

# Synthesis of Liquid Crystalline Polyesterimides by Melt Polymerization and Its Application to Polymer-Dispersed Liquid Crystal

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**ABSTRACT:** *N*-(4-Carboxyphenyl)trimellitimide (DAI) was synthesized from trimellitic anhydride and *p*-aminobenzoic acid by a one-step reaction utilizing *m*-cresol as a solvent. DAI was reacted with hexanediol and nonanediol to give bishydroxyhexyltrimellitimide (BHHI) and bishydroxynonyltrimellitimide (BHNI), respectively. Thermotropic liquid crystalline polyesterimides with BHHI and BHNI as a mesogenic group and 6 and 9 methylene units as a spacer were synthesized by a direct melt-polymerization method similar to the one used in the preparation of commercial polyester. Polyesterimides were characterized by IR, <sup>1</sup>H-NMR, DSC, and a polarized optical microscope. Their application as a matrix (binder) of polymer-dispersed liquid crystal (PDLC) was investigated with 4-heptyloxybenzoic acid as a low molecular weight liquid crystal (LMWLC). From the PDLC experiment, polyesterimides were found to be useful as a matrix for the high-temperature PDLC above 100°C. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1517–1522, 1998

**Key words:** poly(ester imide); liquid crystalline polymer; melt polymerization; polymer dispersed liquid crystal; PDLC

## INTRODUCTION

Various polyesterimides have been synthesized for the purpose of improving the processability and solubility of polyimide by incorporation of an ester group into the main chain of the polyimide.<sup>1–4</sup> Current applications of polyesterimides include a high-temperature-resistant coating for magnet wire.<sup>4–6</sup> Recently, a series of liquid crystalline polyesterimides were synthesized from *N*-(4-carboxyphenyl)trimellitimide and  $\alpha,\omega$ -dihydroxyalkane by Kricheldorf's group.<sup>7–10</sup> The synthesis of ordered-structure polyesterimides were also reported by Lenz's group.<sup>11–13</sup> Synthesis of these polyesterimides, however, involved a rather

complicated procedure in the imide formation or solution polymerization with HCl gas as a by-product. In this study, diacid imide (DAI) was synthesized by a one-step reaction utilizing *m*-cresol as the solvent and polymerization was conducted by direct melt-polymerization as used in the preparation of commercial polyester.

Low molecular weight liquid crystals (LMWLCs) have been used in electrooptic displays and sensors.<sup>14–16</sup> LMWLCs dispersed in the polymer matrix, that is, polymer-dispersed liquid crystals (PDLCs), have also been used in electro- or thermo-optic displays.<sup>17–19</sup> Chien et al. used side-chain liquid crystal polymers as matrices for PDLC display applications.<sup>20,21</sup> In this study, main-chain-type liquid crystalline polyesterimides were synthesized and PDLCs were prepared with 4-heptyloxybenzoic acid as LMWLCs to determine the phase behavior in the high-temperature range.

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## EXPERIMENTAL

### Materials

Trimellitic anhydride, 4-aminobenzoic acid, 1,6-hexanediol, and 1,9-nonanediol were purchased from Aldrich Chemical Co. Zinc acetate dihydrate and antimony oxide used as catalysts and triphenyl phosphate used as a heat stabilizer in the polyesterification were also reagent grades from Aldrich Chemical Co. These chemicals were used without further purification.

