

# Mesomorphism Enhancement of Modified Side-Chain Liquid-Crystalline Polysiloxanes by Copolymerization

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**ABSTRACT:** The liquid-crystalline (LC) monomer 4-allyloxybenzoyloxy-4'-buthylbenzoyloxy-*p*-phenyl ( $M_1$ ), whose LC phase appeared at lower temperatures, from 137 to 227°C, and the modified mesogenic monomer 4-allyloxybenzoyloxy-4'-methoxybenzoyloxy-*p*-biphenyl ( $M_2$ ), whose LC phase appeared at higher temperatures, from 185 to 312°C, were prepared. A series of side-chain LC polysiloxanes containing  $M_1$  and  $M_2$  were prepared by graft copolymerization. Their LC properties were characterized by differential scanning calorimetry, thermogravimetric analysis, polarizing optical microscopy, and X-ray diffraction. The results show that the introduc-

tion of the modified mesogenic monomer  $M_2$  into the polymeric structure caused an additional increase in the clearing point (isotropic transition temperature) of the corresponding polysiloxanes, compared with unmodified polysiloxanes, but did not significantly affect the glass-transition temperature. Moreover, the modified polysiloxanes exhibited nematic phases as the unmodified polymer did. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1196–1201, 2005

**Key words:** liquid-crystalline polymers (LCP); polysiloxanes

## INTRODUCTION

In materials science, one important prerequisite for the rational design of materials with complex physical properties is the understanding of the relationship between molecular structure and the resulting macroscopic properties. Another important concept is the combination of different molecular fragments, which gives rise to different properties in the same material.<sup>1</sup> Recently, liquid-crystalline polymers (LCPs) have received much attention because of their high modulus, strength, and stiffness values. Particularly, polysiloxanes have been used for the preparation of liquid-crystalline (LC) materials with different organic mesogenic units as side-group substituents,<sup>2,3</sup> and there has been much research into the design of molecules to obtain LC phases, for example, by the introduction of crosslinkable groups or ionic groups; however, re-

search has shown that the crosslinkable groups or ionic groups generally decrease mesomorphic properties.<sup>4–8</sup>

In this article, the LC monomer 4-allyloxybenzoyloxy-4'-buthylbenzoyloxy-*p*-phenyl ( $M_1$ ), whose LC phase is found at lower temperatures, and the modified mesogenic monomer 4-allyloxybenzoyloxy-4'-methoxybenzoyloxy-*p*-biphenyl ( $M_2$ ), whose LC phase is found at higher temperatures, were prepared, and a series of side-chain LCPs containing  $M_1$  and  $M_2$  were synthesized by copolymerization. The mesomorphic properties of the monomers and polymers were investigated with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), polarizing optical microscopy (POM), and X-ray diffraction (XRD). The influence of the modified monomer  $M_2$  on the mesomorphic phase of the polysiloxanes is discussed.

## EXPERIMENTAL

### Materials

Polymethylhydrosiloxane (PMHS; weight-average molecular weight = 700–800) was obtained from Jilin Chemical Industry Co. (Jilin, China). 4-Butylbenzoic acid, 4-hydroxybenzoic acid, and 4-methylbenzoic acid were purchased from Beijing Chemical Co. Pyridine was purified by distillation over  $\text{CaH}_2$  before use. All other solvents and reagents were purified by standard methods.

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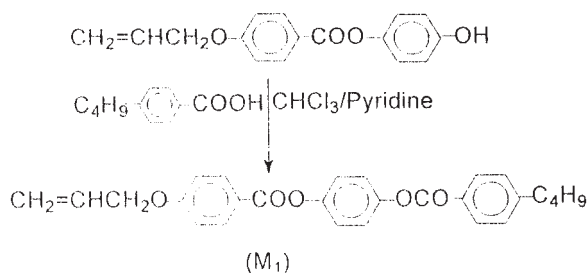
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Scheme 1 Synthetic route of M<sub>1</sub>.

