

## Effect of Branched Methyl Group in Lateral Substituent on Main Chain Liquid Crystalline Polyesters

Koichi FUJISHIRO\* and Robert W. LENZ

*Polymer Science and Engineering Department, University of Massachusetts,  
Amherst, MA 01003*

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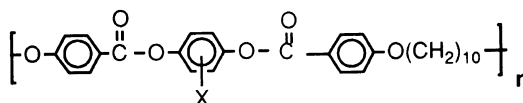
**ABSTRACT:** To investigate the effect of a branched methyl group in a lateral long-chain substituent on liquid crystalline properties, two polyesters containing a decamethylene spacer and a triad mesogen with 2-methyl-1-butoxy and *n*-butoxy substituents, **I** and **II**, respectively, were prepared and characterized by wide angle X-ray diffraction (WAXD), thermal and optical methods. Both polymers exhibited the exactly similar crystalline state and melt transition. In contrast, the isotropization transition of **I** was observed at lower temperature than **II**. The data obtained suggest that the branched methyl group in the butoxy substituent did not influence the formation of the crystal and the melting transition, but it depressed only the isotropization transition.

**KEY WORDS** Liquid Crystalline Polyesters / Lateral Substituent / Wide Angle X-Ray Diffraction / Polymeric Crystal / Melting Transition / Isotropization Transition /

Some wholly rigid aromatic liquid crystalline polyesters derived typically from symmetric monomers such as *p*-hydroxybenzoic acid have high melting transition temperatures over 400°C, which limited both the application of these polymers and characterization of their properties. These high melting transitions can be decreased by several types of structural modifications including either the introduction of a flexible spacer group in the backbone, placement of lateral substituents on the aromatic rings, introduction of molecular kinks or bends in repeating units, or copolymerization with other rodlike comonomers.<sup>1</sup>

Lateral substituents on main chain liquid crystalline polymers (LCPs) generally reduce both the melting,  $T_m$ , and the isotropization transitions,  $T_i$ , because of decrease of the symmetry and axial ratio of the mesogenic

units. In our laboratory, the following series of LCPs with various lateral substituents have been investigated to obtain the systematic effect of the substituents on the liquid crystalline properties.<sup>2-4</sup>



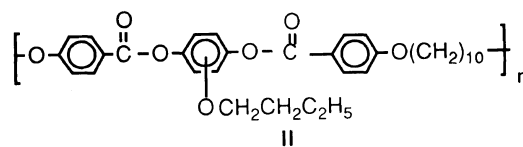
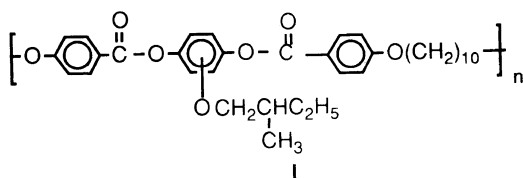
in which X is (CH<sub>2</sub>)<sub>m</sub>CH<sub>3</sub>, O(C<sub>2</sub>H<sub>4</sub>O)<sub>m</sub>CH<sub>3</sub>, etc.

The effects of substituents on  $T_i$  can be divided into two categories: steric and polar effects.<sup>3</sup> Melting transitions,  $T_m$ , of the long-chain lateral substituted polymers decreased in an approximately odd-even effect until the substituent contained six atoms, and leveled off with a further increase in the length of the

\* Present address: Chemicals Laboratory, Advanced Materials & Technology Research Laboratories, Nippon Steel Corporation, 1618 Ida, Nakahara-ku, Kawasaki 211, Japan.

pendent group.<sup>2,4</sup> Furthermore, these polymers exhibited very wide temperature ranges of enantiotropic liquid crystalline phases. In contrast, chiral polyesters with a (*S*)-2-methyl-1-butoxy group showed very narrow temperature ranges in formation of liquid crystalline phases. In addition, they were converted to monotropic LCPs by annealing process just below their  $T_m$ s.<sup>5</sup> These properties may result from the steric requirements of the branched methyl group in the 2-methyl-1-butoxy substituent.

