

## Thermal Properties of Thermotropic Liquid Crystalline Polymer/Polycarbonate Blends

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**ABSTRACT:** The thermal properties of blends of liquid crystalline poly(biphenyl-4,4'-ylene sebacate) (TLCP) and polycarbonate (PC) were investigated by differential scanning calorimetry. The glass transition temperature of blends decreases as the concentration of TLCP increases up to ca. 40% by weight. The observation of a single glass transition temperature indicates that PC is miscible with TLCP in this concentration range. The crystallization rate of TLCP in TLCP/PC blends decreases with increasing PC content. In particular, the crystallization rate is remarkably lower for a TLCP/PC (90/10) blend. However, the transition temperatures of TLCP are almost invariant with blend composition except for TLCP/PC (90/10) blend. The upper critical solution temperature (UCST) behavior was observed in blends containing 20—50 wt% PC whereas the phase separation was not observed in the other compositions.

**KEY WORDS** Thermotropic Liquid Crystalline Polymer / Polycarbonate / Polymer Blend / Crystallization Rate / Cloud Point / UCST /

Liquid crystalline polymers (LCPs) have recently received considerable attention for their excellent chemical resistance, thermal stability and mechanical performance. LCPs can be easily oriented in the melt or in the solution by an external field to form a liquid crystalline phase due to their rigid molecular structure. When processed in the liquid crystalline state, these materials generally possess excellent mechanical properties in the direction of orientation. Furthermore, the viscosity of LCP under processing conditions is lower than that of comparable flexible polymers.<sup>1,2</sup> The blends of LCPs with flexible polymers may have good mechanical properties due to the reinforcing effect of LCP. In particular, when the domain of LCP in blends has a fibrillar shape, the reinforcing effect becomes greater. The basic principle of molecular composites that a rigid rod polymer is dispersed in a flexible coil polymer at a scale no greater than a few nanometers is patented

by Helminak *et al.*<sup>3</sup>

Takayanagi *et al.*<sup>4</sup> studied wholly aromatic and aliphatic polyamide blends. However, the processibility of these blends with a lyotropic liquid crystalline polymer is very delicate due to their poor solubility. Thermotropic liquid crystalline polymers have been focused as materials to overcome the difficulty of this processing. The thermotropic liquid crystalline polymer, which is initially dispersed as spheres or droplets, can be elongated in adequate flow fields to give an *in-situ* reinforcement. Elongated fine fibrils can effectively reinforce the matrix as has been demonstrated by a number of authors.<sup>5-9</sup>

The morphology of such *in-situ* composites depends on the processing condition and thermal properties which can exert profound effect on the mechanical properties of the system. Thermal properties of blends of thermotropic liquid crystalline polymers with thermoplastic polymers have been investigated

by several workers.<sup>10-12</sup> Pracella *et al.*<sup>13</sup> studied the isothermal crystallization kinetics and melting behavior of blends of poly-(butylene terephthalate) (PBT) with poly-(decamethylene-4,4'-terephthaloyldioxydibenzoate). The thermal properties of blends of PBT and liquid crystalline poly(biphenyl-4,4'-ylene sebacate) was also studied.<sup>14</sup> However, the major efforts of these works were focused on the analysis of the influence of the liquid crystalline component on crystallization, melting process and glass transition of the blends.

In this study, the miscibility of poly-(biphenyl-4,4'-ylene sebacate) (TLCP)/polycarbonate (PC) blends are examined. The transition kinetics of TLCP in TLCP/PC blends and phase behavior are also discussed in terms of miscibility of TLCP/PC blends.

## EXPERIMENTAL

Polycarbonate (PC) was supplied by Lucky Co. and used as received without further purification. Poly(biphenyl-4,4'-ylene sebacate) was prepared by melt polymerization. 4,4'-Diacetoxibiphenyl was reacted in the melt with equimolar sebacic acid in the presence of sodium acetate catalyst, in a flask with a capillary tube which served as a nitrogen inlet. The flask was heated to 190°C in a sand bath and a continuous stream of nitrogen bubbles was passed through the capillary tube. The temperature was progressively increased up to 240°C and then the pressure was reduced. The inherent viscosity of TLCP was 0.53 when measured in a phenol/tetrachloroethane (60/40, v/v) solution at 25°C.

The blends were prepared by dissolving two polymers in the mixed solvent of phenol and tetrachloroethane (60/40, v/v). The polymer solutions were then poured into a large excess of methanol. The precipitated polymers were filtered and then dried in a vacuum oven at 120°C for 3 days.