### Techniques

Elementary analysis was conducted with a Carlo Erba Model 1106 elemental analyzer, and IR spectra were recorded with a Midac FTIR spectrometer. <sup>1</sup>H-NMR spectra of oligomer and polymer samples were obtained with a Bruker 300-MHz spectrometer (Model AM-300) in a mixture solvent of CF<sub>3</sub>CO<sub>2</sub>D : CDCl<sub>3</sub> (3 : 1 by volume). Viscosity measurement was conducted with an Ubbelohde viscometer at 20°C in a *N*-methylpyrrolidinone solvent. The intrinsic viscosity [ $\eta$ ] was obtained by extrapolation to the zero concentration according to the Huggins equation. A Perkin–Elmer DSC-7 and a DuPont TA 2000 system DSC-10 differential scanning calorimeter were employed to determine the thermal transition temperatures of LC polymers and PDLC samples. Thermograms were obtained at a 20°C/min rate during the heating and cooling run. All polymer samples were heated to 30°C above the  $T_m$  and then quenched with liquid nitrogen to remove the thermal history.  $T_g$ 's were assigned to the temperatures at which  $\Delta C_p$  became half of the total value. A DuPont TA 2000 system TGA-951 was employed to check the thermal stability of the polymer samples. A Leitz polarized optical microscope equipped with a Mettler FP-82 HT hot stage and a Mettler FP-90 control unit was used to observe the thermal transitions and anisotropic textures of the PDLC samples. A Rheometrics dynamic spectrometer (RDS-II) was employed to observe the rheological properties of the liquid crystalline polyesterimides. Shear rates were varied from 0.1 to 100 rad/s at different temperatures.

### Synthesis

Synthetic routes to the intermediates and polyesterimides are shown in Scheme 1.

#### *N*-(4-Carboxyphenyl) trimellitimide (DAI) (1)

This compound was synthesized by reacting 0.26 mol of trimellitic anhydride and 0.26 mol of 4-

aminobenzoic acid with 700 mL of the *m*-cresol solvent in a glass reactor with a mechanical stirrer at 200°C through a one-step process.<sup>22</sup>

Yield: 84.6%, IR (KBr): 1780, 723; (imide C=O): 1375 (CN). Melting temperature: 370.4°C (by DSC). ANAL. Calcd. for C<sub>16</sub>H<sub>9</sub>NO<sub>6</sub> (311.26): C, 61.74; H, 2.91; N, 4.50. Found: C, 61.82%; H, 2.88%; N, 4.51%.

#### Bishydroxyhexyltrimellitimide (BHBI) (2a) and Bishydroxynonyltrimellitimide (BHNI) (2b)

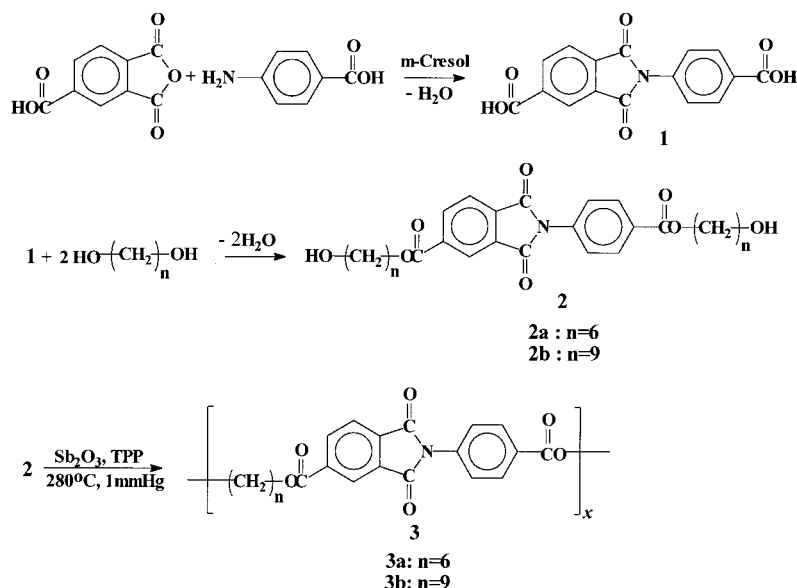
DAI was reacted with hexanediol (HD) and nonanediol (ND) with zinc acetate dihydrate (100 ppm) as a catalyst to give BHBI and BHNI oligomers, respectively. DAI and diol (HD or ND) were charged into a 1 L glass reactor equipped with a mechanical stirrer and condenser at the mol ratio of 1 : 2.5, and the mixture was heated to 240°C. The reaction mixture became clear after 5 h, and then it was further reacted for 1 h. When the water collected from the reaction was above 95% of the theoretical amount, the product (BHBI or BHNI) was poured into an aluminum pan and solidified.