In this study, we have further investigated the effects of a branched methyl group in a long-alkyl substituent on the LC phase behavior of the polymer. For this purpose, the following two polymers were prepared, and their phase behaviors were compared to each other:

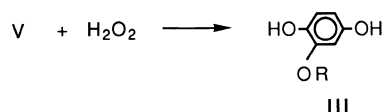
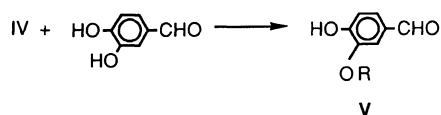
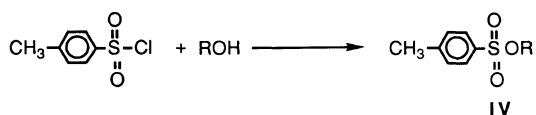


The racemic polymer, **I**, has a branched methyl group in the substituent, while **II** contains a *n*-butoxy group as a substituent. Therefore, both polymers have the same effective length in the side alkyl chain.

## EXPERIMENTAL

### Synthesis of Monomers

Lateral substituted hydroquinones were synthesized in three steps according to the reaction scheme shown below<sup>4</sup>:



in which R is  $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{C}_2\text{H}_5$  (**IIIi**, **IVi**, and **Vi**), or  $-\text{CH}_2\text{CH}_2\text{C}_2\text{H}_5$  (**IIIn**, **IVn**, and **Vn**).

2-[(±)-2-Methyl-1-butoxy]hydroquinone, **IIIi**, was prepared as previously described.<sup>5</sup>

*Butyl p*-toluenesulfonate, **IVn**.<sup>6</sup> In the first step, a mixture of 51 g of pyridine and 9.71 g of 1-butanol was placed in a 200 ml flask, which was cooled below 20°C in an ice bath. To this solution was added 25.7 g of *p*-toluenesulfonyl chloride in small portions with stirring, and the reaction mixture was stirred for 3 hours below 20°C after the addition was completed. A large excess of cold dilute hydrochloric acid and ice was added after completion of the reaction, and the mixture was extracted three times with dichloromethane. The dichloromethane solution was washed with water, dried over anhydrous sodium sulfate, filtered and evaporated to afford 25.9 g of colorless liquid (yield 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ = 0.86 (3H, t, *J* = 7.8 Hz), 1.29–1.39 (2H, m), 1.59–1.66 (2H, m), 2.45 (3H, s), 4.03 (2H, t, *J* = 6.4 Hz), 7.35 (2H, d, *J* = 8.3 Hz), 7.79 (2H, d, *J* = 7.5 Hz). *Elemental Anal.*, Found; C, 57.82%; H, 7.08%; S, 14.10%. Calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>3</sub>S: C, 57.90%; H, 7.01%; S, 14.05%.

3-Butoxy-4-hydroxybenzaldehyde, **Vn**. In the second step, a solution of 15.2 g of 3,4-dihydroxybenzaldehyde in 180 ml of ethanol

was added to 90 ml of 10% sodium hydroxide solution. After the solution was heated at 50°C, 25.0 g of **IV** was added dropwise to the solution. The mixture was stirred at 50°C for 5 hours, after which the solvent was removed by evaporation *in vacuo*, and the residue was dissolved in 200 ml of water and extracted with diethyl ether. The remaining aqueous solution was acidified with dilute hydrochloric acid, extracted with diethyl ether, and the ether solution was washed with a saturated sodium bicarbonate solution and with water, successively, then dried over anhydrous sodium sulfate. After the ether solution was evaporated *in vacuo*, 60 ml of a mixture of chloroform and petroleum ether (1:1 volume ratio) was added to the residue, the precipitate was removed by filtration, and the filtrate was concentrated and purified by column chromatography (silica gel, chloroform) to yield 4.5 g of brown liquid. This liquid was a mixture of the desired product, **Vn**, and 4-butoxy-3-hydroxybenzaldehyde, **V'n**. The molar ratio of **Vn** and **V'n** could be determined by the proton peaks corresponding to the formyl groups. **Vn**:**V'n**=81:19 (mol/mol). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ=0.98 (3H, t, *J*=7.8 Hz), 1.45—1.54 (2H, m), 1.78—1.86 (2H, m), 4.11 (2H, t, *J*=6.8 Hz), 6.45 (1H, s), 7.04 (1H, d, *J*=7.8 Hz), 7.39—7.41 (2H, m), 9.81 (1H, s).