### Characterization

Fourier transform infrared (FTIR) spectroscopy of the synthesized polymers and monomers in the solid state were obtained by the KBr method performed on a Nicolet 510P FTIR spectrometer (Nicolet Instruments, Madison, WI). Thermal transition properties were characterized by a Netzch DSC204 instrument at a heating rate of 20°C/min under a nitrogen atmosphere. Visual observations of LC transitions under cross-polarized light were made with a Linknm THMSE 600 polarizing optical microscope (Leitz, Wetzlar, Germany), equipped with a Leica DMRX (Poole, UK) heating stage. X-ray diffraction measurements were performed with nickel-filtered Cu K $\alpha$  radiation with a Rigaku powder diffractometer (The Woods, TX).

### Synthesis of the monomers

4-Allyloxybenzoic acids and monomer M<sub>1</sub> were prepared according to previously reported synthetic methods.<sup>9-11</sup> The synthetic routes of monomers M<sub>1</sub> and M<sub>2</sub> are outlined in Schemes 1 and 2, respectively.

#### 4-Allyloxybenzoyl-4'-hydroxyl biphenyl (1)

4-Allyloxybenzoic acids (17.8 g, 0.1 mol) and thionyl chloride (25.0 g, 0.21 mol) were added into a round flask equipped with an absorption instrument of hydrogen chloride. The mixture was stirred at room temperature for 2 h, then heated to 60°C, and kept for 3 h in a water bath to ensure that the reaction finished. The excess thionyl chloride was removed under reduced pressure to obtain 4-allyloxy benzoyl chloride. The antioxidant (6.3 g, 0.01 mol) was dissolved in 120 mL of pyridine and tetrahydrofuran to form a solution. 4-allyloxy benzoyl chloride (4.1 g, 0.02 mol) prepared by a similar method was slowly added to the solution and reacted at 50°C for 6 h; the mixture was then cooled and poured into 500 mL of cold water. The precipitate was filtered and washed by acetone; the acetone was removed, and **1** was obtained:

mp = 158°C. Yield = 56%. IR (cm<sup>-1</sup>): 3346 (OH), 2963, 2878 (CH<sub>3</sub>, CH<sub>2</sub>); 1700 (C=O); 1604, 1577, 1510 (Ar).

#### 4-Alloxybenzoyloxy-4'-methoxybenzoyloxy-*p*-biphenyl (m<sub>2</sub>)

4-Methoxybenzoyl chloride was prepared by the same procedure, and 4-allyloxybenzoyl chloride was slowly added to solution containing **1** and was then reacted for 6 h at 60°C. The mixture was poured into water, precipitated, and filtered, and the crude product was washed with ethanol and acetone, respectively. Then, M<sub>2</sub> was obtained:

mp = 185°C. Yield = 80%. IR (cm<sup>-1</sup>): 3045, 3012 (=CH); 2932, 2868 (CH<sub>3</sub>, CH<sub>2</sub>); 1731 (C=O); 1649 (C=C); 1604, 1509 (Ar). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, tetramethylsilane,  $\delta$ , ppm): 3.9 (t, H, —OCH<sub>3</sub>), 4.6–4.7 (d, 2H, —CH<sub>2</sub>—O—), 5.3–5.5 (m, 2H, CH<sub>2</sub>=), 6.0–6.2 (m, 1H, =CH—), 7.0–8.2 (m, 16H, Ar—H).

### Synthesis of the polymers

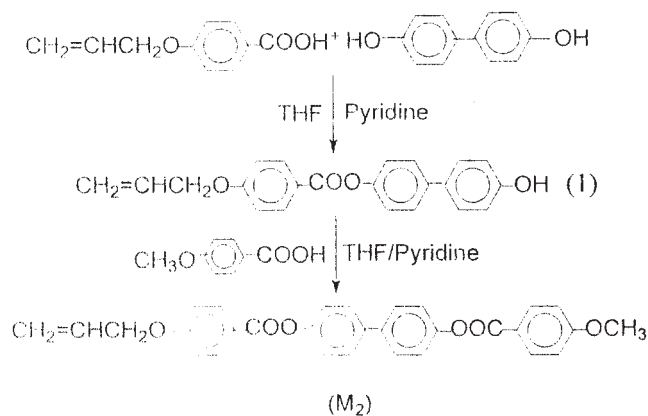
The polymers were synthesized by graft copolymerization. M<sub>1</sub>, M<sub>2</sub>, and PMHS were dissolved in freshly distilled chloroform; the mixture was heated to 65°C under nitrogen and anhydrous conditions, and then, 1 mL of a tetrahydrofuran solution of hexachloroplatinate (IV) catalyst (5 mg/mL) was injected with a syringe. The progress of the reaction was monitored by IR spectroscopy until the Si—H absorption peak of PMHS at 2160 cm<sup>-1</sup> disappeared. The crude polymer was purified by precipitation in chloroform with ethanol and dried *in vacuo*:

IR (KBr, cm<sup>-1</sup>): 2958–2873 (CH<sub>3</sub>— and —CH<sub>2</sub>—); 1734 (C=O); 1607, 1509 (Ar); 1260 (Si—C); 1165 (C—O—C); 1100–1000 (Si—O—Si).

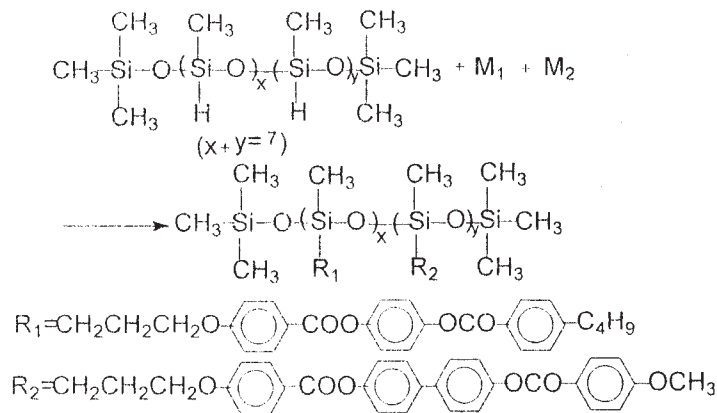
## RESULTS AND DISCUSSION

### Syntheses

The structure of M<sub>2</sub> was characterized by FTIR and <sup>1</sup>H-NMR. The IR spectra of M<sub>2</sub> showed characteristic



Scheme 2 Synthetic route of M<sub>2</sub>.



Scheme 3 Synthetic routes of the copolymers.

bands at 1731 and 1604–1509  $\text{cm}^{-1}$  attributed to ester C=O and aromatic C=C stretching. The  $^1\text{H-NMR}$  spectra of  $M_2$  showed multiplets at 5.3–5.5 and 7.0–8.2 ppm corresponding to olefinic protons and aromatic protons, respectively.

The polymers were prepared by graft copolymerization, in other words, by a hydrosilylation reaction between the Si—H groups of PMHS and the olefinic C=C of  $M_1$  and  $M_2$  in chloroform, with hexachloroplatinate (IV) as catalyst at 65°C. The hydrosilylation reaction catalyzed by hexachloroplatinate (IV) proceeded almost quantitatively. The IR spectra of the polymers showed the complete disappearance of the Si—H stretching band at 2166  $\text{cm}^{-1}$ . Characteristic Si—O—Si stretching bands appeared at 1200–1000  $\text{cm}^{-1}$ . In addition, the absorption bands of ester C=O and the aromatic group still existed. Polymers  $P_1$ – $P_5$  containing both  $M_1$  and  $M_2$  groups were powder and dissolved in  $\text{CHCl}_3$  and dimethylformamide (DMF), but their solubility in  $\text{CHCl}_3$  decreased with the content of  $M_2$ . The synthetic routes are outlined in Scheme 3. The polymerization experiments and yields are summarized in Table I. Representative IR spectra of the polymers  $P_0$ ,  $P_3$ , and  $P_5$  are presented in Figure 1, where % T is equal to % transmittance.