<sup>1</sup>H-NMR (CF<sub>3</sub>COOD/CDCl<sub>3</sub>) for BHBI:  $\delta$  = 8.68 (s; *ortho* H to COO— and imide C=O); 8.61 (d; H *ortho* to COO— and *meta* to imide C=O), 8.17 (d; H *meta* to COO— and *ortho* to imide C=O), 8.26 (d; *meta* Hs to imide CN, 2H), 7.62 (d; *ortho* Hs to imide CN, 2H), 4.44–4.59 (m; COOCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>OH, 10H), 1.85–1.97 (m; COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, 8H), 1.58 (t; COO(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH, 8H). <sup>1</sup>H-NMR (CF<sub>3</sub>COOD/CDCl<sub>3</sub>) for BHNI:  $\delta$  = 8.28 (s; *ortho* H to COO— and imide C=O); 8.17 (d; H *ortho* to COO— and *meta* to imide C=O), 7.67 (d; H *meta* to COO— and *ortho* to imide C=O), 7.81 (d; *meta* Hs to imide CN, 2H), 7.21 (d; *ortho* Hs to imide CN, 2H), 3.98–4.06 (m; COOCH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>OH, 10H), 1.36–1.47 (m; COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>OH, 8H), 0.82–1.04 (t; COO(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>(CH<sub>2</sub>)<sub>2</sub>OH, 20H)

ANAL. Calcd for C<sub>28</sub>H<sub>33</sub>NO<sub>8</sub> (511.58): C, 65.74%; H, 6.50%; N, 2.74%; Found: C, 65.89%; H, 6.45%; N, 2.64%. ANAL. Calcd for C<sub>34</sub>H<sub>46</sub>NO<sub>8</sub> (596.74): C, 68.55%; H, 7.61%; N, 2.35%. Found: C, 68.60%; H, 7.54%; N, 2.39%.

#### Polyesterimides [PEHI (3a), PENI (3b)]

BHBI (or BHNI) was pulverized and placed in a cylindrical glass reactor equipped with a mechanical stirrer and a vacuum line. The Sb<sub>2</sub>O<sub>3</sub> catalyst and triphenyl phosphate thermal stabilizer were added at the 300 and 200 ppm levels, respectively, based on 100 g of the polymer product. The reaction mixture was melted when the temperature of the oil bath was raised to 230°C, and the me-



**Scheme 1** Synthetic routes to (1) DAI intermediate, (2) BHHI and BHNI oligomers, and (3) polyesterimides.

chanical stirrer was turned on. The reaction temperature was further increased to 285°C over a period of about 40 min, while a partial vacuum was applied (reaching about 1 mmHg). At this moment, the rotating speed of the stirrer was set to 150 rpm, and the mixture was further reacted for 1–2 h, while the reaction by-product (HD or ND diol) was removed off the reactor through the vacuum line. As the polycondensation reaction proceeded, the decrease in the rotating speed of the stirrer due to the viscosity buildup of the reaction mixture was measured with a tachometer until the reaction was stopped at the stirrer speed of 40 rpm. The product polymer melt was forced out of the glass reactor into a water pool by applying pressure with N<sub>2</sub>. The resulting polyesterimide sample (PEHI or PENI) was purified by extraction (Soxhlet) with toluene as the solvent. The polymer sample was washed again in acetone and then dried in a vacuum oven for more than 48 h at room temperature prior to characterization.

IR (KBr) for PEHI: 1782, 723 (imide C=O), 1373 CN; IR (KBr) for PENI: 1782, 723 (imide C=O), 1371 CN; <sup>1</sup>H-NMR (CF<sub>3</sub>COOD/CDCl<sub>3</sub>) for PEHI: δ = 8.70 (s; *ortho* H to COO— and imide C=O); 8.64 (d; H *ortho* to COO— and *meta* to imide C=O), 8.18 (d; H *meta* to COO— and *ortho* to imide C=O), 8.28 (d; *meta* Hs to imide CN), 7.63 (d; *ortho* Hs to imide CN), 4.45–4.61 (m; —COOCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>—), 1.97 (s; -to imide CN), 4.45–4.61 (m; —COOCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>—), 1.97 (s;

—COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>—), 1.67 (s; —COO—(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>—). <sup>1</sup>H-NMR (CF<sub>3</sub>COOD/CDCl<sub>3</sub>) for PENI: δ = 8.69 (s; *ortho* H to COO— and imide C=O); 8.63 (d; H *ortho* to COO— and *meta* to imide C=O), 8.17 (d; H *meta* to COO— and *ortho* to imide C=O), 8.27 (d; *meta* Hs to imide CN), 7.63 (d; *ortho* Hs to imide CN), 4.40–4.55 (m; —COOCH<sub>2</sub>(CH<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>—), 1.91 (s; —COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>—), 1.51 (s; —COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>CH<sub>2</sub>—). Intrinsic viscosity (20°C, *N*-methylpyrrolidinone): PEHI: [η] = 0.35 dL/g, PENI: [η] = 0.35 dL/g.

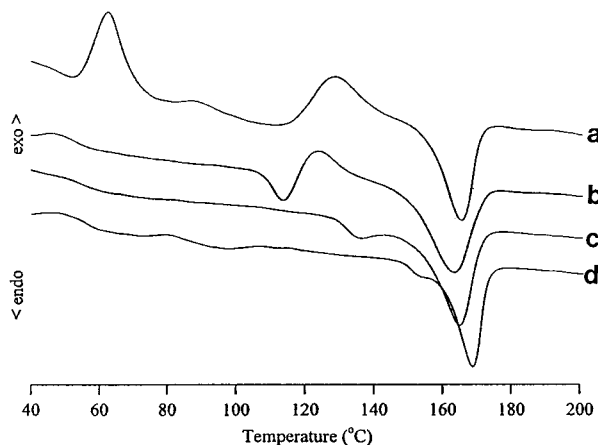
### Preparation of PDLC

A thermally induced phase separation (TIPS) process<sup>15</sup> was employed to prepare the PDLC films with 4-heptyloxybenzoic acid (60% by wt) as LMWLC and PEHI or PENI polyesterimide as the matrix. 4-Heptyloxybenzoic acid exhibited a liquid crystalline property by making the dimer (transition temperatures: K 96 N 147.9 I) as shown in Figure 5. The polyesterimide and 4-heptyloxybenzoic acid mixture was placed between two ITO glasses (12 μm Mylar film as a spacer) and then heated above the *T<sub>m</sub>* of the mixture and cooled slowly to room temperature to induce phase separation.

## RESULTS AND DISCUSSION

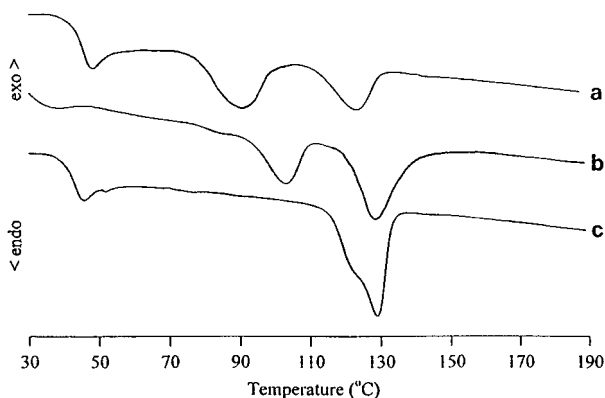
### Thermal and Viscoelastic Properties Polyesterimides

In Figure 1 are shown the DSC traces of PEHI polyesterimide. Trace (a) shows first heating run

