

# Synthesis and Characterization of Block Copolymers Containing PC Segments and PHTH-6 Mesogenic Units

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**ABSTRACT:** Liquid crystalline block copolymers that incorporate both PHTH-6 mesogenic units and polycarbonate (PC) segments in the main chain were synthesized by polycondensation in solution of hydroxyl-terminated PC and acid-chloride-terminated PHTH-6. The copolymer compositions were determined from <sup>1</sup>H-NMR data. The structure, thermal properties, as well as liquid crystalline behavior of the block copolymers were characterized by <sup>1</sup>H-NMR, Fourier transform infrared (FTIR), differential scanning calorimetry (DSC), polarizing optical microscopy (POM), transmission electron microscopy (TEM), and X-ray scattering, etc. A novel kind of morphology of a liquid crystalline block copolymer, a feathery structure, was observed for the first time, in which the PHTH-6 mesogenic microphase dispersed in the PC microdomain in the form of feathery structure. These block copolymers showed a microphase-separation system, for which the geometry on a length scale changes from tens of nanometers to 600 nm and the degree of phase separation was strongly dependent on the segment lengths incorporated. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 283–294, 2002; DOI 10.1002/app.10318

**Key words:** block copolymers; liquid-crystalline polymers; morphology; polycondensation

## INTRODUCTION

The linking of a liquid crystalline polymer with a conventional polymer in the form of a liquid crystalline block copolymer opens up a new approach for the combination of advantageous properties<sup>1</sup> of a liquid crystalline polymer with the favorable properties of amorphous and semicrystalline polymers. Since the issue of the first reports on the synthesis of a liquid crystalline block copolymer in 1985 by Lambert et al.,<sup>2</sup> much effort has

been devoted to this research field. The number of investigations dealing with the synthesis and characterization of block copolymers with liquid crystalline segments has rapidly increased over the last 15 years.<sup>3–11</sup> Interest in these copolymers is basically related to their potential use in the following aspects<sup>9,12–16</sup>: First, block copolymers containing liquid crystalline segments can be used as a reinforcing element due to their rigid molecular structures to realize the concept of molecular or supramolecular self-reinforcement or of molecular composites. Second, these new materials can be of great value in clarifying fundamental aspects of polymer physics. For example, liquid crystalline block copolymers can be used as

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model systems for semicrystalline block copolymers that will provide a new opportunity to obtain equilibrium relations between gross geometrical and topological patterns. Third, the special morphologies of liquid crystalline block copolymers, caused by microphase separation, may provide a new opportunity for the development of new, unexpected behavior or synergistic effects of selected properties, thus allowing the development of *tailor-made materials* by clever coupling of suitable units. Finally, these materials can be used to elucidate the influence of an amorphous block on the phase structure of the liquid crystalline component and the nature of the mesophase transitions in restricted geometries/dimensions.

Recently, polymer blends of thermotropic liquid crystalline polymers (TLCPs) with thermoplastics have provoked increasingly focused interests for their great potential for high-performance composites with outstanding mechanical properties, good thermal stability, and good process ability in the melt due to their low melt viscosity.<sup>17–19</sup> However, their practical application in product design and engineering has been restricted by the poor compatibility between the TLCPs and the thermoplastic matrix due to self-aggregation and phase separation, which results in rough dispersion and poor adhesion of the interfaces toward each other.<sup>20,21</sup> Several different approaches have been developed for enhancing the compatibility between liquid crystalline polymers and thermoplastic polymers.<sup>22–29</sup> Liquid crystalline block copolymers have proved to be an effective compatibilizer in polymer-blend systems of TLCPs with a thermoplastic matrix and also have proved to be efficient in the control of the microphase dimension of the blend system of TLCPs/thermoplastics.<sup>30–32</sup> Enhancement of the interfacial adhesion by a block copolymer is achieved when one block can selectively mix with one component of the polymer blend and the other block can dissolve preferentially the other component. Thus, the liquid crystalline block copolymer can serve as a bridge between TLCPs and the thermoplastic matrix. If the compatibility between thermoplastics and TLCP reinforcement material could be sufficiently increased, the mechanical properties of these blend systems should be enhanced dramatically. So, studies on the synthesis, structure, and properties of the liquid crystalline block copolymers are of considerable interest for potential application and theoretical research as well.<sup>3,33</sup> Different approaches to the preparation of liquid crystalline block copolymers

have been reported, including (1) living and quasi-living polymerization such as anionic,<sup>34,35</sup> cationic,<sup>36</sup> ring-opening metathesis,<sup>37</sup> and group transfer<sup>38</sup>; (2) polycondensation<sup>39,40</sup>; (3) the use of macroinitiators<sup>41,42</sup>; (4) transfer agents<sup>43</sup>; (5) coupling of end-functionalized homopolymers<sup>44,45</sup>; and (6) polymer-analogous reactions of AB-type prepolymers.<sup>46,47</sup>

In this article, we present the synthesis and characterization of a series of liquid crystalline block copolymers with PHTH-6 mesogenic units and polycarbonate (PC) segments by solution polycondensation. In particular, the influence of the segment lengths on the resulting morphology, phase behavior, glass transition, and melting behavior of the block copolymers is discussed. The objective of our work was to enhance the compatibilities in the blends of TLCPs with PC by using PHTH-6-*b*-PC as a compatibilizer wherein the PC segments are identical with the repeating units of the isotropic polymer to be blended. If the compatibility between PC and the TLCP could be sufficiently improved, the comprehensive properties of this blend system should be enhanced. In the following article, we shall describe in detail the mechanical properties, thermal properties, and melt rheological behavior of TLCP/PC blends compatibilized by PHTH-6-*b*-PC block copolymers.

