

# NOTES

## Liquid Crystalline Polymers: A Comparison of Two Synthetic Approaches to Thermotropic Polymers

### INTRODUCTION

Segmented thermotropic main-chain polymers that melt to form a structured fluid phase have been of considerable interest for the past two decades.<sup>1</sup> These thermotropic materials are becoming more prominent in the development of high-performance materials such as fibers, films, and molded parts.<sup>2</sup> Synthetically, a variety of polymerization strategies have been employed in the preparation of liquid crystalline polymers (LCPs).<sup>3</sup> One common strategy relies on the simultaneous construction of the mesogenic unit during polymerization. This method was introduced by Wegner<sup>4</sup> and has been used extensively in the preparation of LCPs that incorporate triad mesogens.<sup>5,6</sup> A second commonly used strategy makes use of a triad monomer unit that can be polymerized directly with a variety spacer groups.<sup>7,8</sup> Both methods yield high molecular weight polymers. However, neither method has been found to be very convenient for large-scale preparations of polymers due to the number of synthetic transformations necessary to yield LCPs.

Recently, Bilibin developed a direct route to triad "mesogenic monomers."<sup>9,10</sup> These new monomers are viable alternatives for the synthesis of high molecular weight LCPs and may be used to circumvent some of the problems associated with the previously described methods.

In this note we report on the properties of a series of LCPs prepared by two different synthetic routes. The first, method A, utilizes the simultaneous construction method, while the latter, method B, employs Bilibin's "mesogenic monomer" method. The synthetic strategies are outlined in Scheme 1.

### EXPERIMENTAL

#### Materials

Terephthaloyl chloride, 2-bromoterephthalic acid, *p*-hydroxybenzoic acid, methyl-*p*-hydroxybenzoate, benzylchloride, 5% palladium on carbon, and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (Aldrich) were used as received. Tetrachloroethane,

triethylamine, pyridine, 4-dimethylaminopyridine, thionyl chloride, triethylene glycol, decanediol, and dodecanediol (Aldrich), as well as methylene chloride, chloroform, and diphenylether (Fisher Scientific), were purified using standard techniques. Silica gel (60 mesh flash), was obtained from Universal Scientific Inc.

#### Characterization

IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer using KBr pellets. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were obtained on a Bruker AC300 in deuteriochloroform using tetramethylsilane (TMS) as the internal standard. Inherent viscosities were determined with a Cannon-Ubbelohde type viscometer at a concentration of 0.5 g/dL in chloroform at ambient temperatures, unless otherwise stated. Gel permeation chromatography (GPC) (Waters 150-GPC, 2 × 10 micron Polymer Labs mixed columns, chloroform) was used to determine polydispersity as well as  $\bar{M}_n$  and  $\bar{M}_w$  values. Molecular weights were calibrated versus polystyrene standards. The thermal properties were investigated with a Perkin-Elmer DSC 7 at heating/cooling rates of 20 K/min unless otherwise indicated. A Zeiss Universal polarized microscope equipped with cross polarizers and a Leitz Wetzlar model 350 hot stage was used for optical microscopy.

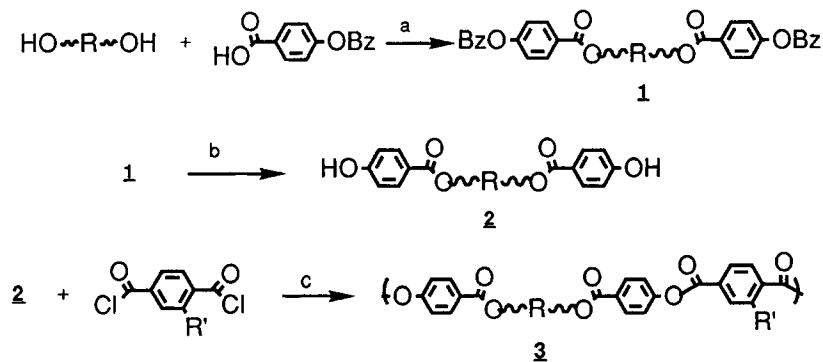
#### Monomer Synthesis

The diacid chlorides of 2-bromoterephthalic acid and terephthalic acid were prepared by refluxing the acid in an excess of thionyl chloride. After complete dissolution, the excess thionyl chloride was removed by distillation. The crude 2-bromoterephthaloyl chloride was purified by vacuum distillation, 110°C < 1 mm, while terephthaloyl chloride was recrystallized from dry hexane. The (trifluoromethyl) terephthaloyl chloride was synthesized as previously reported.<sup>11</sup>