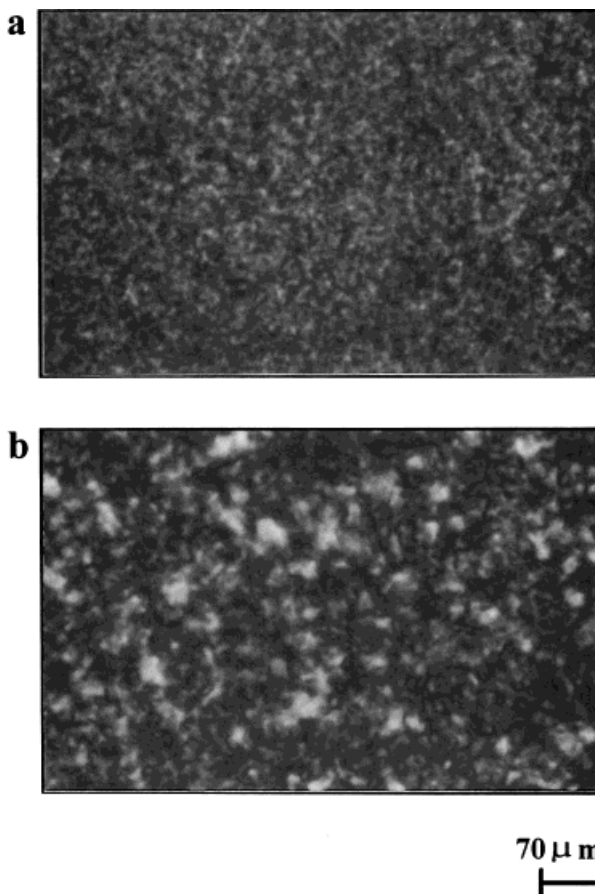


**Figure 1** DSC traces of PEHI: (a) first heating after quenching with liquid  $N_2$ ; (b) heating after annealing for 1 h at  $100^\circ\text{C}$ ; (c) heating after annealing (1 h,  $120^\circ\text{C}$ ); (d) heating after annealing (1 h,  $140^\circ\text{C}$ ).

after the PEHI sample was quenched with liquid nitrogen from the melt state. In this run, the glass transition temperature ( $T_g$ ) is obscure due to exotherm peak at  $65^\circ\text{C}$  caused by crystallization of the polymer chain. When PEHI was annealed for 1 h at  $100^\circ\text{C}$  and subjected to the DSC heating run at  $20^\circ\text{C}/\text{min}$  rate (trace b), the crystallization peak disappeared and two endotherm peaks at 110 and  $164^\circ\text{C}$  were observed. These peaks were assigned to be melting (at  $110^\circ\text{C}$ ) and liquid crystalline to isotropic (at  $164^\circ\text{C}$ ) temperature. As the annealing temperature was increased to  $120^\circ\text{C}$  (trace c) and  $140^\circ\text{C}$  (trace d), the melting peaks became smaller and both the  $T_m$  and  $T_{iso}$  points moved toward the higher temperatures. The  $T_g$  of PEHI was assigned to be about  $58^\circ\text{C}$  (trace d), corresponding to the half of  $\Delta C_p$  value.



**Figure 2** DSC traces of PENI: (a) first heating after quenching with liquid  $N_2$ ; (b) heating after annealing for 5 h at  $60^\circ\text{C}$ ; (c) heating after annealing for 5 h at  $100^\circ\text{C}$ .

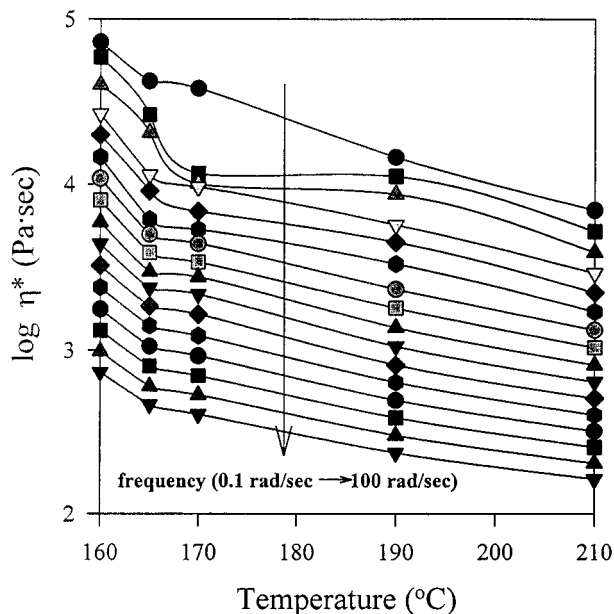


**Figure 3** Polarized optical micrographs of polyesterimides during cooling run: (a) PEHI at  $155^\circ\text{C}$ ; (b) PENI at  $112^\circ\text{C}$ .