**2-Butoxyhydroquinone, III<sub>n</sub>**. In the third step, 4.1 g of the mixture of **Vn** and **V'n** was dissolved in 29 ml of 1.5*N* sodium hydroxide solution, and to this solution was added dropwise 2.46 g of a 30% hydrogen peroxide solution with stirring. The solution was stirred for 2 hours, and the temperature of the solution was kept at less than 30°C during the reaction. The reaction mixture was acidified with dilute hydrochloric acid and extracted three times with diethyl ether. The ether solution was washed with sodium metabisulfite solution and water, respectively, then dried over anhydrous sodium sulfate. After evaporation *in vacuo*, the residue was purified by column chromatography (silica gel, di-

chloromethane). After the eluent was evaporated, the residual solid was recrystallized with a mixture of hexane and chloroform (65:35 volume ratio) to afford 1.64 g of gray crystal (yield 42%). mp 81.4—92.8°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ=0.97 (3H, t, *J*=7.3 Hz), 1.42—1.53 (2H, m), 1.73—1.81 (2H, m), 3.97 (2H, t, *J*=6.3 Hz), 4.7—5.0 (1H, s), 5.3 (1H, s), 6.30 (1H, dd, *J*=8.6 Hz, 2.9 Hz), 6.43 (1H, d, *J*=2.9 Hz), 6.76 (1H, d, *J*=8.8 Hz). *Elemental Anal.*, Found: C, 65.90%; H, 7.80%. Calcd for C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>: C, 65.95%; H, 7.69%.

The 4,4'-dichloroformyl- $\alpha,\omega$ -diphenoxydecane monomer was prepared according to a method previously described.<sup>7</sup>

#### Polymer Synthesis

The polymers were prepared by the solution polymerization of **III** with 4,4'-dichloroformyl- $\alpha,\omega$ -diphenoxydecane monomer. In 20 ml of dry dichloromethane (distilled over phosphorous pentoxide) was dissolved 1.0 g of **III** with 1.4 ml of triethylamine (distilled over potassium hydroxide), and a solution of an equimolar amount of 4,4'-dichloroformyl- $\alpha,\omega$ -diphenoxydecane in 20 ml of dry dichloromethane was added dropwise. The reaction mixture was stirred at room temperature for 24 hours and at reflux temperature for 24 hours. The reaction mixture remained homogeneous throughout the entire polymerization. The polymer solution was poured into 250 ml of methanol, and the precipitated polymer was washed three times with methanol and dried at 70°C *in vacuo*. The yield and the characterization data for the two polymers are collected in Table I.

**I**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ=0.7—0.9 (6H, m), 1.3—2.0 (19H, m), 3.7—3.9 (2H, m), 4.05 (4H, t, *J*=6.3 Hz), 6.80 (1H, d, *J*=8.5 Hz), 6.86 (1H, s), 6.98 (4H, d, *J*=8.6 Hz), 7.19 (1H, d, *J*=8.5 Hz), 8.14 (4H, d, *J*=8.5 Hz).

**II**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ=0.84 (3H, t, *J*=7.8 Hz), 1.3—1.6 (14H, m), 1.6—1.7 (2H, m), 1.83 (4H, t, *J*=6.8 Hz), 3.96 (2H, t, *J*=6.3 Hz), 4.05 (4H, t, *J*=6.8 Hz), 6.81 (1H,

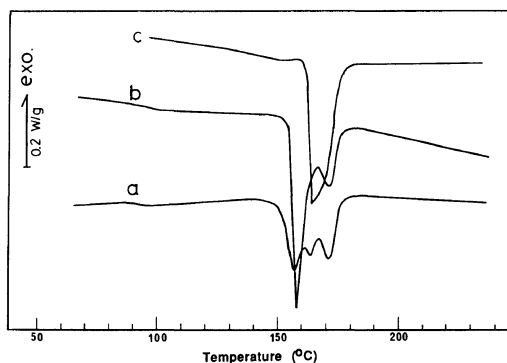
**Table I.** Yields and molecular weights of polymers, I and II

Polymer	Yield	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	molecular weight			
	%			
I	89	29000	65000	2.2
II	95	35000	99000	2.8

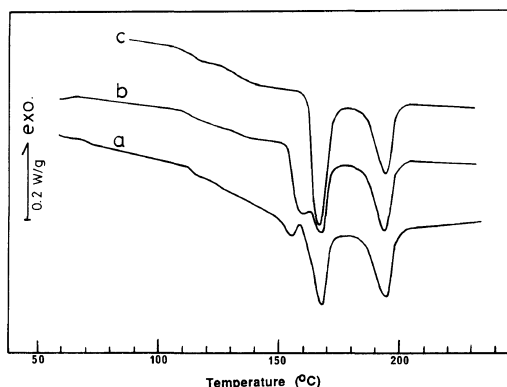
dd,  $J=8.6$  Hz, 2.0 Hz), 6.82 (1H, d,  $J=2.0$  Hz), 6.97 (4H, d,  $J=8.3$  Hz), 7.17 (1H, d,  $J=8.3$  Hz), 8.14 (4H, m).