### Thermal analysis

The mesomorphic properties of monomers  $M_1$  and  $M_2$  were characterized by DSC. The corresponding phase-transition temperatures are summarized in Table II. According to the data listed in Table II,  $M_1$  and  $M_2$  showed enantiotropic LC behavior. The mesomorphic phase ranges of  $M_1$  were from 137°C [melting temperature ( $T_m$ )] to 227°C [isotropic transition temperature ( $T_i$ )] during the heating cycle and from 195°C [temperature taken as isotropic to liquid crystalline ( $T_c$ )] to 105°C [crystallized temperature, ( $T_k$ )] during the cooling cycle. The mesomorphic phase ranges of  $M_2$  were from 185°C ( $T_m$ ) to 312°C ( $T_i$ ) during the heating cycle and from 254°C ( $T_c$ ) to 120°C ( $T_k$ ) during the cooling cycle.  $M_1$  and  $M_2$  had broad LC ranges; meanwhile, the mesomorphic phase of  $M_2$  appeared at higher temperatures, from 185 to 312°C, compared with  $M_1$ , whose mesomorphic phase appeared at 137 to 227°C. This suggests that  $T_m$  and LC to  $T_i$  increased with increasing rigidity of the monomer structure.

The mesomorphic properties of polymers  $P_0$ – $P_5$  were also determined with DSC. Representative DSC curves of the polymers are presented in Figure 2. The corresponding phase-transition temperatures, obtained dur-

TABLE I  
Polymerization of the Polymers

Polymer	Feed (mmol)			$M_2$ (mol %) <sup>a</sup>	Yield (%)	Solubility <sup>b</sup>	
	PMHS	$M_1$	$M_2$			$\text{CHCl}_3$	DMF
$P_0$	0.5	3.50	0.00	0.00	89	+	+
$P_1$	0.5	3.25	0.25	8.33	86	+	+
$P_2$	0.5	3.00	0.50	16.67	88	+	+
$P_3$	0.5	2.75	0.75	21.42	89	+	+
$P_4$	0.5	2.50	1.00	33.30	92	+	+
$P_5$	0.5	2.00	1.50	42.86	90	+	+

<sup>a</sup> Molar percentage of  $M_2$  based on  $M_1 + M_2$ .

<sup>b</sup> + = soluble.

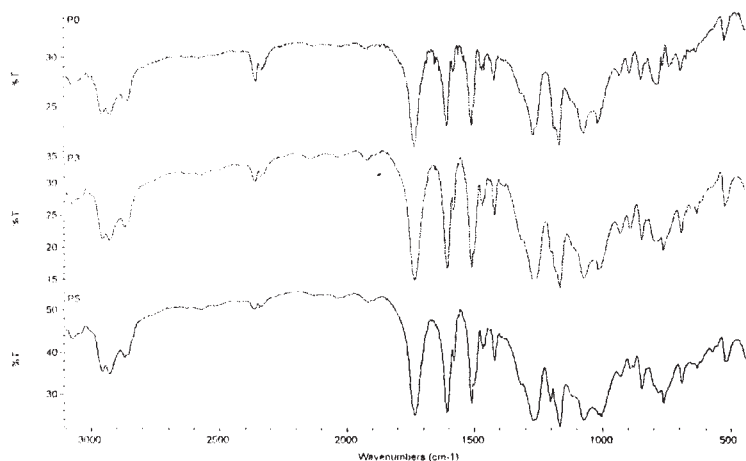


Figure 1 IR spectra of polymers P<sub>0</sub>, P<sub>3</sub>, and P<sub>5</sub>.

ing the second heating scan, are summarized in Table III. All phase transitions were reversible.

The DSC thermograms of P<sub>0</sub>–P<sub>5</sub> showed the glass transition at low temperatures and the LC to isotropic transition at high temperatures. As shown by the data in Table III, the content of M<sub>2</sub> did not significantly affect the glass transition of the LCPs; however, it had a strong influence on the isotropic transition. Figure 3 shows the effect of the content of M<sub>2</sub> on the phase-transition temperatures of the polymers, obtained during the second heating cycles. It characterizes the effect of the content of M<sub>2</sub> on the phase-transition temperatures, the glass-transition temperature ( $T_g$ ) and  $T_i$ , and the mesomorphic temperature range ( $\Delta T = T_i - T_g$ ) of the copolymers and indicates that the  $\Delta T$  of the copolymers that contained M<sub>1</sub> and M<sub>2</sub> prepared by copolymerization was wider than that of the corresponding homopolymer P<sub>0</sub>, which only contained M<sub>1</sub>. Compared with P<sub>0</sub>'s  $\Delta T$  of 155°C, the  $\Delta T$  of P<sub>5</sub> increased to 255°C.