In the DSC experiment of PENI polyesterimide (Fig. 2), the liquid nitrogen quenched sample (trace a) did not show an exothermic peak as in PEHI but two endothermic peaks at  $90^\circ\text{C}$  ( $T_m$ ) and at  $116^\circ\text{C}$  ( $T_{iso}$ ). The absence of an exothermic peak and a lower  $T_m$  and  $T_{iso}$  of PENI than those of PEHI were considered to be due to the increased flexibility of PENI with a longer spacer compared to PEHI. The shift of both  $T_m$  and  $T_{iso}$  (traces b and c) toward higher temperature in the annealed sample were the same as that of PEHI.

The liquid crystalline property of polyesterimides was examined with a polarized optical microscope. In Figure 3 are shown polarized optical micrographs of PEHI and PENI taken at 155 and  $112^\circ\text{C}$ , respectively, during the cooling run at  $2^\circ\text{C}/\text{min}$  from the melt state. Threadlike textures<sup>23,24</sup> were observed. The size of the LC texture in PENI was larger than that of PEHI, indicating a higher ordering due to increased flexibility.

The liquid crystalline property of polyesterimide was also checked by the viscoelastic property



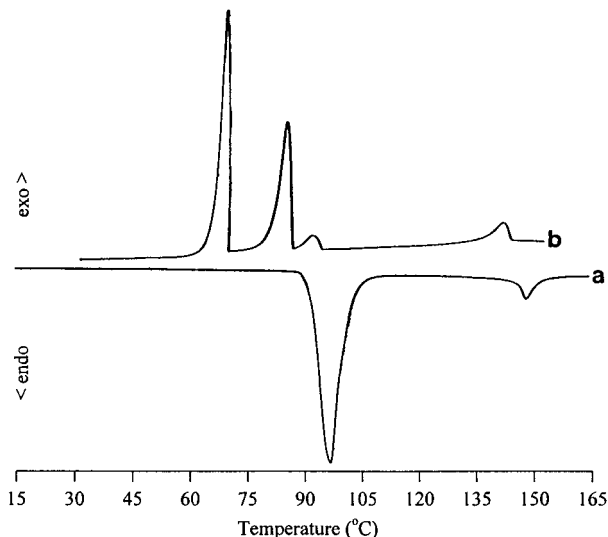
**Figure 4** Plot of temperature versus  $\log \eta^*$  for PEHI.

of the melt samples. In Figure 4 are shown the plots of  $\log \eta^*$  versus temperature in the PEHI sample under various shear rates. The drop in this type of plot under a low shear rate in the neighborhood of the isotropic temperature of PEHI (164°C) was not as sharp as the typical liquid crystalline polymer reported by Kim and Han.<sup>25,26</sup> This may be due to the presence of highly polar imide linkages in the polyesterimide chain.

#### Theroptical Properties of PDLC

Polymer-dispersed liquid crystal (PDLC) samples were prepared by a thermally induced phase separation (TIPS) method with 4-heptyloxybenzoic acid as LMWLC (60% by wt) and polyesterimide (40% by wt) as the matrix. The DSC traces of the LMWLC and PDLC sample with PEHI as the matrix are shown in Figures 5 and 6, respectively.

In the case of PEHI-PDLC (Fig. 6), four thermal changes appeared at 53°C ( $T_1$ ), 94°C ( $T_2$ ), 145°C ( $T_3$ ), and 154°C ( $T_4$ ). The first one at 53°C ( $T_1$ ) was assigned to the glass transition temperature of the PEHI matrix. The different shape of the thermal transition at 53°C from the normally observed  $T_g$  seemed to be due to the presence of LMWLC in the sample. The endotherms at 94°C ( $T_2$ ) and 145°C ( $T_3$ ) were assigned as the phase-separated melting and isotropic temperatures of LMWLC in the PDLC, respectively. The  $T_{iso}$  of LMWLC in the PDLC was lower than that of pure