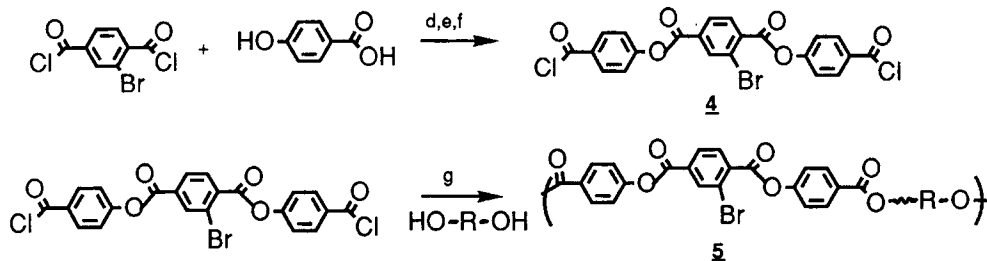
#### *Triethyleneglycol-bis-benzyloxybenzoate*

A 12-L three-neck round-bottom flask equipped with a magnetic stirrer and a nitrogen inlet was charged with 32.00 g of *p*-benzyloxybenzoic acid, 10.53 g triethylene glycol (distilled, 111°C, 0.11 mmHg), 4.0 L methylene chloride, 25.7 g 4-dimethylaminopyridine, and 40.3 g 1-

## Method A



## Method B



Scheme 1 Synthetic strategy for the preparation of triad LCPs.

(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI).<sup>12</sup> The reaction mixture was stirred at room temperature for 3 days. The reaction mixture was then concentrated to 600 mL by removal of the methylene chloride under reduced pressure, then washed with saturated sodium bicarbonate (3 × 500 mL) and water (2 × 600 mL). The aqueous layers were combined and extracted with methylene chloride (300 mL). All the organic layers were combined and dried over sodium sulfate. The solvent was removed under reduced pressure leaving a yellow solid, which was purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, 98.5/1.5%). The fractions containing the product (*R<sub>f</sub>* = 0.7) were combined and evaporated to a white solid 34.5 g (86%), m.p. 74–75°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz) δ (ppm) 8.0 (*d*, 4H Ar-H *o* to ester) 7.4 (*m*, 10H ph Ar-H) 7.0 (*d*, 4H, *o* to O-Bz) 5.1 (*s*, 4H, OCH<sub>2</sub>-Ph) 4.45 (*t*, 4H, CH<sub>2</sub>-OCO) 3.8 (*t*, 4H, OCH<sub>2</sub> β to ester) 3.6 (*s*, 4H, OCH<sub>2</sub>CH<sub>2</sub>O γ to ester). IR (KBr) 3060, 3030 (*m*, Ar-H) 2990–2775 (*s*, aliphatic CH), 1710 (*vs.*, ester C=O), 1605 cm<sup>-1</sup> (*s*, aromatic C=C).

*Triethyleneglycol-bis-hydroxybenzoate*

In a Parr hydrogenator bottle, 10.50 g (0.018 mol) of triethyleneglycol-bis-benzyloxybenzoate was suspended in absolute ethanol and degassed by bubbling nitrogen into the solution for 10 min. The catalyst, 5% palladium on

carbon, was added, and the bottle was placed on a Parr hydrogenator at 50 psig for 24 h. After this period the reaction was shown to be complete by thin-layer chromatography (TLC) (2.5% CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub>); the catalyst was removed by filtration with a Millipore filter, and the solutions were concentrated. The combined products were recrystallized from methanol/water (90/10) followed by filtering and drying (vacuum oven for 48 h at 70°C); this procedure yielded 6.68 g (93%) of a white crystalline compound, m.p. 137–140°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm) 9.0 (*s*, 2H, AR-OH) 8.0 (*d*, 4H, *o* to AR-CO<sub>2</sub>) 7.0 (*d*, 4H, *o* to AR-O) 4.35 (*t*, 4H, CH<sub>2</sub>-OCO) 3.8 (*t*, 4H, OCH<sub>2</sub>β to ester) 3.6 (*s*, 4H, OCH<sub>2</sub>CH<sub>2</sub>O γ to ester). IR (KBr) 3600–3040 (*s*, Ar-OH) 2990–2775 (*s*, aliphatic CH), 1710 (*vs.*, ester C=O), 1605 cm<sup>-1</sup> (*s*, aromatic C=C).

