Phase Behavior of Polymer/Liquid Crystal Blends

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ABSTRACT: The thermodynamic phase behavior of blends of a low molecular-weight liquid crystal (LC), 4-cyano-4′-*n*-heptylbiphenyl (7CB), and each of two amorphous polymers, poly(methyl methacrylate) (PMMA) and polystyrene (PS), was studied as a function of temperature or LC concentration. Phase diagrams for both the binary PMMA/7CB and PS/7CB blends were constructed from DSC and optical microscopic observations showing that 7CB was partially miscible in both PMMA and PS. The study revealed an important observation that there existed a polymer/isotropic LC two-phase state at a given composition besides the polymer/nematic LC two-phase state and the polymer/solid crystalline LC two-phase state. The polymer/isotropic LC two-phase morphology was clearly observed by the phase-contrast optical microscope in the temperature range between the homogeneous single-phase state and the polymer/nematic LC two-phase state, while DSC or cross-polarized light microscopy failed to detect the existence of the polymer/isotropic LC two-phase state. This was also confirmed by a light-scattering experiment. At a low ratio of LC in both the PMMA/7CB and PS/7CB blends, direct transformation between the homogeneous single-phase state and the polymer/nematic LC two-phase state was observed without going through the polymer/isotropic LC two-phase state.

Introduction

Many studies on the phase behavior in binary polymer blends[1-7] as well as polymer/liquid crystal (LC) mixtures[8-25] have been reported in recent years, and the experimental results were often compared with theoretical predictions on the basis of mean-field theory.[20-26,38] There also exists enormous interest due to the technological importance of the blends for the commercial applications with improved properties.[27-37] Especially for polymer/LC systems, the topic has led to the development of self-reinforcing blends to improve the mechanical strength using molecular anisotropy[8,10] or to the search for hosting materials of LC for the electrooptical applications.[28-29] Other studies emphasized the thermodynamic aspects of polymer/LC blends to get the theoretical basis of the phase behavior.[18-24]

Since the miscibility or phase behavior of a polymer/LC blend controls the performance and/or morphology of the material, it is important to understand the phase behavior and phase separation kinetics of the polymer/LC blend. Kronberg et al.[18] studied the phase behavior of the blend of (*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA) with PS or poly(ethylene oxide) (PEO) at very low polymer concentrations. Dubault et al.[19] performed independently the same experiment for the PS/*p*-azoxyanisole (PAA) and PEO/EBBA systems and obtained the phase diagrams of polymer/LC blends showing the superposition of the phase transition curve on the polymer–liquid phase separation diagram. Patwardhan and Belfiore[9] constructed phase diagrams, using data obtained from DSC and C^{13} NMR measurements, of a partially miscible blend of Bisphenol A polycarbonate (BPAPC) with *p*-(pentyloxy)cinnamic acid (5OCA) and a blend of poly(ethylene glycol) (PEG) with *p*-(hexyloxy)benzoic acid (6OBA) which becomes completely miscible above the nematic–isotropic transition temperature (T_{NI}) of the LC but immiscible below T_{NI}. Ballauff[20-23,38] used the extended Flory lattice theory to describe the main features of those phase diagrams by considering the effect of isotropic interactions between the components and successfully predicted the phase behavior of polymer/LC blends including liquid–liquid phase separation in the isotropic phase. More recently, although the system was not exactly a polymer/LC blend, Orendi and Ballauff[38] observed an isotropic two-phase state as well as an isotropic–nematic two-phase state by using *p*-azoxyanisole and tetracosane and successfully proved that the extended lattice model was applicable. However, the works of Kronberg et al. and Dubault et al. were only concerned with the region of very low polymer concentration and the results of Belfiore et al. did not show the polymer–isotropic LC phase separation at the temperature above T_{NI} in the whole range of polymer concentrations.[9] Since the majority of the experiments have used DSC or the cloud point measurement, it is obvious that these techniques can hardly detect an optically isotropic but phase-separated two-phase state. If the refractive index difference between a polymer and an isotropic LC is not very large, the conventional cloud point measurement is not suitable to observe the polymer/isotropic LC two-phase state. Even with DSC, the evolved heat flow in the phase separation process is too small to verify the existence of the polymer/isotropic LC two-phase state.