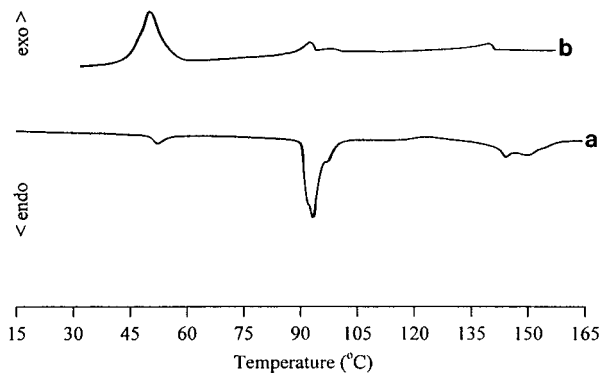


**Figure 5** DSC trace of 4-heptyloxybenzoic acid: (a) heating run; (b) cooling run.

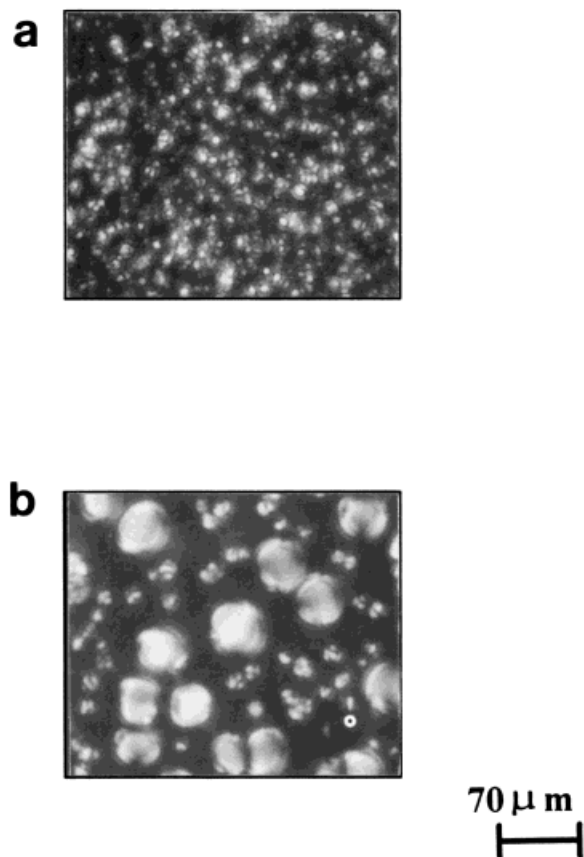
LMWLC (Fig. 5) due to intermixing of the LMWLC and PEHI matrix. The endotherm at 154°C ( $T_4$ ) was assigned as the isotropic temperature of PEHI-PDLC, lowered significantly from that of pure PEHI (164°C) by the presence of LMWLC.

The thermo-optical properties of the PDLC samples were observed through a polarized optical microscope. In Figure 7, microphotographs (a) and (b) were taken during the cooling run (at 2°C/min) of PEHI-PDLC and PENI-PDLC prepared with 4-heptyloxybenzoic acid as the LMWLC.

The white dispersed domains in (a) and (b) represent the LMWLC phase-separated from the homogeneous melt state of PDLC. The sizes of domains in (b) were larger than those of (a), reflecting the more flexible nature of PENI matrix.



**Figure 6** DSC trace of PEHI-PDLC: (a) heating run; (b) cooling run.



**Figure 7** Polarized optical micrographs of PDLC: (a) PEHI-PDLC at 141.6°C during cooling run; (b) PENI-PDLC at 116°C during cooling run.

## CONCLUSIONS

Polyesterimides with the *N*-(4-carboxyphenyl)-trimellitimide unit as the mesogenic group and 6 and 9 methylene units as the spacer (PEHI and PENI) were prepared by a direct melt-polymerization method. The PEHI and PENI polyesterimides showed crystalline properties as observed by DSC and a polarized optical microscope. The confirmation of the liquid crystalline property by rheological measurement was, however, not as clear as the typical main-chain LC polymer due to the presence of polar imide linkages in the chain. The thermo-optical observation of the PDLC with 4-heptyloxybenzoic acid as the LMWLC and polyesterimides as the matrix indicated that poly-

esterimides could be useful matrices working at higher temperature.

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