ANAL: Calcd. for C<sub>20</sub>H<sub>22</sub>O<sub>8</sub>: C, 61.53%; H, 5.68%.

Found: C, 61.41%; H, 5.72%.

*2-Bromoterephthaloyloxybenzoic acid*

The preparation of this material parallels the procedure by Bilbin.<sup>9</sup> After acidification the desired diacid was isolated and dried under vacuum for 3 days at 70°C. M.p. > 300°C (*d*), yield 86%. The diacid was then converted

to the corresponding diacid chloride (see below) without further purification.

#### 2-Bromoterephthaloyloxybenzoyl chloride

The acid chloride was prepared by refluxing a slurry of 2-bromoterephthaloyloxy bisoxybenzoic acid in an excess of thionyl chloride with 1 mL of dimethylformamide acting as catalyst. When gas evolution ceased (3–5 h), the reaction was complete and the excess thionyl chloride was removed by distillation. The remaining off-white residue was recrystallized twice from dry toluene and washed with hexanes to yield a white crystalline solid (yield 77%), m.p. 186–188°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 8.58 (s, 1H, *o* to Ar-Br) 8.25 (m, 5H, 4 *o* to Ar-COCl and 1 *p* to Ar-Br) 8.17 (d, 1H *m* to Br) 7.42 (pair of *d*, 4H *o* to Ar-OOC-). IR (KBr) 3060, 3030 (*m*, Ar-H), 1775 (*s*, formoyl chloride) 1725 (*s*, ester C=O) 1600 (*s*, aromatic C=C).

ANAL. Calcd for C<sub>22</sub>H<sub>11</sub>BrCl<sub>2</sub>O<sub>6</sub>: C, 50.60%; H, 2.12%; Br, 15.30%; Cl, 13.57%.

Found: C, 50.78%; H, 2.26%; Br, 15.32%; Cl, 13.10%.

## POLYMER SYNTHESIS

### Method A

A general procedure for the polymerization of the bis-phenolic monomers with a diacid chloride is as follows.

To a stirred slurry of 7.0 g (0.0179 mol) of triethyleneglycol-bis-4-hydroxybenzoate in 100 mL dry methylene chloride was added 12.47 mL (0.0895 mol) of tri-

ethylamine. After stirring for 15 min a clear solution was obtained. The appropriate diacid chloride (0.0179 mol) was then added dropwise via a pipet over a 20-min period. The mixture became cloudy after the addition; stirring was continued for 3 h. After this time, IR analysis indicated that the reaction was complete. However, the mixture was stirred for an additional 16 hs to ensure complete polymerization.

The solution was then partitioned between methylene chloride and 1 N HCl; the organic layer was washed again with 1 N HCl followed by washing with saturated sodium chloride and precipitated into rapidly stirred solution of hexanes. The resulting white stringy polymer was filtered, washed with hexane, and dried for 24 h in a vacuum oven (yield 89%). Refer to Table I for polymer notation.

Polymer AI: <sup>1</sup>H-NMR 8.45 (*s*, 4H, terephthaloyl Ar-H), 8.1 (*d*, 4H, oxybenzoate *o* to Ar-CO<sub>2</sub>), 7.5 (*d*, 4H, oxybenzoate *o* to Ar-O) 4.4 [*t*(app), 4H, CH<sub>2</sub>-OCO], 3.8 (*t*, 4H, OCH<sub>2</sub> β to ester) 3.6 (*s*, 4H, OCH<sub>2</sub>CH<sub>2</sub>O γ to ester). IR (KBr) 3040 (*m*, aromatic Ar-H), 2910–2820 (vs., aliphatic CH), 1740, 1720 (*s*, ester C=O's) 1600 cm<sup>-1</sup> (*m*, C=C).