## EXPERIMENTAL

### Materials

Methyl *p*-hydroxybenzoate, 1,6-hexanediol, Bisphenol A (BPA), 1,6-dioxane, tetrabutyl orthotitanate, phenol, and trifluoroacetic acid (TFA) were used without further purification. Diphenyl carbonate (DPCB) was of polymer-grade purity and was used as received. 1,1,2,2-Tetrachloroethane (TCE) was distilled prior to use. Terephthaloyl chloride (TC) was purified by distillation under a vacuum and then recrystallized from *n*-hexane.

### Synthesis of ( $\alpha,\omega$ )Bis(4-hydroxybenzoyloxy)hexane (I)

Methyl *p*-hydroxybenzoate and 1,6-hexanediol were added to a three-neck flask according to a molar ratio of 2.1:1. Tetrabutyl orthotitanate was also added as a transesterification catalyst. The reaction mixture was heated to 150°C under a

nitrogen atmosphere and kept at that temperature for 0.5 h. Then, the temperature was increased gradually to 200°C and kept there until no methanol was distilled out. The products were washed three times with water and then recrystallized by 80% ethanol. The melting point and elemental analysis of the compound were as follows: 183°C. ANAL. Calcd: C, 67.1%; H, 6.1%. Found: C, 67.1%; H, 6.4%.

#### Synthesis of Acid-chloride-terminated PHTH-6 (II)

The polycondensation reaction was performed in a three-neck flask equipped with a N<sub>2</sub> inlet and a stirrer. Before starting the polycondensation, the flask was purged three times with nitrogen. Afterward, TC and ( $\alpha,\omega$ )bis(4-hydroxybenzoyloxy)hexane (I) with a certain molar ratio were put into the flask and dissolved in 40 mL TCE under vigorous stirring. The reaction mixture was slowly heated to 145°C and kept there for about 12 h until there was no hydroxyl absorption on FTIR spectroscopy.

#### Synthesis of Hydroxyl-terminated PC (III)

An appropriate amount of BPA, DPCB, Sb<sub>2</sub>O<sub>3</sub> ( $3 \times 10^{-4}$  BPA), and Zn(OAc)<sub>2</sub> · 2H<sub>2</sub>O ( $3 \times 10^{-4}$  BPA) were added into a three-neck flask equipped with a nitrogen (N<sub>2</sub>) inlet, a stirrer, and a distillation head. The reaction mixture was stirred under a nitrogen atmosphere and then heated gradually to 180°C; 15 min later, the reaction system was evacuated to 50 mmHg. Then, the mixture was allowed to react for about 4 h under this condition. Afterward, the temperature was increased at a heating rate of 1°C/min to 250°C and kept at this temperature for 0.5 h. At the same time, the pressure was reduced gradually to 20 mmHg. At last, the reaction temperature was further increased to 270–280°C in 20 min and the pressure was reduced to 2–3 mmHg. After another 2–2.5 h, the product was scratched out of the vessel. The resulting product was precipitated from 1,4-dioxane into methanol and finally dried under a vacuum at 70°C for 24 h. The inherent viscosity ( $\eta_{inh}$ ) of the PC oligomer was 0.26 dL/g and the number-average molecular weight ( $M_n$ ) was 4950, which were determined by VPO investigation.

#### Synthesis of PHTH-6-*b*-PC Block Copolymer

An appropriate amount of the hydroxyl-terminated PC (III) dissolved in 25 mL TCE was added

to the above (II) reaction solution. Then, the polycondensation reaction was continued for another 12 h. Afterward, the reaction mixture was cooled to room temperature and the block copolymer was precipitated in methanol. At last, the final product was extracted with 1,4-dioxane for about 24 h to remove any unreacted PC oligomers and then dried under a vacuum at 70°C for 24 h.