This study tried to concentrate on verifying the existence of the polymer/isotropic LC two-phase state and the fact that the polymer–isotropic LC interaction was an important parameter in a polymer/LC blend, as predicted by Ballauff. Two blend systems of 7CB in PMMA and PS were investigated in a wide concentration range of LC. DSC and cross-polarized as well as phase-contrast optical microscopy were utilized to verify the existence of the polymer/isotropic LC two-phase state and to construct the phase diagrams. Results from DSC and optical microscopic observations were reconfirmed by light-scattering experiments as well.

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Table I
Characteristics of the Materials

materials	manufacturer	characteristics
poly(methyl methacrylate) (PMMA)	Polysciences, Inc.	M_w = 94 000 M_n = 49 000 T_g = 105 °C n = 1.490
polystyrene (PS) (GP125)	Hannam Chemical Co., Korea	M_w = 290 000 M_n = 152 000 T_g = 95 °C n = 1.590
4-cyano-4′-n-heptylbiphenyl (7CB)	BDH Chemical Co. Ltd., U.K.	T_{CN} = 19.5 °C T_{NI} = 43.0 °C n_o = 1.520 n_e = 1.690

Experimental Section

A low molecular-weight liquid crystal, 7CB, was purchased from BDH Chemical Co. Ltd. Its crystalline–nematic transition temperature (T_{CN}) and nematic–isotropic transition temperature (T_{NI}) were observed by DSC to be 19.5 and 43.0 °C, respectively. The molecular weights and the polydispersities of PMMA and PS were determined by gel permeation chromatography (GPC) calibrated with PS standards in tetrahydrofuran (THF). The characteristics of these materials are summarized in Table I. These materials were used as received without further purification.

The predetermined amounts of 7CB and polymers were dissolved in appropriate solvents, i.e. methylene chloride for the PMMA/7CB and methyl ethyl ketone (MEK) for the PS/7CB. The solutions were cast into petri dishes, and the residual solvents were completely removed in a vacuum oven at 60 °C for 24 h. Typically, 10 mg of the sample was cut from the cast film for DSC experiments. For the optical microscopy or light-scattering experiments, the samples were prepared very carefully in order not to introduce unwanted dust particles and about 30-μm-thick films sandwiched between two cover glasses were used.

A Perkin-Elmer DSC-4 calorimeter with the data station was used for thermal analysis. The scanning rate of 10 °C/min was applied under the nitrogen atmosphere. Glass transition temperatures (T_g) of the polymer/7CB blends were measured from the midpoint of the transition range of the thermogram whereas the onset temperatures were used to determine T_{CN} or T_{NI}. The phase transition temperatures of the blends were also observed by cross-polarized and phase-contrast optical microscopy (Leitz Orthodox II microscope) during heating of the blends on a hot stage with a programmable proportional-integral-derivative (PID) temperature controller. The temperature of the hot stage was calibrated using several organic crystalline materials with known melting temperatures. The cross-polarized mode was employed to observe the isotropic–nematic transition of the LC domains below T_{NI}, and the phase–contrast mode to observe the phase-separated but isotropic domains above T_{NI}. The phase-separated state was more clearly observed by using the phase-contrast mode for the blends above T_{NI} since the refractive indices of the two domains were not very different from each other.

The results of the thermal analysis and optical microscopic observation were again confirmed by the light-scattering experiment. The detailed experimental setup was described elsewhere.[5,6] A He–Ne laser of 10 mW was used as the light source with the wavelength of 632.8 nm. Each of 30-μm-thick sample films was placed in a sample cell, and the scattered light intensity as a function of the scattering angle covering 0–40° was measured at a fixed temperature with a heating or cooling rate of 1 °C/min.