Polymer AII<sub>1</sub>: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz) δ (ppm) 8.53 (*s*, 1H, *o* to Ar-Br) 8.18 (*m*, 6H, Ar-H *o* to Ar-CO<sub>2</sub>) 7.37 (4H, *o* to Ar-O) 4.45 (*t*, 4H, CH<sub>2</sub>-OCO) 3.8 (*t*, 4H, OCH<sub>2</sub> β to ester) 3.6 (*s*, 4H, OCH<sub>2</sub>CH<sub>2</sub>O γ to ester). IR (KBr) 3040 (*m*, aromatic Ar-H), 2910–2820 (vs., aliphatic CH), 1740, 1720 (*s*, ester C=O's) 1600 cm<sup>-1</sup> (*m*, C=C).

Polymer AIII: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz) δ (ppm) 8.65 (*s*, 1H, *o* to Ar-CF<sub>3</sub>) 8.5 (*d*, 1H, *p* to Ar-CF<sub>3</sub>) 8.18 (*m*, 5H; 4H *o* to Ar-CO<sub>2</sub>, 1H *m* to Ar-CF<sub>3</sub>) 7.37 (4H, *o* to Ar-O) 4.5 (*t*, 4H, CH<sub>2</sub>-OCO) 3.8 (*t*, 4H, OCH<sub>2</sub> β to ester)

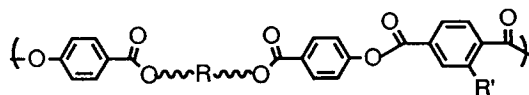
Table I Molecular Weight Data for Polymers Prepared by Methods A and B

Polymer	R	R'	Yield %	η <sub>inh</sub> <sup>a</sup>	$\bar{M}_n$ (10 <sup>-3</sup> ) <sup>b</sup>	$\bar{M}_w / \bar{M}_n$
Method A						
AI	—CH <sub>2</sub> (CH <sub>2</sub> O—CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> —	H	95	0.41 <sup>c</sup>		
AII <sub>1</sub>	—CH <sub>2</sub> (CH <sub>2</sub> O—CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> —	Br	99	0.18	8.9	2.2
AII <sub>2</sub>	—CH <sub>2</sub> (CH <sub>2</sub> O—CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> —	Br	94	0.28	15.2	1.9
AII <sub>3</sub>	—CH <sub>2</sub> (CH <sub>2</sub> O—CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> —	Br	95	0.35	14.7	2.8
AIII	—CH <sub>2</sub> (CH <sub>2</sub> O—CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> —	CF <sub>3</sub>	100	0.19		
Method B						
BI	—CH <sub>2</sub> (CH <sub>2</sub> O—CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> —	Br	89	0.58	24.7	2.0
BII <sub>1</sub>	—(CH <sub>2</sub> ) <sub>10</sub> —	Br	91	0.72	24.5	2.9
BII <sub>2</sub>	—(CH <sub>2</sub> ) <sub>10</sub> —	Br	88	0.43	21.3	2.4
BIII	—(CH <sub>2</sub> ) <sub>12</sub> —	Br	93	0.87	31.0	2.9

<sup>a</sup> Inherent viscosities, dL/g, determined in chloroform using a Cannon-Ubbelohde viscometer at a solution concentration of 0.5 g/dL at ambient temperature.

<sup>b</sup> Number-average molecular weight determined by GPC vs. polystyrene standards.

<sup>c</sup> Solvent CF<sub>3</sub>CO<sub>2</sub>H.



3.75 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>O  $\gamma$  to ester). IR (KBr) 3040 (m, aromatic Ar-H), 2910–2820 (vs., aliphatic CH), 1740, 1720 (s, ester C=O's) 1600 cm<sup>-1</sup> (m, C=C).

### Method B

Two separate polymerization methods were used in the polymerization of 2-bromoterephthaloyloxy-bis-benzoyl chloride with a variety of diols.

The first method parallels that reported by Bilibin<sup>9,10</sup> using high-temperature solution condensation with diphenyl ether as the solvent. After polymerization, the resulting polymer/solvent mixture was precipitated into acetone; the polymer was separated by filtration and continuously extracted in a Soxhlet with acetone for 10 h followed by drying in a vacuum oven at 60°C.