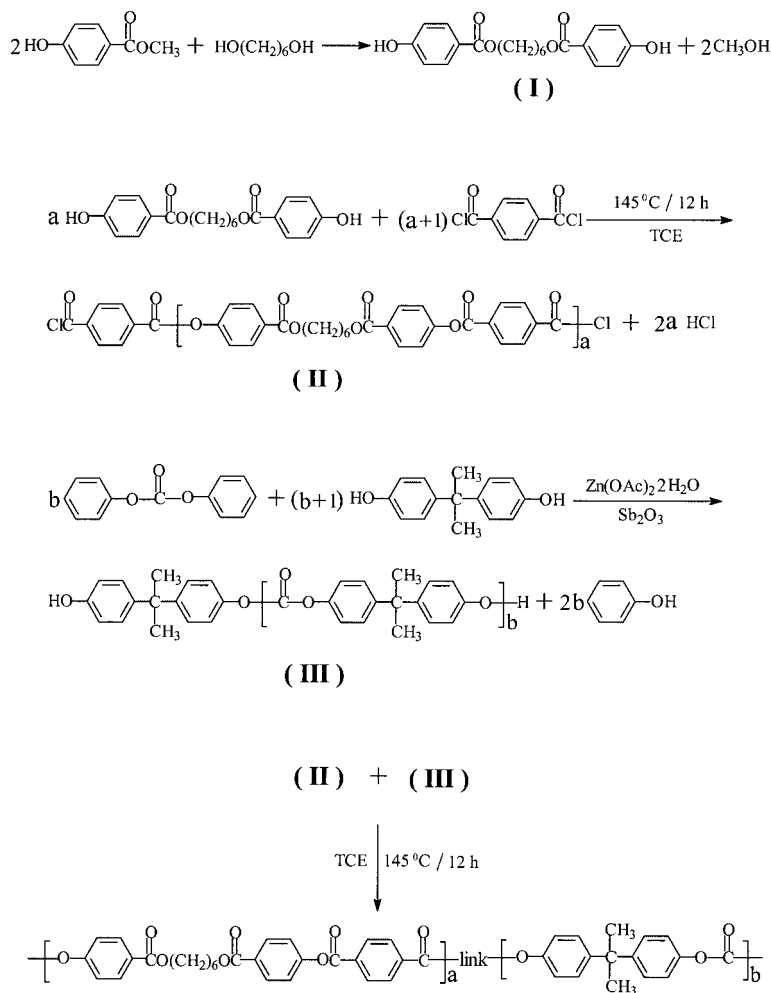
#### Measurements

FTIR spectra were collected on a Nicolet 5DXFT-IR spectrometer. Inherent viscosities of the liquid crystalline polymer as well as of their corresponding block copolymers were measured at a concentration of 0.5 dL/g in a phenol/TCE mixture [1:1 (wt)], using an Ubbelohde viscometer at 25°C. The elemental analysis was carried out using a Carlo Erba Model 1102 analyzer. <sup>1</sup>H-NMR spectra were recorded on an ARX 400 spectrometer. The samples were prepared in deuterated TFA (CF<sub>3</sub>COOD), and the spectra were calibrated using tetramethylsilane (TMS) as an internal standard. The optical characterizations were carried out on a Leitz polarizing optical microscope (POM) equipped with a hot stage, at a magnification of 200×. Room-temperature wide- and small-angle X-ray diffraction (WAXD and SAXD, respectively) patterns were taken on a Rigaku D/max-2400 X-ray diffractometer (CuK $\alpha$  radiation, 40 kV, 100 mA), and the range of measurement was 5–60° for WAXD and 0.7–5° for SAXD, respectively. Transmission electron micrographs were recorded using a JEM-200CX TEM. The samples were prepared as thin films from a polymer solution in TFA/CHCl<sub>3</sub> by spreading on distilled water. DSC was performed on a DuPont 2100 thermal analyzer under a nitrogen flow at a heating rate of 20°C/min. The transition temperature was taken as the maximum point of the endotherm.

## RESULTS AND DISCUSSION

#### Synthesis and Liquid Crystalline Behavior

The synthetic procedure used for the preparation of the liquid crystalline block copolymers PHTH-6-*b*-PC can be roughly divided into three steps (Fig. 1): In the first step, the acid-chloride-terminated liquid crystalline polymer PHTH-6 was prepared by solution polycondensation of TC and the monomer (I). Instead of the multistep reaction



**Figure 1** Synthetic route of liquid crystalline block copolymer PHTH-6-*b*-PC.

utilized in the literature,<sup>48</sup> here, the monomer (I) was synthesized by a one-step transesterification reaction of methyl *p*-hydroxybenzoate and 1,6-hexanediol. Furthermore, to enhance the polycondensation reaction rate, the reaction temperature of polycondensation in solution was increased to 145°C. By changing the molar ratio of TC to the monomer (I), PHTH-6 with different molecular weights can be obtained; the corresponding results are given in Table I.

In the second step, the hydroxyl-terminated PC oligomers (III) with different molecular weights were synthesized by selecting the molar ratio of BPA to DPCB through transesterification. In the last step, the liquid crystalline block copolymers with different PHTH-6 and PC segment lengths were formed by polycondensation in a solution of hydroxyl-terminated PC and acid-chloride-terminated PHTH-6. To make it easy to separate un-

reacted oligomers from the block copolymers, the hydroxyl-terminated PC was fed in excess.

A POM is one of the most useful instruments to investigate liquid crystalline properties, which

**Table I** Properties of PHTH-6 Synthesized by Changing the Ratio of TPC and (I)

Samples	TPC : (I) (mol/mol)	$\eta_{inh}$ (dl/g)	Phase Transition Data <sup>a</sup>
PHTH-6-1	1.10 : 1	0.38	C 234.8 N 337.5 I
PHTH-6-2	1.06 : 1	0.46	C 239.1 N 343.5 I
PHTH-6-3	1.04 : 1	0.55	C 241.1 N 347.3 I
PHTH-6-4	1.03 : 1	0.59	C 244.2 N 351.6 I
PHTH-6-5	1.02 : 1	0.65	C 248.3 N 357.7 I

<sup>a</sup> C: crystalline state; N: nematic phase; I: isotropic liquid state.

**Table II** Composition and Inherent Viscosity of Block Copolymer PHTH-6-*b*-PC

Samples	Synthesis	Content in PHTH-6- <i>b</i> -PC (mol %) <sup>a</sup>		$\eta_{inh}$ (dL/g)
		PC	PHTH-6	
B1	PHTH-6-1 ( $X_n = 10$ ) + PC ( $X_n = 19$ )	64.6	35.4	0.68
B2	PHTH-6-2 ( $X_n = 17$ ) + PC ( $X_n = 19$ )	51.6	48.4	0.71
B3	PHTH-6-3 ( $X_n = 25$ ) + PC ( $X_n = 19$ )	45.9	54.1	0.77
B4	PHTH-6-4 ( $X_n = 33$ ) + PC ( $X_n = 19$ )	41.5	58.5	0.80
B5	PHTH-6-5 ( $X_n = 49$ ) + PC ( $X_n = 19$ )	30.2	69.8	0.86