Thermal analysis was performed on a du Pont 910 differential scanning calorimetry

(DSC). After the samples were maintained at 290°C for 1 min to destroy the thermal history, they were cooled to 100°C at a rate of 20°C min<sup>-1</sup> and then heated to 300°C at a rate of 20°C min<sup>-1</sup>. Using this dynamic thermal program, thermal transition temperatures such as the liquid crystallization temperature ( $T_{is}$ ), solid crystallization temperature ( $T_{sk}$ ), melting temperature ( $T_m$ ) and isotropization temperature ( $T_i$ ) were measured. For the measurement of glass transition temperature, the samples were melted at 290°C for 1 min, quenched into liquid nitrogen and then heated from 20°C to 220°C at a heating rate of 20°C min<sup>-1</sup>.

Cloud points were measured on a hot plate. The samples were placed on a glass slide with a groove and covered with another glass slide. The samples were placed on a hot plate maintained at 310°C which is above  $T_i$  of TLCP. The samples were then heated at a heating rate of 7°C min<sup>-1</sup> and the temperature at which the opaque sample became completely transparent by visual inspection was taken as a cloud point.

## RESULTS AND DISCUSSION

### *Transesterification*

Blends of polyester with PC often exhibit transesterification.<sup>15,16</sup> When such blends are held at higher temperatures, *i.e.*, near their melting points, an interchange reaction could occur leading eventually to random copolymers. Transesterification certainly leads to an improved compatibility of the two components of the blend. Therefore, in a discussion on the thermal behavior of TLCP/PC blends, the possibility of transesterification during the thermal treatments can not be overlooked.

Figures 1 and 2 show the DSC thermograms of TLCP/PC blends when the blends are isothermally maintained at different time intervals at 290°C and 300°C, respectively. The lower transition temperature is assigned to the melting temperature ( $T_m$ ) and the higher to the isotropization temperature ( $T_i$ ) of TLCP.  $T_m$ ,

## Thermal Properties of LCP/PC Blends

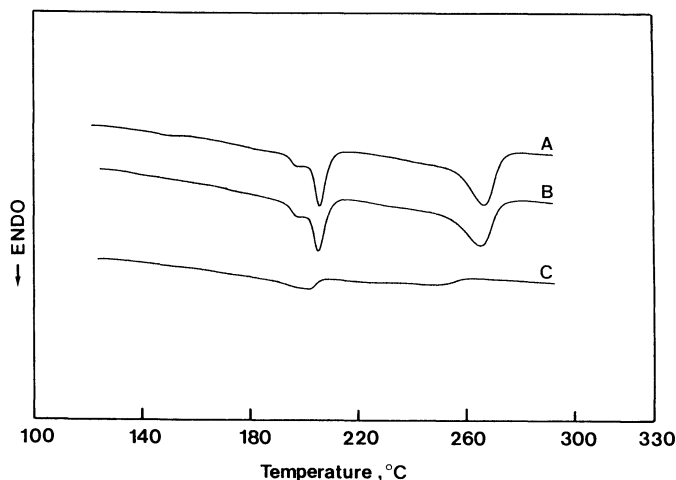


Figure 1. DSC thermograms of TLCP/PC (80/20) blend held at 290°C: (A) 1 min; (B) 4 min; (C) 5 min.

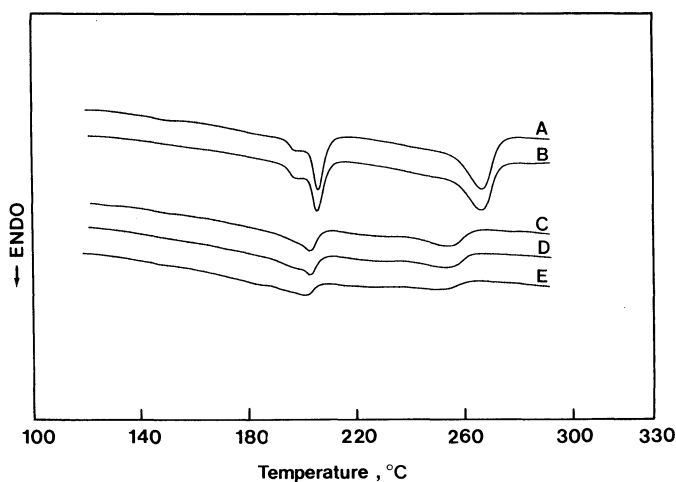


Figure 2. DSC thermograms of TLCP/PC (80/20) blend held at 300°C: (A) 1 min; (B) 2 min; (C) 3 min; (D) 4 min; (E) 5 min.