#### Characterization of Polymers

$^1\text{H}$  NMR spectra were obtained with a JOEL EX-400 spectrometer on solutions in deuterated chloroform ( $\text{CDCl}_3$ ). The molecular weights of the polymers were also determined on a Waters GPC instrument with a refractive index detector using tetrahydrofuran as an eluent and polystyrene standards for calibration. Liquid crystalline transitions were characterized by a differential scanning calorimetry (DSC), by a polarized light microscope, and by wide angle X-ray diffraction (WAXD). Thermal analyses of the polymers were obtained on a Mettler TA-3000 System at a scanning rate of  $10^\circ\text{C min}^{-1}$ . The peak maxima of the phase transitions were recorded for each sample after the first heating and cooling scans. For the annealing experiment of the polymers, all of the thermograms were taken after the polymers were cooled below their isotropization temperatures at a cooling rate of  $10^\circ\text{C min}^{-1}$ , then reheated to a given temperature, annealed at that temperature for 3 hours, and cooled to  $50^\circ\text{C}$  at a cooling rate of  $10^\circ\text{C min}^{-1}$ . Textures were observed with a Olympus optical microscope equipped with a hot stage. Oriented fibers were drawn at  $50^\circ\text{C}$  above the isotropic temperature,  $T_i$ , and annealed at  $20^\circ\text{C}$  below the melting temperature,  $T_m$ , for 12 hours under nitrogen atmosphere. WAXD patterns of the oriented



**Figure 1.** DSC thermograms of polymer I (19.0 mg) in heating scans: (a) without annealing; (b) annealed at  $145^\circ\text{C}$ ; (c) annealed at  $155^\circ\text{C}$ .



**Figure 2.** DSC thermograms of polymer II (19.4 mg) in heating scans: (a) without annealing; (b) annealed at  $147^\circ\text{C}$ ; (c) annealed at  $157^\circ\text{C}$ .

fibers were obtained on Rigaku R-AXIS IIC equipped with an imaging plate using Ni filtered Cu radiation.

## RESULTS AND DISCUSSION

DSC thermograms for the two polymers with different substituents (I, 2-methyl-1-butoxy; II, butoxy) are shown in Figures 1 and 2, respectively. Both thermograms of the polymers, I (Figure 1a) and II (Figure 2a), without annealing contained three endotherms. Two lower temperature endotherms were observed at the similar temperatures for both

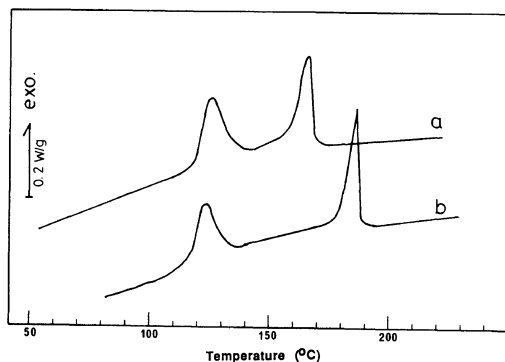
polymers, **I** and **II**, while the highest temperature endotherm of **II** was observed at higher temperature than that of **I**. Visual examination of the polymers on a hot-stage of a polarizing microscope verified that the highest temperature endotherms corresponded to the clearing or isotropization temperatures,  $T_i$ , and lower temperature transitions to melting transitions,  $T_m$ .

As multiple melting endotherms have been found in several polymers described in our previous report<sup>5</sup> and in the studies by Griffin and Havens,<sup>7</sup> annealing processes increase degrees of crystallinity of the polymers and influence the melting transitions. Therefore, thermograms of the polymers after annealing close at the melting transitions are also shown in Figures 1 and 2. By the annealing treatment, the endotherm was shifted to a higher transition temperature with a larger enthalpy than those without annealing, finally, only one melting transition was observed at the same temperature for both polymers. In contrast, the last endotherm, which corresponded to the isotropization transition, was not varied by the annealing.