<sup>a</sup> Calculated values from <sup>1</sup>H-NMR.

can provide direct information on the liquid crystalline phase, such as its formation and transition, as well as the determination of the type of liquid crystalline and phase-transition temperature. Examination of all block copolymers under a POM shows them to be highly birefringent and liquid crystalline. The liquid crystalline texture is not altered in comparison to that of the pure PHTH-6 oligomer. A uniform threaded nematic texture was observed in all cases when the sample was heated above 240°C and no detectable phase separation was found on a macroscopic scale. As the temperature reaches about 280°C, some dark regions begin to appear, as opposed to the highly birefringent regions. These dark regions were examined under the polarizer alone to ascertain that they contained polymer and not air bubbles, which may be attributed to the isotropic transition of the block copolymers with lower molecular weight. As the temperature increased, the dark regions grew in size. The complete disappearance of liquid crystallinity of the samples occurs around 320–340°C, which was well consistent with the DSC results.

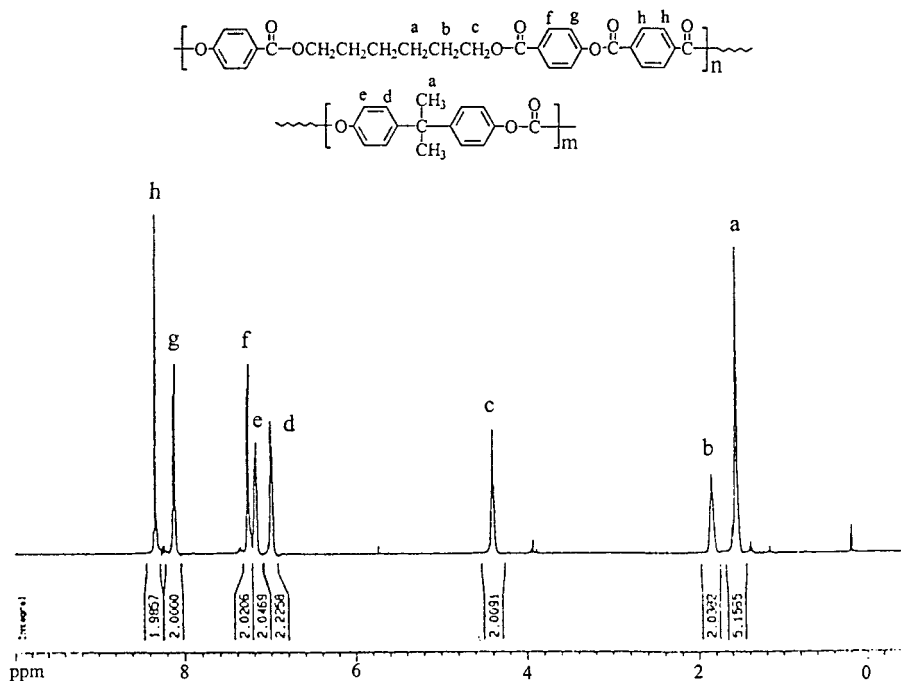
### Composition and Structure

The molar compositions of block copolymers calculated from the <sup>1</sup>H-NMR results and inherent viscosities are listed in Table II. It can be seen that the molar percentage of PHTH-6 segments in PHTH-6-*b*-PC increases with increasing molecular weights of PHTH-6 oligomers as the molecular weights of PC oligomers were unchanged. A similar trend was also obtained by the measurement of the inherent viscosity of the liquid crystalline block copolymers. In addition, it is clear from Tables I and II that the inherent viscosities of all the liquid crystalline block copolymers were

markedly larger than were those of the corresponding PC and PHTH-6 oligomers. The above results obviously revealed that the PC segments and PHTH-6 segments have been linked together by chemical bonds.

To further confirm the formation of a liquid crystalline block copolymer, <sup>1</sup>H-NMR spectrum analysis was carried out (see Fig. 2). The terephthalate protons ascribed to PHTH-6 segments appear at 7.3, 8.1, and 8.3 ppm, while the peaks at 7.0 and 7.1 ppm correspond to the terephthalate protons of the PC segments. The peaks that appeared at 4.4, 1.8, and 1.5 ppm belong to the methylene protons of the PHTH-6 segments. It is noticed that the peak at 1.5 ppm associated with the methyl protons of the PC segments showed a superimposition with that originating from the methylene protons of the PHTH-6 segments.

Figure 3 illustrates the FTIR difference spectra of the liquid crystalline block copolymer PHTH-6-*b*-PC and the mixture consisting of PHTH-6 and PC oligomers minus pure PHTH-6, along with the spectrum of the pure PC. From Figure 3, we found that the difference spectrum of the mixture sample minus pure PHTH-6 was completely identical with that of pure PC, which indicates the absence of interactions between PHTH-6 and PC oligomer molecular chains in the PHTH-6/PC mixture. In other words, each polymer component keeps its individual properties, especially its own molecular environment, unaffected by the presence of the other polymer components in the mixture. In the case of the FTIR difference spectrum of PHTH-6-*b*-PC minus pure PHTH-6, it became more complex than was the spectrum of pure PC, clearly indicating that the configuration and location of some bands were quite different from those in the mixture. In other words, the adjacent struc-