$T_g$  and LC to  $T_i$  are two important parameters in connection with the structures and properties of LC polymers. For side-chain LCPs,  $T_g$  and  $T_i$  are influenced by the nature of the polymer backbone, the rigidity of the mesogenic groups, the length of flexible spacers, and the copolymer composition. In general, mesomorphic groups that contain four phenyl groups impose additional constraints on the motion of chain segments due to a steric hindrance effect and cause an increase in  $T_g$ .

However, the effect was small for low contents of M<sub>2</sub>; thus,  $T_g$  only increased from 31°C for P<sub>1</sub> to 40°C for P<sub>5</sub> when the content of M<sub>2</sub> side groups increased from 8.33 to 42.86 mol %, but  $T_i$  was influenced significantly.  $T_i$  increased from 186°C for P<sub>1</sub> to 295°C for P<sub>5</sub> during the heating cycle when the same content change of M<sub>2</sub> occurred. The reason was that the  $T_g$  involves the movement of segments in polymers, whereas  $T_i$  involves the whole-chain movement of polymers. M<sub>1</sub> and M<sub>2</sub> were both rod-like monomers; the effect of M<sub>2</sub> for the movement of segments in the polymers at lower temperatures was weak when the extent of M<sub>2</sub> was lower. With the length of M<sub>2</sub> mesogenic groups increasing and the terminal polar group (OCH<sub>3</sub>) appearing, the orientation order of the M<sub>2</sub> mesogenic group at higher temperatures was predominant, especially when the orientation of M<sub>1</sub> mesogenic groups disappeared at about 227°C. M<sub>2</sub> mesogenic groups were of orientation order as before until 312°C, so the LC to  $T_i$  of the polymers containing M<sub>1</sub> and M<sub>2</sub> increased, and their mesomorphism was enhanced.

The TGA results of the polymers are also shown in Table III. A representative TGA thermogram of P<sub>4</sub> is presented in Figure 4 (where TG is equal to thermogravimetry). The TGA results show that the temperatures at which 5% weight loss occurred ( $T_d$ 's) were higher than 340°C for P<sub>1</sub>–P<sub>5</sub>, which accounted for the fact that the synthesized polymers had high thermal stabilities.

TABLE II  
Phase-Transition Temperatures of the Monomers

Monomer	Heating			Cooling		
	$T_m$ (°C)	$T_i$ (°C)	$\Delta T$ (°C)	$T_c$ (°C)	$T_k$ (°C)	$\Delta T$ (°C)
M <sub>1</sub>	137	227	90	195	105	90
M <sub>2</sub>	185	312	127	254	120	134

Heating:  $\Delta T = T_i - T_m$ . Cooling:  $\Delta T = T_c - T_k$ .

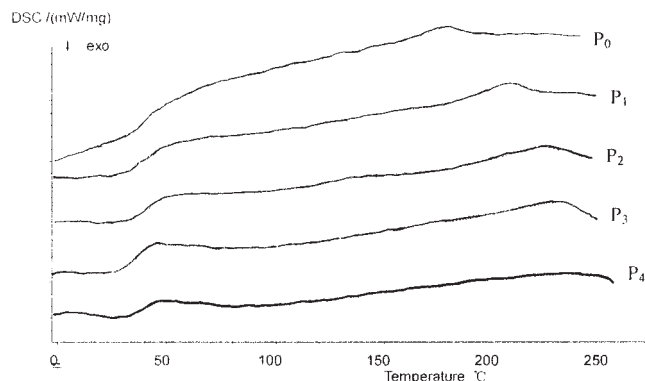


Figure 2 DSC curves of the polymers.

### Texture analysis

The optical textures of the monomers  $M_1$  and  $M_2$  were studied by hot-stage POM. The POM observations showed that  $M_1$  and  $M_2$  exhibited nematic threadlike textures during the heating and cooling cycles. When  $M_1$  was heated to a  $T_m$  of 137°C, the obvious threadlike texture appeared, and the texture did not change until the clearing point temperature of 227°C. When the isotropic state was cooled from the isotropic phase, a droplet texture was observed at first, which then turned to a threadlike texture, which remained until the crystallizing point temperature. The mesomorphic properties of  $M_2$  were similar to those of  $M_1$ .