$T_i$  and the heats of transitions decrease with the increase of the thermal treatment time. The transition peaks of blends held at 290°C are almost the same until 4 min, while the transition peaks of blends held at 300°C are significantly changed even at 3 min. This suggests the progressive incorporation of PC units in the TLCP chains, which causes a disruption of the chain periodicity and of the lamellar organization of TLCP.

### Phase Behavior

The glass transition temperature of TLCP/PC blends decreases as the concentration of TLCP increases up to 40 wt%, as shown in Figure 3. A single glass transition temperature indicates that TLCP is miscible with PC in this concentration range; however, the heat capacity change during the glass transition decreases with the increase of TLCP concentration and finally the glass transition temperature could not be observed with the sensitivity of our

instrument at a concentration higher than 50 wt% of TLCP.

The melting and isotropization behavior of TLCP/PC blends are shown in Figure 4. The transition temperatures of TLCP are almost invariant with blend composition except for a TLCP/PC (90/10) blend. The transition peaks of a TLCP/PC (90/10) blend were broadened and shifted to lower temperatures. Figure 5

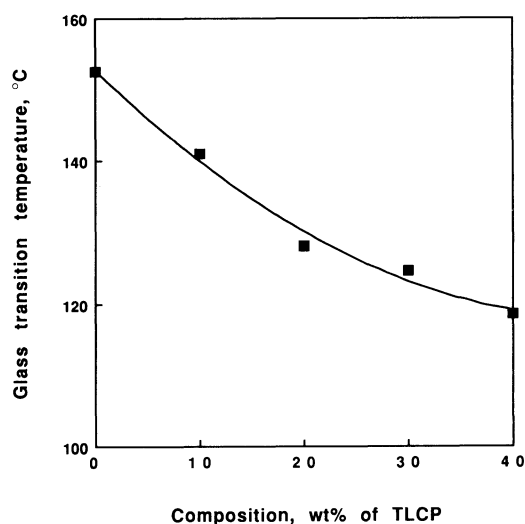


Figure 3. Glass transition temperatures for TLCP/PC blends versus the weight percent of TLCP.

shows cloud points above which TLCP/PC blends become a homogeneous phase, indicating that the blends show the upper critical solution temperature (UCST) behavior. The transesterification reaction might occur during the measurement of cloud points, which may enhance the miscibility and have an effect to lower the cloud point. However the successive cooling and heating in our experiment does not alter the cloud points of Figure 5 within experimental error. The cloud points are observed in blends containing 20–50 wt% PC while a TLCP/PC (90/10) blends is clear above the isotropization temperature. For a TLCP/PC (90/10) blend, the sample was cooled to observe the cloud point at the cooling mode; however, the cloud point is hardly observed because the temperature at which the sample becomes opaque is very close to  $T_{is}$  of TLCP.

Figure 6 shows the DSC thermograms of a TLCP/PC (90/10) blend when the sample is annealed at 230°C for different annealing times. As can be seen in Figure 6, the broad peaks become sharper and the transition temperatures shift to higher temperatures as the annealing time increases. Finally the DSC thermograms of a TLCP/PC (90/10) blend becomes similar to those of blends containing

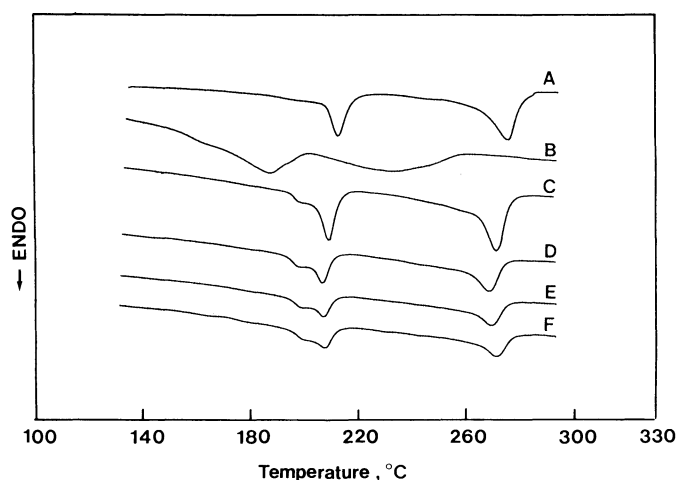


Figure 4. DSC thermograms of TLCP/PC blends at heating rate of 20°C min<sup>-1</sup>: (A) TLCP 100; (B) TLCP 90; (C) TLCP 80; (D) TLCP 70; (E) TLCP 60; (F) TLCP 50 wt%.