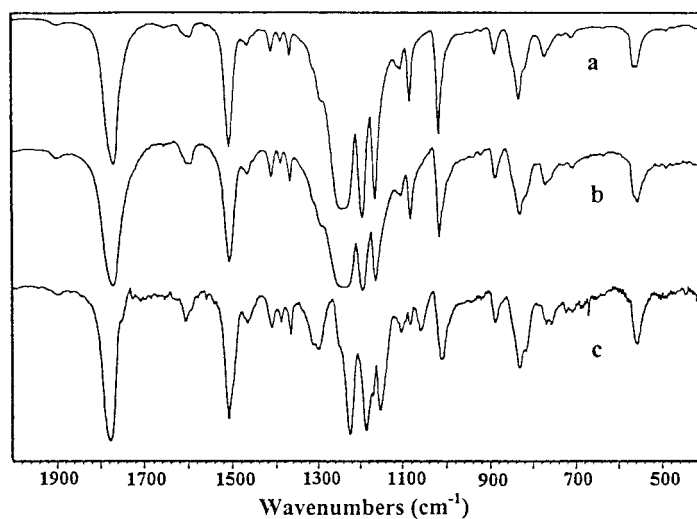


**Figure 2**  $^1\text{H-NMR}$  spectrum of liquid crystalline block copolymer B2.

ture and molecular environment of some groups were changed due to the linking of PHTH-6 segments and PC segments by chemical bonds.

The solid-phase structures of PHTH-6-*b*-PC along with the liquid crystalline polymer PHTH-6 were examined using room-temperature X-ray diffraction experiments (see Fig. 4). The corresponding results are listed in Table III. It can be seen that the completely identical diffuse peaks

were found in both the liquid crystalline polymer PHTH-6 oligomer and the PHTH-6-*b*-PC block copolymer sample, clearly indicating that the block copolymers have the same crystalline structure as that of PHTH-6. In other words, the crystallization of the block copolymer is caused by the PHTH-6 segment. On the other hand, owing to that PC oligomers are completely amorphous, it can be concluded that PHTH-6-*b*-PC exhibited a



**Figure 3** FTIR spectra of (a) PC, (b) difference spectrum of mixture minus PHTH-6-1, and (c) difference spectrum of B1 minus PHTH-6-1.

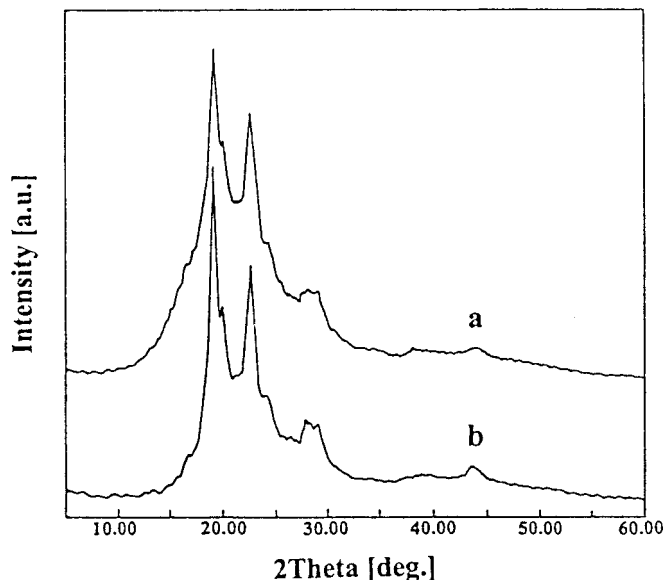


Figure 4 X-ray diffraction patterns of (a) B2 and (b) PHTH-6-2.

microphase-separated structure, which is characterized by the coexistence of an amorphous PC phase and a lateral-ordered nematic PHTH-6 phase. It is well known that each segment in the block copolymer keeps its own individual characteristics on the whole, with the segments capable of crystallization forming their own crystalline microregion, which is completely consistent with our experimental results. Very similar diffraction spectra were also recorded for other block copolymers.