Results and Discussion

PMMA/7CB Blends. DSC thermograms of pure PMMA and PMMA/7CB blends with different compositions are shown in Figure 1. The measured T_g of the PMMA is 105 °C and agrees well with the literature value.[39] T_g of the PMMA/7CB blend decreases gradually from 105 °C as the concentration of 7CB increases up to 30 wt % in the blend. But T_g of the blend with over 30 wt % 7CB was not observed in DSC thermograms. Under 30 wt % 7CB in the blend, therefore, most of the LC seemed to be molecularly mixed with PMMA acting as a plasticizer. Similar phenomena were also reported in the BPAPC/5OCA[9] or PS/EBBA (or TBBA) system.[10] The transition peaks of T_{NI} and T_{CN} of 7CB at 50 and 70 wt % LC in the blend are shown in Figure 1, while T_g of the plasticized PMMA phase in the blends is not clearly observed. The DSC thermogram proves that there must be a phase separation between PMMA- and LC-rich phases in the blend with a high LC content.

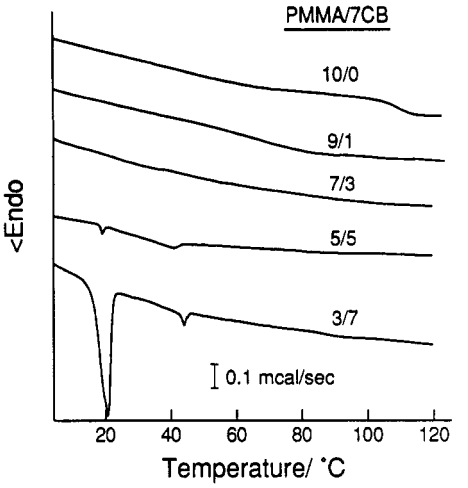

Figure 1. DSC thermograms of the binary PMMA/7CB blends.

It is worth noting that the peak for T_{CN} of the LC-rich phase in the blend with the LC concentration of 50 wt % starts to appear at 20 °C but the peak position shows little change from that of pure 7CB, whereas T_{NI} tends to increase with an increase of the LC concentration in the blend. This indicates that the LC-rich domains below T_{CN} are little perturbed by PMMA. In other words, the LC-rich domains have the polymer molecules mixed in the LC but pushed aside to the boundary of the LC clusters while the PMMA-rich phase, on the other hand, can hold homogeneously 7CB molecules up to 30 wt %.

It is reasonable to imagine that a polymer/LC blend shows a phase separation below the critical temperature and the system is composed of two phases, i.e. PMMA- and LC-rich phases. If the critical temperature is higher than T_{NI}, the LC-rich domain may be isotropic above T_{NI} and nematic below T_{NI}. It is, however, probed that the polymer/isotropic LC two-phase state was not experimentally observed previously. It means that either a DSC study or polarized light microscopy generally employed for the phase separation study does not detect the existence of the isotropic LC-rich domains and only observes the transition of the nematic LC.

It is, however, possible to check the existence of the two conditions in the LC-rich domains above T_{CN}. Optical microscopy and the light-scattering technique were employed to prove the existence of a polymer/isotropic LC two-phase state. Optical micrographs for a PMMA/7CB blend with a ratio of 3/7 shown in Figures 2 and 3 were obtained at fixed temperatures during heating and cooling with a scanning rate of 1 °C/min. Both series A and B were taken under the cross-polarized and the phase-contrast mode, respectively. Several points become obvious from these figures. Figure 2 shows, at 30 °C, two-phase morphology composed of LC-rich domains in the nematic state and PMMA-rich domains. There is no difference between light micrographs from the cross-polarized mode (A-1) and from the phase-contrast mode (B-1). However, the field of view under the microscope becomes darkened and nothing is observed in the cross-

