-carbonate)s **4b–i** composed of symmetric aromatic di-imide rings, owing to the disorder of the polymer chain linearity introduced by the combination of the pentamethylene chain with the interconnecting carbonate linkage having lower bond angles than the ester linkage [28–29]. However, our previously reported copoly(imide-carbonate)s [25], having traditional biphenyl mesogen units and aliphatic spacers between the carbonate linkage (scheme 1), show nematic phases independent of the copolymer compositions. These results suggest that the 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide unit still behaves as a good mesogen and plays an important role in the LC formation, together with the neighbouring aliphatic chains, in these kinds of semi-rigid copoly(imide-carbonate) described above.

Further details of the synthesis and characterization of the copolymers may be given. The monomers **1** and **2**, and the copolymers **4b–i** were prepared according to our previously described methods [24, 26]. A typical polycondensation procedure for the copolymer **4c** is described: a mixture of **1** (4.8 mmol, 0.223 g) and **2** (1.2 mmol, 0.0682 g) in a mol ratio of **1**:**2** = 0.8:0.2, and diphenyl carbonate (7.2 mmol, 0.154 g) was heated with stirring at 180°C for 2 h in the presence of zinc acetate (5 mg) in a nitrogen atmosphere. Then the mixture was allowed to react at 190°C for 30 min at a pressure of 16–17 Torr and finally at 200°C for 30 min at 1 Torr. After the polycondensation, the product was dissolved in chloroform and the solution poured into methanol to reprecipitate the polymer. The resulting polymer **4c** was collected by filtration, washed thoroughly with water and boiling methanol three times, and dried at 60°C for 24 h; yield 92%. Elemental analysis: calc. for (C<sub>28.6</sub>H<sub>27.6</sub>N<sub>2</sub>O<sub>7</sub>)<sub>n</sub> (511.38)<sub>n</sub>, C 67.17, H 5.45, N 5.48; found, C 67.10, H 5.57, N 5.45%. The 3,4,3'',4''-*p*-terphenyltetracarboxdi-imide-rich copolymers **4f–i** were polymerized under the following conditions: 180°C for 2 h under nitrogen, 200–205°C for 30 min at 16–17 Torr and finally at 220–225°C for 30 min at a pressure of

1 Torr; yield 85%. Elemental analysis for the copolymer **4h**: calc. for (C<sub>33.4</sub>H<sub>32.4</sub>N<sub>2</sub>O<sub>7</sub>)<sub>n</sub> (573.87)<sub>n</sub>, C 69.90, H 5.70, N 4.88; found, C 69.90, H 5.61, N 4.82%.

The <sup>13</sup>C NMR spectra were obtained with a JEOL LMN EX270 spectrometer using CDCl<sub>3</sub> as solvent. The FTIR spectra were recorded on a Jasco FTIR 5300 spectrometer using KBr disks. The DSC measurements were performed with a Shimadzu DSC-60 calorimeter at heating and cooling rates of 10°C min<sup>-1</sup> under nitrogen. The optical textures of polymers were observed with a polarizing microscope (Nikon) equipped with a hot stage (magnification × 200). The variable temperature X-ray analyses were carried out using a Rigaku Denki RINT 2500 generator equipped with a temperature controller with CuK<sub>α</sub> irradiation. The number average molecular masses ( $\bar{M}_n$ ) and molecular mass distributions ( $\bar{M}_w/\bar{M}_n$ ) were estimated by size exclusion chromatography with a Jasco 930-RI refractometer and a column combination (K-803/K-804) (Shodex), using polystyrene standards and chloroform as eluent.

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