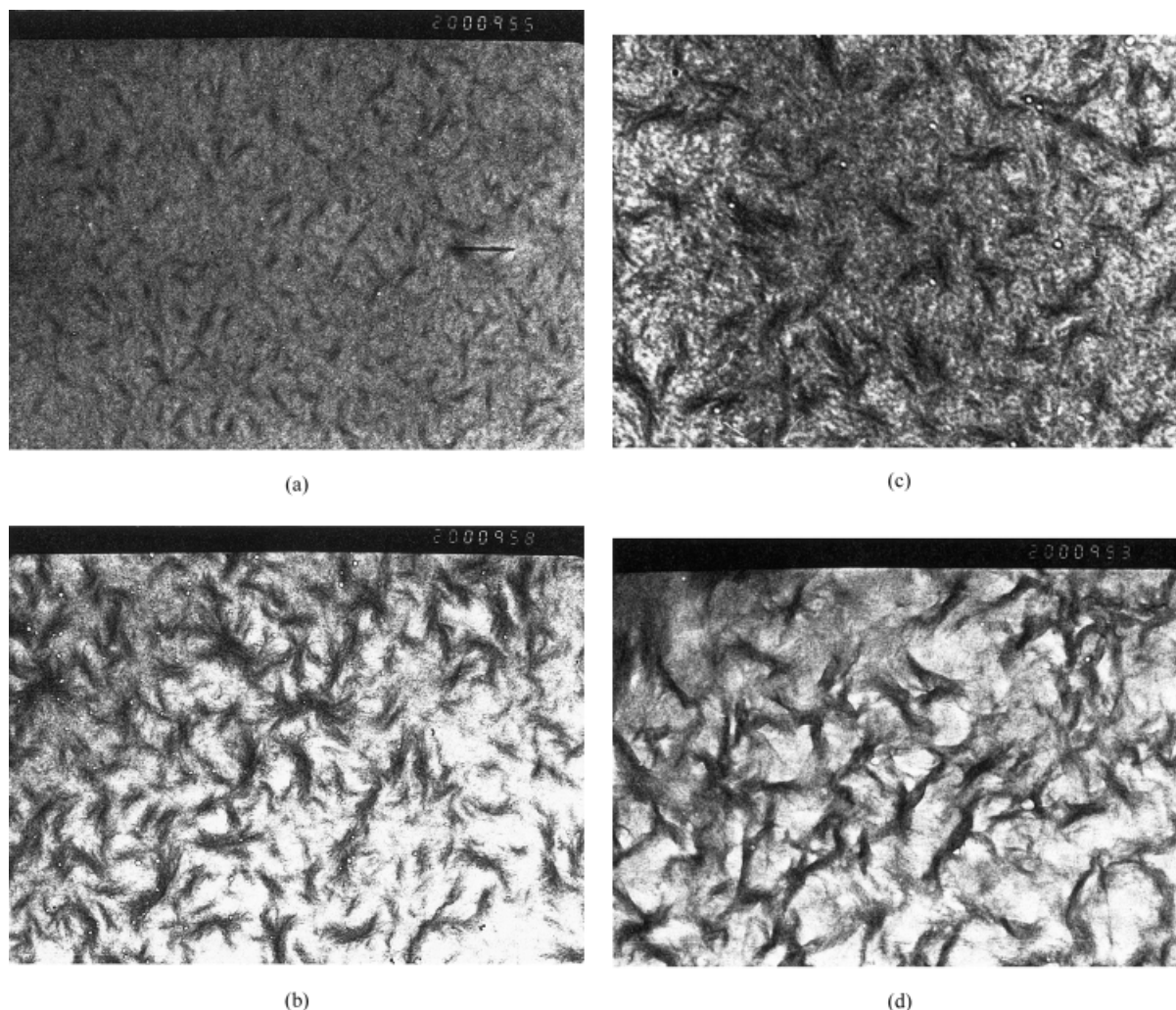
To obtain a deeper insight into the microphase separation of block copolymers as well as to investigate the effect of the segment length of the

incorporated block on the morphology of the resulting copolymers, TEM analyses were carried out using thin films obtained by spreading a TFA/chloroform solution on the distilled water surface. In general, block copolymers composed of incompatible polymer segments form the microdomain morphology in the solid state. Owing to the chemical linkage between the noncompatible polymer components, phase separation is usually limited to the nanoscopic scale. The phase separation is dependent mainly on the thermodynamic interaction parameters, the volume fraction of the different components, the temperature, the composition of the blocks, as well as the molecular weight and the molecular weight distribution of the constituent component chains.<sup>10,49,50</sup> Depending on the different conditions mentioned above, several different morphologies<sup>51-53</sup> were observed for the block copolymers. These include spherical and cylindrical structures, an ordered bicontinuous structure, a gyroid structure, a double-diamond structure, a zigzag structure, a hollow cylinder structure, a punched sheets structure, and a catanoid lamellae structure.

In this research, we focused special attention on the effect of the molecular weight of the segments incorporated into the microphase separation of the resulting block copolymers. Figure 5 illustrates TEM micrographs of the block copolymers with different mesogenic segment molecular weights, along with the mixture consisting of PHTH-6 and PC. A novel kind of morphology of a

Table III Distance Between Face of Crystal of PHTH-6-2 and B2 as Well as Corresponding  $2\theta$  and Relative Intensity of Diffuse Peaks

B2			PHTH-6-2		
$2\theta$	$I/I_{\max}$	$D$ (Å)	$2\theta$	$I/I_{\max}$	$D$ (Å)
3.40		25.96	3.42		25.89
18.18	72	4.87	18.28	45	4.85
18.98	100	4.67	19.30	100	4.60
20.48	68	4.33	20.90	51	4.25
22.80	66	3.90	22.50	39	3.94
23.08	68	3.85	23.40	69	3.80
25.30	40	3.51	25.60	28	3.48
27.98	32	3.18	28.08	24	3.18
29.20	32	3.05	29.50	27	3.03

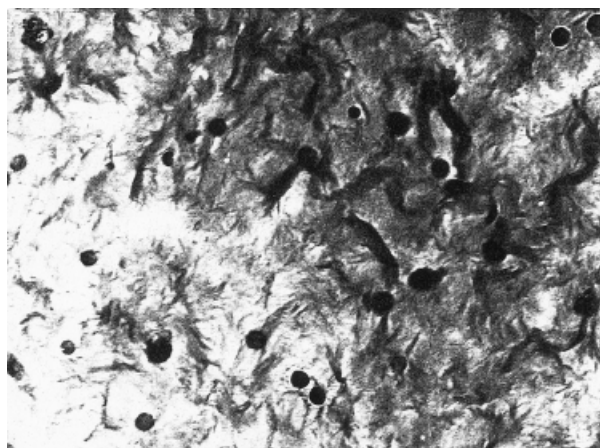


**Figure 5** TEM micrographs of (a) B1, (b) B2, (c) B3, (d) B4, (e) B5, and (f) mixture of PC and PHTH-6-1 oligomers (at a magnification of  $2 \times 10^4 \times$ )