Alternatively, room temperature solution condensation using tetrachlorethane with pyridine was also found to be an effective mode of preparation for these polymers.<sup>13</sup> After the polymerization was complete, the reaction mixture was precipitated into a large volume of methanol, the polymer was filtered washed with methanol, soxhlet extracted with acetone and vacuum dried at 60°C. Refer to Table I for polymer notation.

Polymer BI: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm) 8.53 (s, 1H, *o* to Ar-Br) 8.18 (m, 6H, *o* to Ar-CO<sub>2</sub>) 7.37 (4H, *o* to Ar-O) 4.45 (t, 4H, CH<sub>2</sub>-OCO) 3.8 (t, 4H, OCH<sub>2</sub>  $\beta$  to ester) 3.6 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>O  $\gamma$  to ester). IR (KBr) 3040 (m, aromatic Ar-H), 2910–2820 (vs., aliphatic CH), 1740, 1720 (s, ester C=O's) 1600 cm<sup>-1</sup> (m, C=C).

Polymer BII: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm) 8.53 (s, 1H, *o* to Ar-Br) 8.18 (m, 6H, *o* to Ar-CO<sub>2</sub>) 7.37 (4H, *o* to Ar-O) 4.35 (t, 4H, CH<sub>2</sub>-OCO) 1.7 (t, 4H, CH<sub>2</sub>  $\beta$  to ester) 1.4 [m (broad), 12H, internal CH<sub>2</sub>]. IR (KBr) 3040 (m, aromatic Ar-H), 2910–2820 (vs., aliphatic CH), 1740, 1720 (s, ester C=O's) 1600 cm<sup>-1</sup> (m, C=C).

Polymer BII<sub>2</sub>: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm) 8.53 (s, 1H, *o* to Ar-Br) 8.18 (m, 6H, *o* to Ar-CO<sub>2</sub>) 7.37 (4H, *o* to Ar-O) 4.35 (t, 4H, CH<sub>2</sub>-OCO) 1.7 (t, 4H, CH<sub>2</sub>  $\beta$  to ester) 1.4 [m (broad), 12H, internal CH<sub>2</sub>]. IR (KBr) 3040 (m, aromatic Ar-H), 2910–2820 (vs., aliphatic CH), 1740, 1720 (s, ester C=O's) 1600 cm<sup>-1</sup> (m, C=C).

Polymer BIII: <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm) 8.53 (s, 1H, *o* to Ar-Br) 8.18 (m, 6H, *o* to Ar-CO<sub>2</sub>) 7.37 (4H, *o* to Ar-O) 4.38 (t, 4H, CH<sub>2</sub>-OCO) 1.8 (t, 4H, CH<sub>2</sub>  $\beta$  to ester) 1.4 [m (broad), 16H, internal CH<sub>2</sub>]. IR (KBr) 3040 (m, aromatic Ar-H), 2910–2820 (vs., aliphatic CH), 1740, 1720 (s, ester C=O's) 1600 cm<sup>-1</sup> (m, C=C).

## RESULTS AND DISCUSSION

### Synthesis

*Method A:* In the preparation of the bisphenolic prepolymers, a direct esterification of *p*-benzyloxybenzoic acid with either triethylene glycol or decanediol was achieved

using 4-dimethylaminopyridine and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride. The esterification was followed by a catalytic hydrogenation that was necessary to deblock the bisbenzyl ether and generate the desired product. The resulting bisphenolic compound can be purified by recrystallization, NMR, and IR spectroscopy support the proposed structure.

Polymers were prepared from the bisphenolic monomers by using solution condensation techniques in methylene chloride or chloroform with triethylamine, an acid acceptor, and catalyst. After polymerization, precipitation of the viscous polymer solution followed by vacuum drying yielded the white polymeric materials.