The textures of polymers  $P_0$ – $P_5$  observed with POM exhibited thermotropic LC properties during the heating and cooling cycles.  $P_0$  and  $P_1$ – $P_5$  showed typical nematic threadlike textures.<sup>12</sup> The phase-transition temperatures determined by DSC were consistent with POM observation results. These results indicate that copolymer composition did not affect mesogenic type and texture. The optical textures of monomers  $M_1$  and  $M_2$  and polymers  $P_2$  and  $P_4$  are shown as examples in Figure 5.

### XRD analysis

XRD studies were carried out to obtain more detailed information on LC phase structure. In general, a sharp and strong peak at a low angle ( $1^\circ < 2\theta < 4^\circ$ ) in

TABLE III  
Thermal Properties of the Polymers

Polymer	$M_2$ (mol %)	$T_g$ (°C)	$T_i$ (°C)	$\Delta T$ (°C)	$T_d$ (°C)
$P_0$	0.00	31	186	155	365
$P_1$	8.33	34	218	184	357
$P_2$	16.67	35	236	201	349
$P_3$	21.42	33	246	213	351
$P_4$	33.30	33	279	246	355
$P_5$	42.86	40	295	255	368

$$\Delta T = T_i - T_g$$

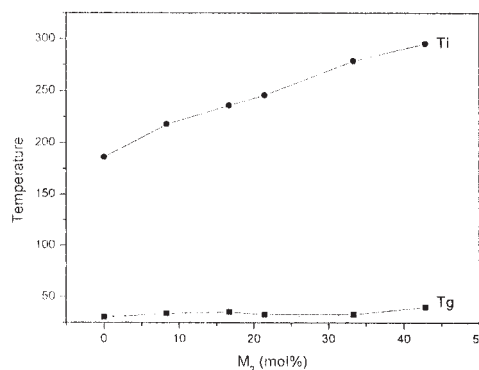


Figure 3 Phase-transition temperatures of the polymers.

small-angle X-ray scattering curves and a broad peak associated with lateral packing at  $2\theta \approx 20^\circ$  can be observed in wide-angle X-ray diffraction curves for smectic structure; no peak appeared at a low angle, and a broad peak at  $2\theta \approx 20^\circ$  was also observed for nematic structure. For cholesteric structure, no peak appeared at a low angle, and a broad peak occurred only at  $2\theta \approx 17^\circ$ .<sup>13,14</sup> All of the polymers prepared showed amorphous diffuse peaks at about  $2\theta = 20^\circ$  and a few diffuse peaks at about  $2\theta = 10^\circ$ . Moreover, no sharp peak in the lower Bragg angle region was observed. The results suggest that the LCPs  $P_0$ – $P_5$  exhibited nematic mesophase.<sup>15</sup> Representative XRD curves of quenched samples are shown in Figure 6. This also indicates that the structure of  $M_2$  in the polymers did not change their mesogenic types.

### CONCLUSIONS

Two kinds of LC monomers,  $M_1$ , whose LC phase appeared at lower temperatures during the heating cycle (137–227°C), and  $M_2$ , whose LC phase appeared at higher temperatures during the heating cycle (185–312°C), were prepared, and a series of side-chain LC polysiloxanes containing  $M_1$  and  $M_2$  were synthesized