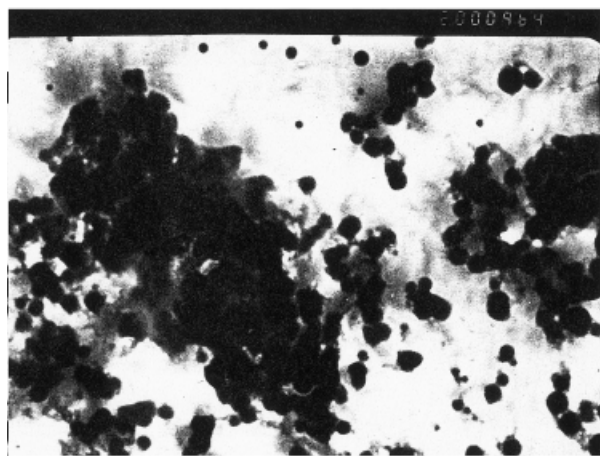
liquid crystalline block copolymer was found for the first time, in which the PHTH-6 microphase dispersed in the PC microdomain in the form of a feathery structure which is obviously different from that reported in other literature. Furthermore, it should be noted that the block copolymers exhibited a distinct microphase separation to a different extent, although showing a uniform liquid crystalline texture under a polarizing microscope. The dark region is the PHTH-6 microdomain, while the bright region is the PC microdomain. With increase of the molecular weight of the PHTH-6 segment, the dimensions of the PHTH-6 microdomain increase accordingly. The geometry on a length scale changes from about tens of nanometers to 600 nm. It can be stated that the degree of phase separation of the block

copolymers is dependent on its segment length. In other words, the morphology of the block copolymer covering the range of less phase-separated copolymers to samples with a high degree of phase separation can be controlled by the variation of the PHTH-6 segment lengths. Moreover, a very interesting morphology was observed for the block copolymer B5 [Fig. 5(e)], in which the PHTH-6 feathery microphase was accompanied by numbers of PHTH-6 spherical domains, which was quite different from the morphology observed in other block copolymers. The reason is not very clear at present. It is may be due to the aggregation of the longer PHTH-6 segment fraction of the block copolymers. In addition, a significant difference of morphology was observed in the PHTH-6/PC mixture [Fig. 5(f)], for which the PHTH-6





(e)



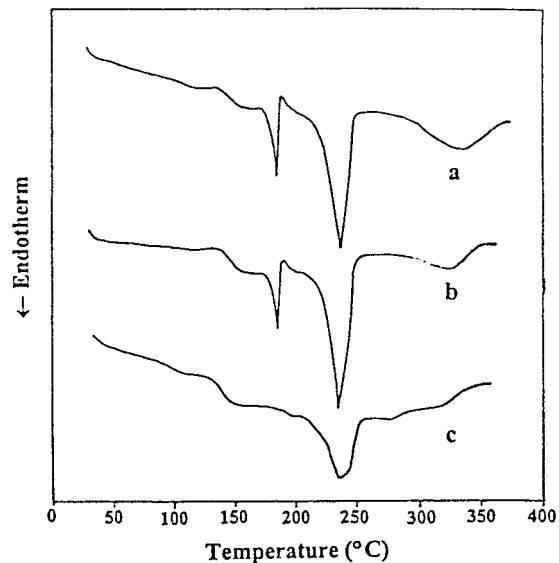
(f)

**Figure 5** (Continued from the previous page)

phase dispersed in the PC matrix in the form of a larger aggregation, revealing an obvious two-phase structure.

### Thermal Property

The structure formation of liquid crystalline block copolymers is basically understood and has been extensively reviewed. However, due to the anisotropic phase structure of the liquid crystalline segment in block copolymers, a new question arises concerning how the size and type of the isotropic and liquid crystalline microphases, which can be controlled by their corresponding segment molecular weight and composition, affects the glass transition and the liquid crystalline behavior of a liquid crystalline block copolymer. Although many different liquid crystalline block copolymers have been synthesized during



**Figure 6** DSC thermograms of (a) B3, (b) B2, and (c) B1.

the last 15 years, only a few works have dealt with detailed examinations of the physical properties<sup>10</sup>; thus, so far, no general answers to the physics of liquid crystalline block copolymers could be given. Therefore, it is clear that more work is required to motivate further research in this new field.

Figure 6 shows DSC traces of the block copolymers with different molecular weights of the incorporated PHTH-6 segments, and their corresponding transition temperatures are summarized in Table IV. Upon heating from 20 to 350°C, the block copolymers B2, B3, B4, and B5 show four different transitions: an indication of a glass transition around 140–150°C and two sharp en-

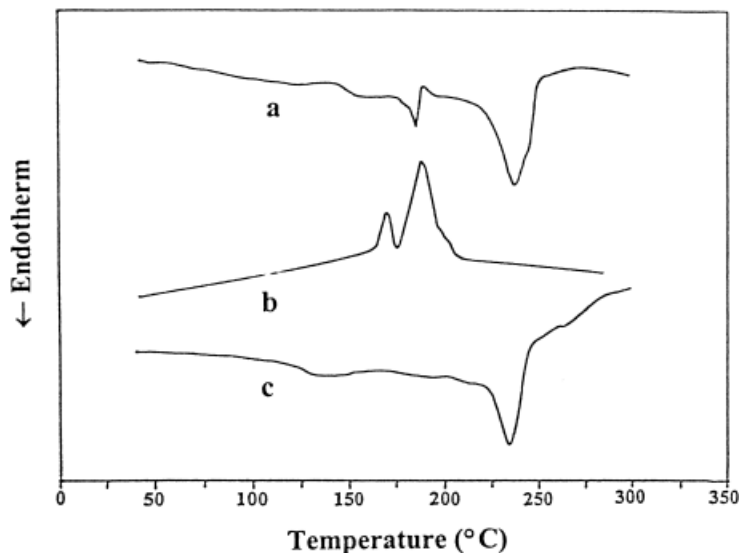
**Table IV** Phase-Transition Temperature of Block Copolymers with Different PHTH-6 Segment Molecular Weights