In the cooling scan from the isotropic state, thermograms of both polymers are shown in Figure 3. The transitions from the isotropic state to the LC state were observed at 166°C and 185°C for polymers **I** and **II**, respectively, while the transitions from the LC state to the crystal were observed at 125°C for both polymers. These thermograms were not affected by the annealing treatment.

In order to obtain information on molecular packing of the polymers in the solid state, oriented samples with the annealing treatment were prepared for WAXD studies. The WAXD pattern of oriented specimen of **II** is seen in Figure 4, and the equatorial WAXD profiles of both polymers are shown in Figure 5. Surprisingly, the exactly same WAXD patterns were obtained for both polymers as seen in Figures 4 and 5.

To sum up the DSC and WAXD results,



**Figure 3.** DSC thermograms of polymers **I** and **II** in cooling scan: (a) polymer **I** (19.0 mg); (b) polymer **II** (19.4 mg).

both annealed polymers exhibited the same crystalline state, which behaved the similar melting transition, while they showed different the isotropization transitions. The same WAXD patterns of spacings on the meridian were expected for both polymers because they came from the effective lengths, 30 Å, of the repeating unit parallel to the same polymeric backbone. Even the same pattern on the equator indicates that the branched methyl group in the butyl chain did not dominate the molecular packing in the solid state. In contrast, the branched methyl group influenced the liquid crystalline phase to depress the isotropization transition temperature.

The phase behaviors of these polymers can be interpreted according to the thermodynamics proposed by Keller, Unger, and Percec.<sup>8</sup> A schematic free energy diagram for the present polymers is shown in Figure 6. The free energies of the crystals,  $G_k$  for both polymers are exactly identical to each other because both polymers exhibited the same type of crystal. The free energies in the liquid crystalline state,  $G_{lc}$ , for both polymers also must be likely equal because the melting transitions were observed at the same temperature range. Additionally, the liquid crystalline property must come from the triad-ester mesogen, whose axial ratio is defined as the length of

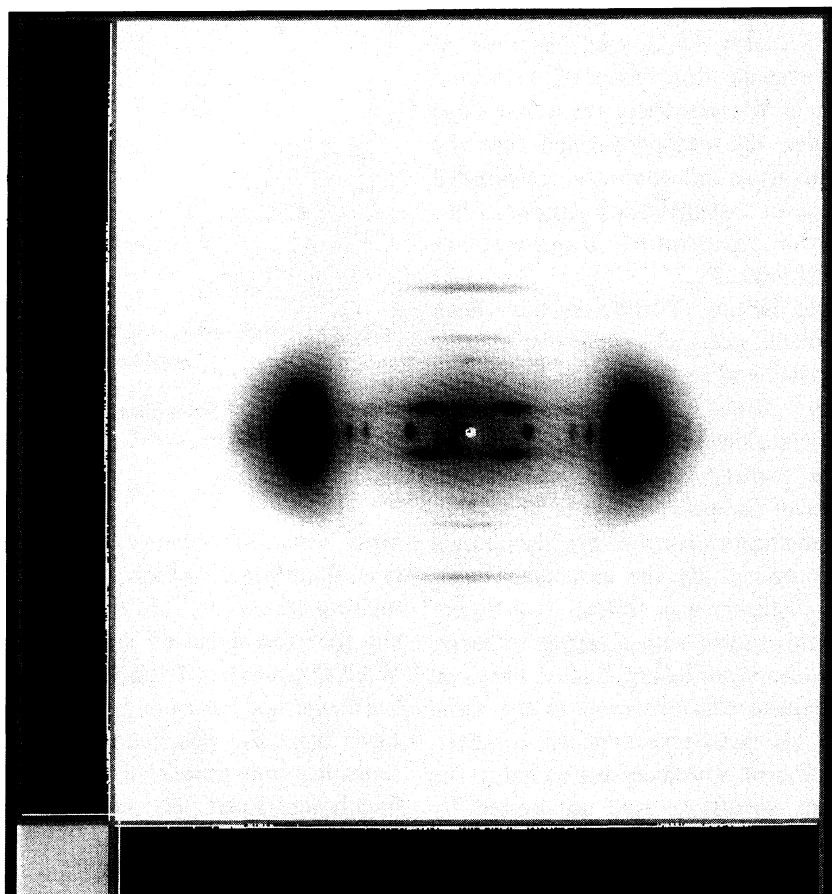


Figure 4. WAXD data of oriented specimen of II.