*Method B:* The synthetic procedure used to prepare the mesogenic monomer paralleled the procedure outlined by Bilibin,<sup>9,10</sup> substituting 2-bromoterephthaloyl chloride for terephthaloyl chloride. Once prepared, the 2-bromoterephthaloyloxybenzoyl chloride was polymerized by using either a room-temperature or a high-temperature condensation reaction. In the case of the high-temperature reaction, diphenyl ether was used as an inert reaction medium and the polymerizations were run at  $\sim$ 190°C while HCl, the condensation byproduct, was vented from the reaction vessel. Room-temperature polycondensations were run in tetrachloroethane using pyridine as a catalyst and acid acceptor. After polymerization, precipitation, soxhlet extraction (with acetone), and drying, the polymers were obtained as white stringy solids. The results of the two polymerization methods are summarized in Table I.

The yields from both polymerization techniques are in excess of 85%. The resulting polymers are white and are soluble in a variety of chlorinated solvents. The IR and NMR spectra for comparative materials indicate that the two methods yield polymers of similar if not identical chemical makeup. The molecular weights, as indicated by inherent viscosity measurements, range from a low value of 0.18 dL/g to a high value of 0.87 dL/g. In general, polymers prepared by method B are of higher molecular weight than method A. The lower molecular weight of the polymers by method A may be attributed to the bisphenolic monomer's being hygroscopic. Only after exhaustive drying of the bisphenolic monomer were polymeric materials possible by method A. Finally, from examining the BII polymers prepared using the mesogenic monomer method, it appears that higher molecular weights are achievable using high-temperature solution condensation versus room-temperature solution condensation. This result is consistent with Bilibin's examination of similar type materials.<sup>9</sup>

### Thermal Properties

The thermal properties of the mesogenic polymers are summarized in Table II. Differential scanning calorimetry (DSC) and optical polarizing microscopy (OPM) were used to determine the solid to mesophase transition tem-

**Table II Thermal Transitions of Polyesters by DSC and OPM**

Polyesters	DSC Transition Temperature (°C) <sup>a</sup>		Optical Polarizing Microscopy Transition Temperature (°C) <sup>b</sup>	
	$T_m$	$T_i$	$T_m$	$T_i$
AI	189	195	208	191
AII <sub>1</sub>	88		117	110
AII <sub>2</sub>	89		118	
AII <sub>3</sub>	91		119	
AIII	40		117	58
BI	120		166	130
BII <sub>1</sub>	150	163	210	140
BII <sub>2</sub>	149	160	215	154
BIII	156		191	150

<sup>a</sup> Determined at a heating rate of 20°C/min.

<sup>b</sup> Samples observed between glass plate and cover slide.

perature ( $T_m$ ) as well as the mesophase to isotropic phase transition temperatures ( $T_i$ ).

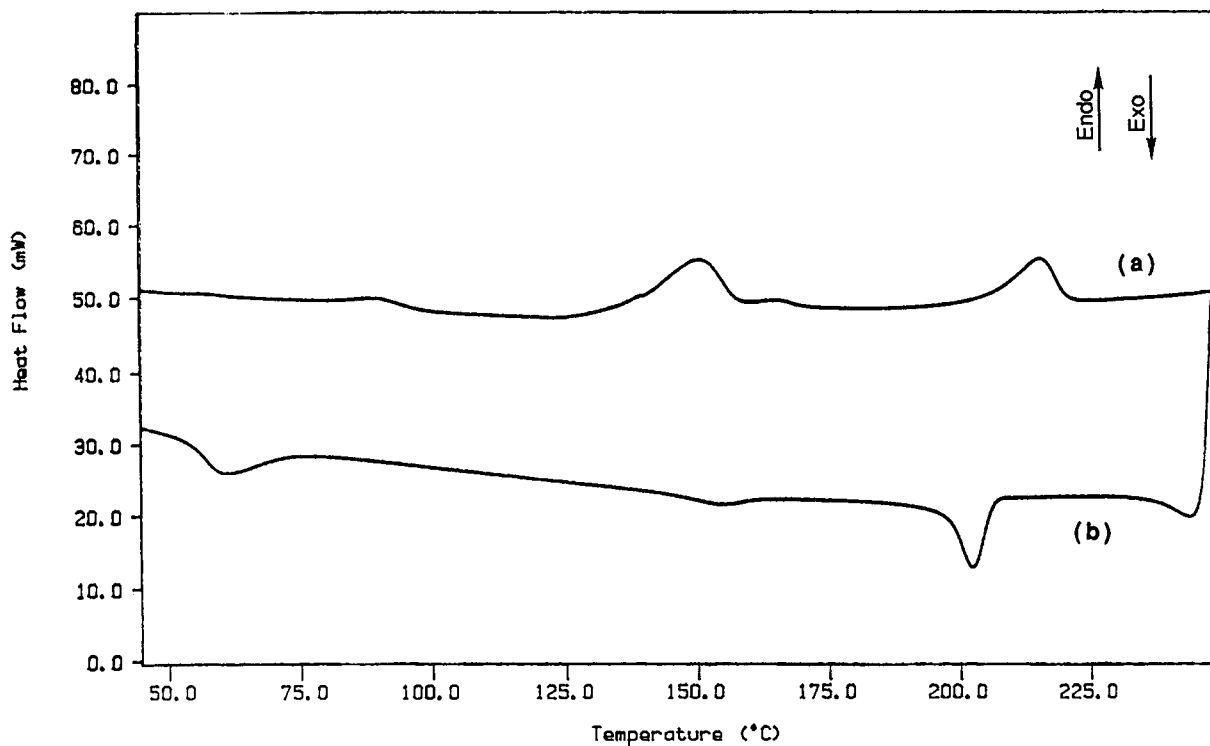
DSC: Both polymerization methods gave polymers that exhibit reproducible multiple melting and clearing tran-