20–50 wt% PC. This suggests that the TLCP component in the blend phase separates on cooling from 290°C to 230°C and then the TLCP domain crystallizes as it is annealed. Therefore, it is reasonable to say that the phase separation occurs between 230°C and 290°C for a blend of TLCP/PC (90/10).

In an attempt to investigate the phase separation behavior of TLCP/PC (90/10)

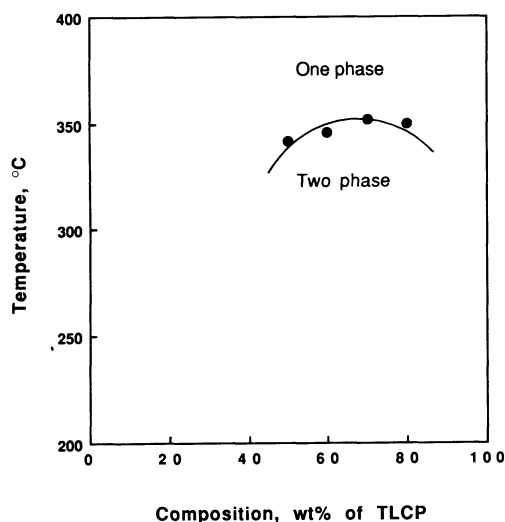


Figure 5. Cloud points for TLCP/PC blends versus the weight percent of TLCP.

blend, the samples were annealed at various annealing temperatures for 4 min. As shown in Figure 7, the sample shows dual melting endotherms and dual isotropization endotherms when annealed at 230°C. The lower peaks of both melting endotherms and isotropization endotherms may be attributed to small crystallites which are formed during the cooling from 290°C to the annealing temperature. The higher peaks of both melting endotherms and isotropization endotherms may be attributed to crystallites which are formed from a separated phase as it is annealed. The magnitude of the lower peak decreases with the increase of the annealing temperature up to 250°C while the magnitude of the higher peak increases. The transition peaks are again broadened and shifted to lower temperatures as the annealing temperature is further raised above 260°C, indicating that the TLCP/PC (90/10) blend shows a single phase at temperatures above 260°C and the crystallization is inhibited by the miscibility. Consequently, it is conclusive that the phase separation temperature lies between 250°C and 260°C.

The TLCP/PC (90/10) blends is miscible in the isotropic state and the phase separation

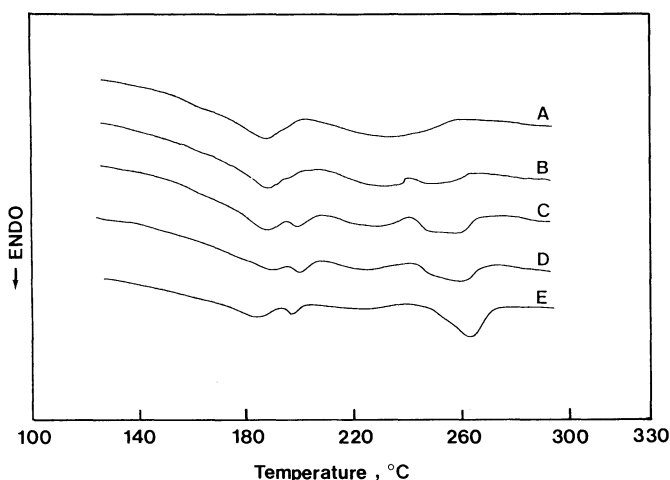


Figure 6. DSC thermograms of TLCP/PC (90/10) blend annealed at 230°C for different periods of time: (A) 0 min; (B) 1 min; (C) 4 min; (D) 10 min; (E) 30 min.