the triad mesogen along the long axis to the diameter described by the butoxy substituent, so that the branched methyl group presumably does not contribute to the free energy of the liquid crystal,  $G_{lc}$ . In contrast, the free energy of the isotropic liquid of I,  $G_i'$  must be lower than that of II,  $G_i''$ , since the branched methyl group decreases the rigidity of the triad mesogen compared to II. In this situation, the polymer should be in the lowest free energy state represented by the lowest free energy path shown in Figure 6. That is, the crossing point of  $G_k$  and  $G_{lc}$  corresponds to the melting point,  $T_m$ , which of both polymers were identical. In contrast, the other cross section of  $G_{lc}$  and  $G_i$ , which corresponds to

the isotropization transition ( $T_i$ ),  $T_i'$  of I came close to  $T_m$ , while  $T_i''$  of II appeared at higher temperature than  $T_i'$ . The annealing treatment of the polymer decreased  $G_k$  to increase the melting point slightly.

Weissflog and Demus reported the different effect of a branched methyl group in a lateral alkyl substituent on phase behaviors of low molecular weight liquid crystals (LMWLCs) based on 2,4-dihydroxybenzoate.<sup>9</sup> In those cases, the lateral branched methyl group strongly enhanced the melting temperature, and it also lowered the isotropization remarkably. The different influence on the melting transition in this polymeric system presumably causes that the macromolecular backbone

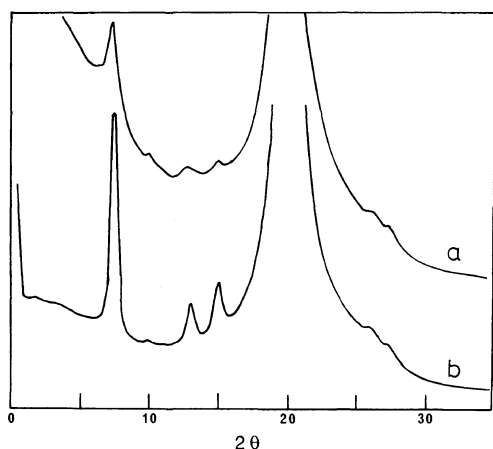


Figure 5. Equatorial WAXD profiles: (a) polymer I; (b) polymer II.

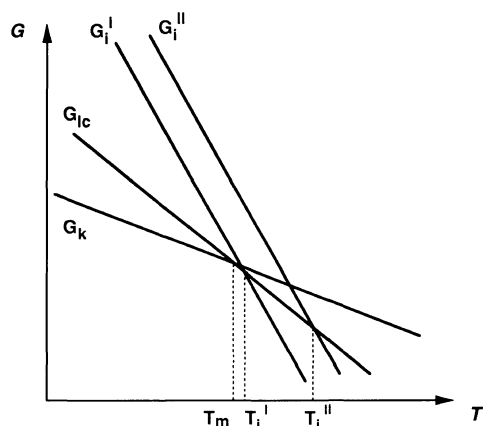


Figure 6. Schematic free energy diagram for the present polymers:  $G_k$ , free energy of the crystal;  $G_{lc}$ , free energy of the liquid crystal;  $G_i^I$ , free energy of the isotropic liquid I;  $G_i^{II}$ , free energy of the isotropic liquid II;  $T_m$ , melt transition temperature;  $T_i^I$ , isotropization transition temperature of I;  $T_i^{II}$ , isotropization transition temperature of II.

contributes relatively more on formation or melting transition of the crystal than the long lateral substituent compared to the LMWLCs.

## CONCLUSION

Both polymers, I containing 2-methyl-1-butoxy substituent and II containing *n*-butoxy substituent, exhibited the exactly similar crystalline state and melting transition. In contrast, the isotropization transition of I was observed at lower temperature than II. The data obtained suggest that the branched methyl group in the butoxy substituent did not influence the formation and the melting transition of the crystal, but it depressed the isotropization transition. These phase behaviors could be interpreted according to the thermodynamics.

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