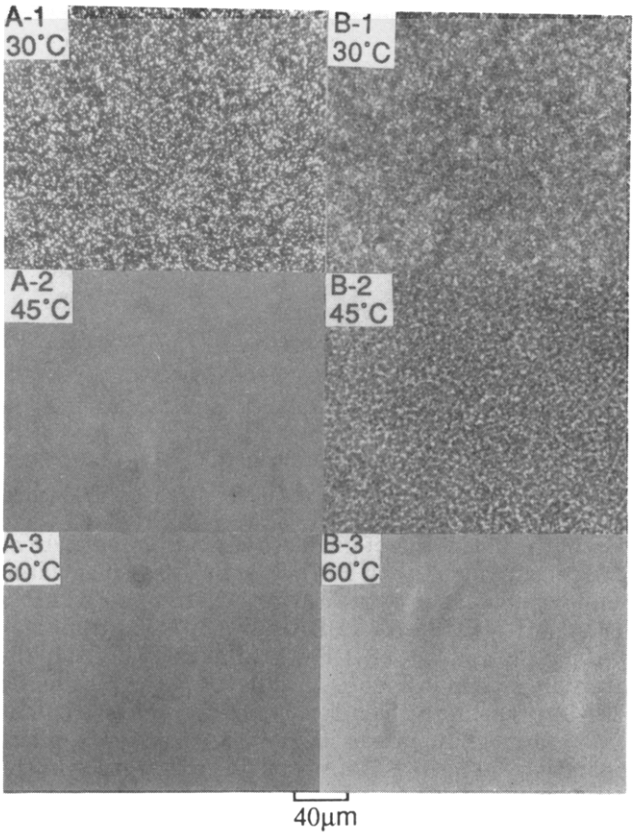

Figure 2. Optical micrographs of the PMMA/7CB 3/7 blend at fixed temperatures during heating with a rate of 1 °C/min: series A, by the cross-polarized mode; series B, by the phase-contrast mode with polarizer only.

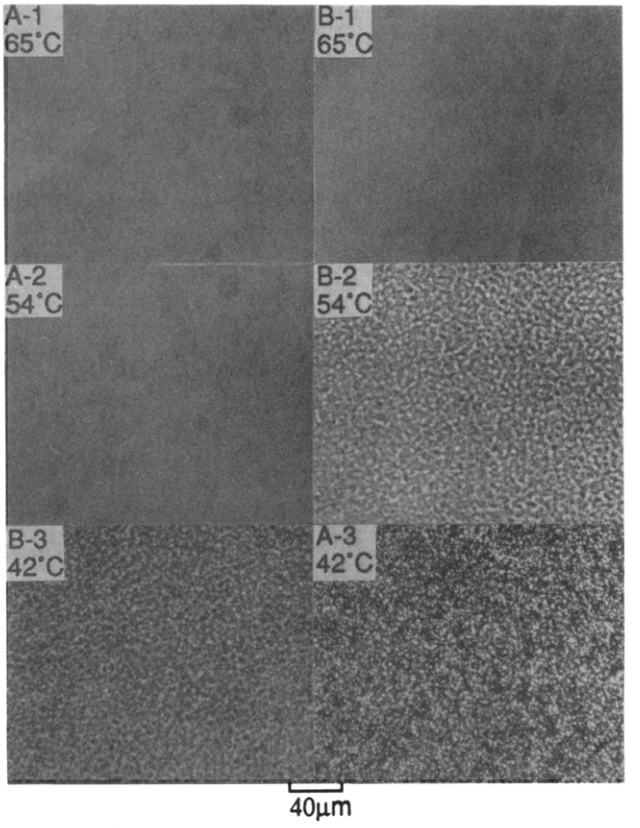

Figure 3. Optical micrographs of the PMMA/7CB 3/7 blend at fixed temperatures during cooling with a rate of 1 °C/min: series A, by the cross-polarized mode; series B, by the phase-contrast mode with polarizer only.

polarized mode as shown in Figure 2A-2 when the temperature is increased to 45 °C. This indicates that the nematic state of LC in the LC-rich domains is transformed into the isotropic state. Since there is no order or orientation in the PMMA-rich or the LC-rich domains at 45 °C, no anisotropic texture is observed by the cross-polarized optical microscope. On the contrary, the phase-contrast technique, which utilizes the difference in refractive indices, clearly shows the existence of the PMMA/isotropic LC two-phase morphology above T_{NI} of LC, as shown in Figure 2B-2. Further heating transforms the polymer/isotropic LC two-phase state into a homogeneous single-phase state, and both the cross-polarized and the phase-contrast modes detect no morphology, as shown in Figure 2A-3,B-3.