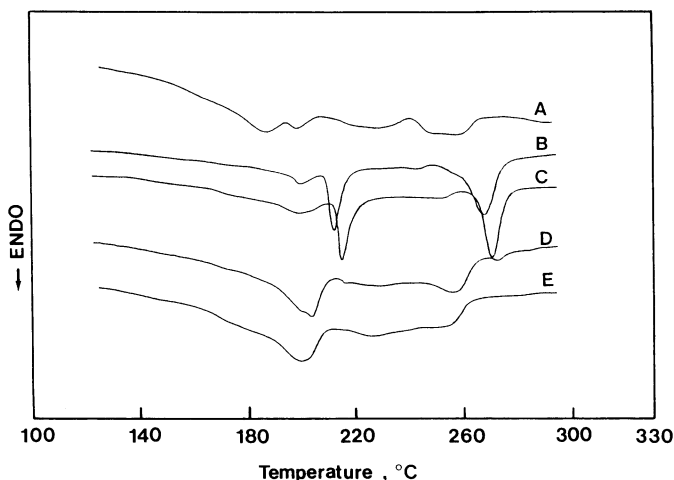


Figure 7. DSC thermograms of TLCP/PC (90/10) blend annealed for 4 minutes at various temperatures: (A) 230°C; (B) 240°C; (C) 250°C; (D) 260°C; (E) 270°C.

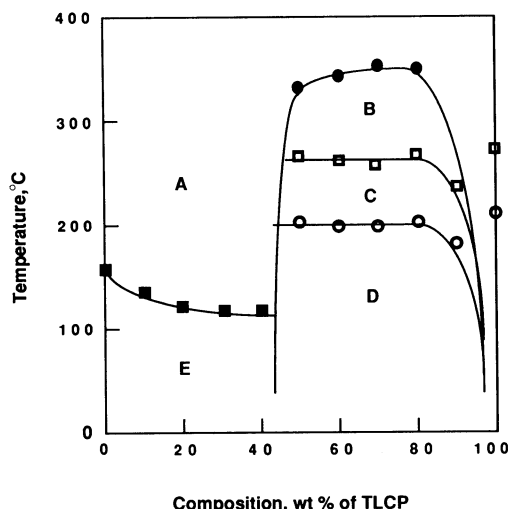


Figure 8. Phase diagram for TLCP/PC blends: (■)  $T_g$ ; (○)  $T_m$ ; (□)  $T_i$ ; (●) cloud points.

takes place on cooling. The phase separation temperature of a TLCP/PC (90/10) blend is lower than  $T_i$  of TLCP, which prevents most of the TLCP from undergoing liquid crystallization. Based on the cloud points and the transition temperatures of blends, it is possible to construct an approximate equilibrium phase diagram for the TLCP/PC system as shown in Figure 8. The regions indicated in the phase

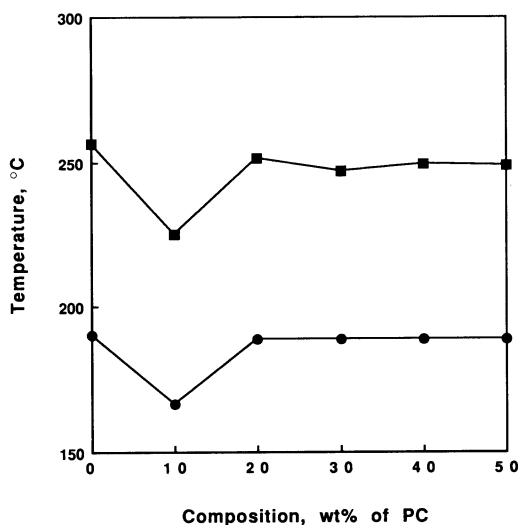
diagram is described as follows:

- (1) Region A is a one-phase mixture existing in an isotropic molten state.
- (2) Region B is a two-phase mixture of PC with isotropic TLCP.
- (3) Region C is a two-phase mixture of PC with smetic TLCP.
- (4) Region D is a two-phase mixture of PC with solid crystal TLCP.
- (5) Region E is a one-phase mixture of glassy PC with TLCP.

#### Non-Isothermal Crystallization

In the case of small molecule liquid crystalline materials, the kinetics of liquid crystallization and solid crystallization have been studied by several authors.<sup>17-19</sup> Liquid crystallization in these systems is characterized by a very small degree of supercooling and a very high rate of transformation. It was found that these transitions were nucleation-controlled and can be described by an Avrami-type equation.<sup>20</sup>

The crystallization temperatures of TLCP/PC blends are shown in Figure 9. It is interesting that the crystallization temperature of a TLCP/PC (90/10) blend is lower than those of any other blends. The kinetics of non-



**Figure 9.** Crystallization temperatures for TLCP/PC blends versus the weight percent of PC: (■) isotropic → mesophase; (●) mesophase → solid crystal.