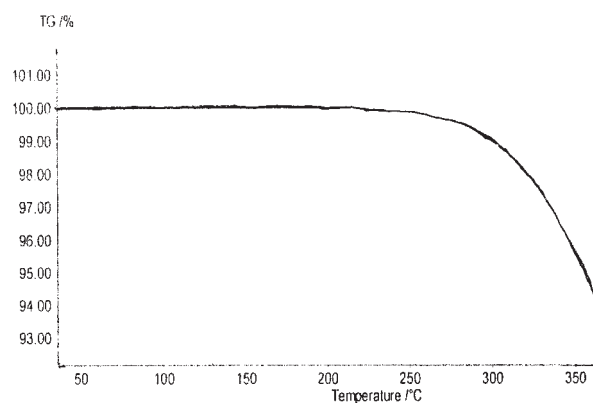
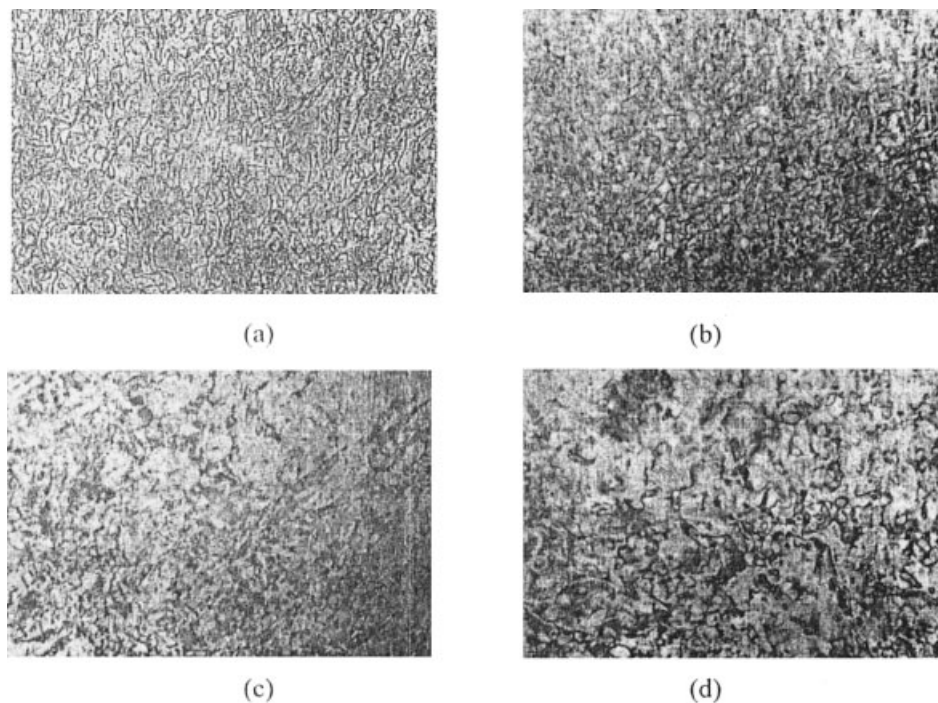


Figure 4 TGA thermogram of polymer  $P_4$ .

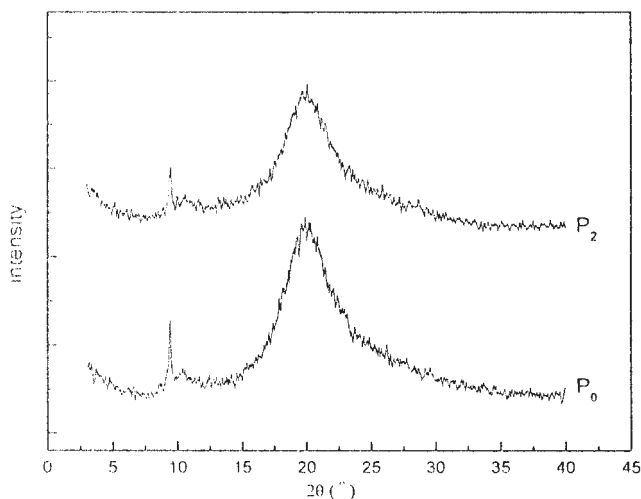




**Figure 5** Polarized optical micrographs of the polymers (200 $\times$ ). Textures of (a)  $M_1$  on heating to 145 $^{\circ}\text{C}$ , (b)  $M_2$  on heating to 200 $^{\circ}\text{C}$ , (c)  $P_0$  on heating to 189 $^{\circ}\text{C}$ , and (d)  $P_2$  on heating to 200 $^{\circ}\text{C}$ .

by hydrosilylation. Their LC properties showed that the mesogenic phases of the polymers became wider because of the orientational order of  $M_2$  mesogenic

groups at higher temperatures, and mesomorphism was enhanced. The structure of  $M_2$  in the polymers did not change their mesogenic types.



**Figure 6** X-ray diffractograms of the quenched samples  $P_0$  and  $P_2$ .

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