sitions. The transitions are enantiotropic, and some supercooling was observed for both clearing and melt transitions. A representative DSC for polymer BII<sub>2</sub> is given in Figure 1.

The thermal properties of polymers like polymer AI have been reported elsewhere.<sup>7,9</sup> The thermal transitions reported here for AI compare favorably with those in the literature despite significant differences in molecular weight.

A molecular weight effect, which is common for LCPs,<sup>14</sup> is exemplified by comparing the AII polymers with polymer BI. The AII polymers have  $\eta_{inh}$  ranging from 0.18 to 0.35 dL/g, and have roughly the same thermal behavior, namely, a  $T_m$  at ~ 88°C and a  $T_i$  at ~ 117°C. Polymer BI, which is of substantially higher molecular weight ( $\eta_{inh}$  0.58 dL/g), exhibits a  $T_m$  at 120°C and a  $T_i$  at 166°C; an increase of 32°C for  $T_m$  and 49°C for  $T_i$  over the AII polymers.

Structural modifications in the polymer lead to changes in the thermal properties of the LCPs.<sup>15</sup> The incorporation of substituents on the mesogenic moiety decreases thermal transitions and broadens the temperature range of liquid crystalline phase. This is demonstrated in polymers AI, AII, and AIII, which have, respectively, an H, Br, and CF<sub>3</sub> substituent on the central terephthaloyl unit. Increasing the length of the spacer, as in polymer BII(C<sub>10</sub>) and BIII(C<sub>12</sub>), results in a convergence of  $T_i$  with  $T_m$ , thus indicating a destabilization of the LC phase. These changes in the thermal properties are typical of LCPs and have been reported in a number of systematic studies.<sup>16,17</sup>



**Figure 1** DSC curves of polymer BII<sub>2</sub>: (a) first heating; (b) first cooling.

Optical microscopy shows that all the polymers melt to give viscous, birefringent liquids. The temperature for  $T_m$  and  $T_i$  correspond roughly with those observed by DSC; the difference may be due to variations in heating rates. The textures observed are generally grainy although annealing samples for long periods leads to the formation of well-developed Schlieren textures.<sup>18</sup>

## CONCLUSIONS

The two polymerization methods each offer distinct advantages. Method A allows for the systematic study of LCPs with varying mesogenic composition. This is achievable through polymerization of the bisphenolic monomer with different diacid chlorides. Method B, on the other hand, lends itself to the systematic study of LCPs with varying spacer groups. Both synthetic methods generate reasonably high molecular weight polymers. As in any polycondensation reaction, monomer purity and stoichiometry is of extreme importance. Both methods yield polymers that are virtually identical by IR and NMR spectroscopy. However, method B consistently gave higher molecular weight polymers than method A, which may be related to the relative ease of purification of the fully formed mesogenic unit.

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