Samples	Phase-Transition Temperature (°C)			
	$T_g^a$	$T_{m1}^b$	$T_{m2}^c$	$T_i$
B1	137.7	—	238.4	321.0
B2	142.3	183.4	236.6	324.8
B3	148.0	183.3	236.9	330.4
B4	151.8	183.7	239.7	333.7
B5	153.2	182.2	242.2	340.1

<sup>a</sup> Amorphous PC regions.

<sup>b</sup> Melt transition before *K-N* transition.

<sup>c</sup> *K-N* transition.



**Figure 7** DSC thermograms of B2: (a) first heating; (b) first cooling; (c) second heating.

dotherms at  $\sim 180$  and  $\sim 240^\circ\text{C}$ , respectively, followed by one broad endothermic peak at  $320$ – $340^\circ\text{C}$ . POM studies revealed that the endothermic peak around  $\sim 240^\circ\text{C}$  was attributed to the crystal–nematic ( $K \rightarrow N$ ) transition, and the peak around  $320$ – $340^\circ\text{C}$ , to the nemati–isotropic ( $N \rightarrow I$ ) transition. The endotherm observed around  $180^\circ\text{C}$  is present only in the first heating scan and it disappears in the subsequent thermal cycle [see Fig. 7(c)]. The origin of this peak is not clearly understood at the present time. A similar phenomenon was also observed in the case of a Triad-4-*co*-PBT block copolymer by Kantor et al.,<sup>54</sup> which was considered to be due to some crystal–crystal transition. For copolymer B1, on the other hand, only three transitions were found, while the endotherm at  $180^\circ\text{C}$  was no longer present. Thus, this endotherm may be associated with the extent of phase separation of the block copolymer PHTH-6-*b*-PC; the less phase separation will be in favor of the formation of a more perfect crystal for PHTH-6-*b*-PC, but good understanding of this endotherm will require additional studies to characterize it more completely.

The block copolymers are expected to exhibit two  $T_g$ 's corresponding to the PC and PHTH-6 segments. However, because of the rigidity, the  $T_g$  of the PHTH-6 segment was not detected in the DSC thermogram, but we observed a  $T_g$  of about  $48^\circ\text{C}$  for the PHTH-6 oligomers using dynamic mechanical analysis (DMA) at a heating rate of  $1^\circ\text{C}/\text{min}$  and an oscillation frequency of  $1\text{ Hz}$ .<sup>55</sup>

Therefore, it is reasonable to believe that the  $T_g$  of the block copolymer that appeared at about  $140$ – $150^\circ\text{C}$  corresponds to the glass transition of the amorphous PC phase, which is consistent with a  $T_g$  of  $152.6^\circ\text{C}$  for the corresponding PC oligomers. In addition, it is noticed from Table IV that the glass transition temperature of the amorphous PC phase in the block copolymer increases with an increasing molecular weight of the PHTH-6 segment when the molecular weight of the PC segment remains unchanged. This effect may be attributed to a combination of two factors: First, the rigid PHTH-6 mesogenic phase can reinforce the amorphous PC phase. Second, with increase of the PHTH-6 segment length, the extent of phase separation increases (see Fig. 5), each phase of the block copolymer tending to exhibit its own independent thermal response ( $T_g$ ). Moreover, an increase in the isotropic temperature ( $T_i$ ) and  $T_{m2}$  of the block copolymers was also noticed with an increasing molecular weight of the PHTH-6 segment. Therefore, the properties of the block copolymers can be tailored by controlling the mesogenic segment lengths incorporated. Furthermore, in comparing the thermal behavior of the block copolymers and the PHTH-6 oligomers collected in Tables I and IV, it is easy to see that the isotropic temperatures ( $T_i$ 's) of all the block copolymers are lower than are those of the corresponding PHTH-6 oligomers. This suggested that the stability of the liquid crystalline phase decreased due to the introduction of PC segments.

All these can refer to the interactions between the different blocks, which are caused by their chemical bonds.

## CONCLUSIONS

A series of liquid crystalline block copolymers, PHTH-6-*b*-PCs, containing PHTH-6 mesogenic segments and PC segments were synthesized. By using polycondensation schemes in solution with appropriate starting materials and reaction conditions, PHTH-6-*b*-PCs with different liquid crystalline segment lengths were successfully prepared and characterized. A new kind of morphology of a liquid crystalline block copolymer, a feathery structure, was observed in this study. The characterization evidence proves that the block copolymers exhibit a microphase-separation system, for which the geometry on a length scale changes from tens of nanometers to 600 nm depending on the different liquid crystalline segment molecular weights. The coupling of longer PHTH-6 segments results in the formation of higher-phase-separated systems. On the other hand, the thermal analysis of block copolymers shows that the introduction of longer liquid crystalline segments results in an increase of both the glass transition temperature and the mesophase-isotropic transition temperature. Therefore, it can be concluded that the segment lengths incorporated, to some extent, can control the morphologies and properties of block copolymers. In other words, the properties of the block copolymers can be tailored by the coupling of segments with suitable molecular weights.

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