isothermal crystallization was analyzed by the use of Ziabicki's approximate theory<sup>21</sup> or Jeziorny's approach.<sup>22</sup> These theories are based on the assumption that crystallization can be represented by the first order kinetics:

$$dX_t/dt = K(T)(1 - X_t) \quad (1)$$

where  $X_t$  is the degree of crystallinity after time  $t$  of the crystallization process, and the rate constant  $K(T)$  is dependent only on the temperature. It is assumed that the  $K(T)$  curve is equal to the DSC thermogram. The kinetic crystallizability  $G$  represents the degree of crystallinity over the entire crystallization range and can be calculated as follows:

$$G = \left( \frac{\pi}{\ln 2} \right)^{1/2} K_{\max} \left( \frac{D}{2} \right) \quad (2)$$

where  $K_{\max}$  is the maximum value of the rate constant and  $D$  is the half width of the  $K(T)$  curve.

$$K_{\max} = \frac{C_k}{t_{\max}} \quad (3)$$

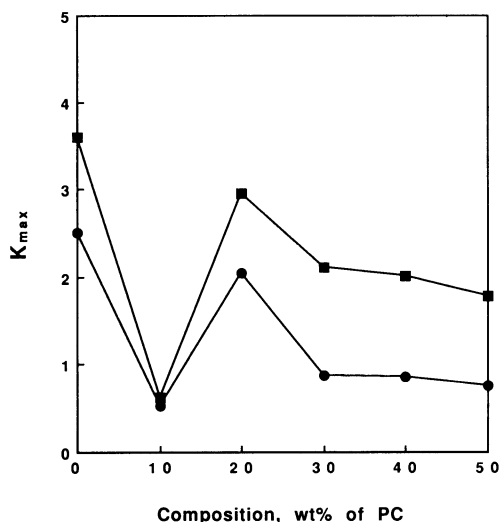
where  $t_{\max}$  is the time corresponding to the maximum value of rate constant  $K_{\max}$  and

**Table I.** Parameters characterizing the non-isothermal crystallization kinetics of TLCP/PC blends (isotropic → mesophase): cooling rate = 20°C min<sup>-1</sup>

TLCP/wt%	$D/K$	$K_{\max}$	$G/K \text{ min}^{-1}$
50	24.0	0.76	19.47
60	19.0	0.85	17.23
70	20.0	0.87	18.50
80	8.5	2.04	18.50
90	18.0	0.53	10.12
100	8.8	2.50	23.38

**Table II.** Parameters characterizing the non-isothermal crystallization kinetics of TLCP/PC blends (mesophase → solid crystal): cooling rate = 20°C min<sup>-1</sup>

TLCP/wt%	$D/K$	$K_{\max}$	$G/K \text{ min}^{-1}$
50	8.5	1.79	16.21
60	8.0	2.02	17.20
70	8.0	2.12	18.05
80	6.3	2.96	19.85
90	18.0	0.63	12.06
100	5.5	3.59	21.02



**Figure 10.** Maximum crystallization rate for TLCP/PC blends versus the weight percent of PC: (●) isotropic → mesophase; (■) mesophase → solid crystal.

$C_k$  is the ratio of crystallinity before and after  $t_{\max}$ .

For the present system, the values of pa-

rameters determined from eq 2, 3, and 4 are listed in Tables I and II. The larger value of  $K_{\max}$  indicates that the polymer crystallizes more rapidly.  $K_{\max}$  values are plotted against blend composition in Figure 10. The crystallization rate of TLCP in TLCP/PC blends decreases with the increase of PC concentration. In particular, the crystallization rate of a TLCP/PC (90/10) blend is lower than that of other compositions. This can be explained in relation to the phase separation temperature. Unlike other blends, the TLCP/PC (90/10) blends is a single phase in the isotropic state and the phase separation temperature is lower than  $T_i$  of TLCP. Therefore, the liquid crystallization and solid crystallization of the TLCP/PC (90/10) blend are retarded on cooling from 290°C.

### CONCLUSION

The upper critical solution temperature (UCST) was observed in TLCP/PC blends. The cloud points were only observed in blends containing 20–50 wt% PC while the other blends were clear in the isotropic state. The phase separation temperature of a TLCP/PC (90/10) blend was lower than  $T_i$  of TLCP, which prevented most of TLCP from undergoing liquid crystallization. This seems to be closely related with the phenomena that the crystallization rate was lower for a TLCP/PC (90/10) blend and that the transition peaks of TLCP/PC (90/10) blend were broadened and shifted to lower temperatures.

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