In many cases of polymer/polymer or polymer/solvent systems, the phase separation is easily determined by the cloud point (T_{cloud}) measurement. However, similar refractive indices between the two materials make the T_{cloud} measurement impossible or difficult at least. T_{NI} in a polymer/LC system is often misinterpreted as T_{cloud}, and the resulting phase diagram becomes somewhat ill-represented because the phase boundary in the polymer/nematic LC two-phase state becomes a very strong light scatterer compared with that of a polymer/isotropic LC two-phase state, as will be discussed later. This fact explains why optical microscopy fails to observe the morphology of a polymer/isotropic LC two-phase state and leads to misinterpretation of the polymer/isotropic LC two-phase state as a homogeneous single-phase state. Since the difference in the refractive indices between PMMA and isotropic 7CB is about the order of 10^{-2}, only the phase-contrast optical microscopy or the light-scattering technique is suitable for the detection of the polymer/isotropic LC two-phase state. Micrographs ob-

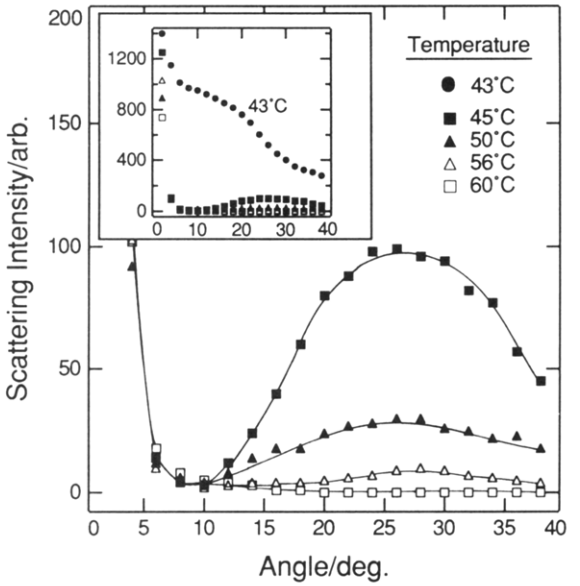

Figure 4. Light-scattering intensities as a function of scattering angle and temperature of the PMMA/7CB 3/7 blend at fixed temperatures during cooling with a rate of 1 °C/min.

tained while cooling the sample in the homogeneous single-phase state show the reversible process of the phase separation and the isotropic–anisotropic transition, as seen in Figure 3.

Existence of the polymer/isotropic LC two-phase state from the optical microscopic observations was reconfirmed by the light-scattering experiment, as shown in Figure 4. It showed the angular-dependent light-scattering intensities of the blend at fixed temperatures during cooling with a scan rate of 1 °C/min from 70 °C at which the blend

was in a homogeneous single-phase state. At 60 °C, the scattering intensity showed no feature, indicating that the polymer/LC blend was in a homogeneous single-phase state. When the temperature was lowered around 56 °C, the scattering intensity began to increase and showed the maximum at around 28° revealing that the phase separation into the polymer/isotropic LC two-phase state had occurred. The scattering intensity continued to increase with lowering the temperature to 45 °C. The temperature range for holding the polymer/isotropic LC two-phase state is from 45 to 56 °C. Since the intensity maximum is about 28° and the refractive index of the blend is about 1.5 at the wavelength of 632.8 nm, the mean LC domain size deduced from the scattering profile[4,41,42] is about the order of 1 μm and agrees well with the optical microscopic results.

Another interesting observation in the scattering intensity profile is that the scattering angle of the maximum intensity is not changed very much. Since the phase separation takes place very quickly in the case of the polymer/solvent mixture (usually less than 10 s), one may expect that the domain size or the scattering angle at the maximum intensity will change during a 30-min light-scattering experiment, as seen in polymer/polymer blend systems.[5,6] However, the PMMA/7CB system in the isotropic two-phase state shows no change in its LC domain size in this study. Our understanding of this behavior is as follows: if the PMMA/7CB system reaches the polymer/isotropic LC two-phase state just below T_{cloud}, the LC-rich domains are immediately formed as the separated phase as in polymer/solvent systems and the domains are already too large to move around through the viscous PMMA-rich phase. Since the phase separation took place very quickly, as in the case of a usual polymer/solvent system, it was difficult to judge from Figure 4 whether the phase separation occurs by a nucleation-and-growth mechanism or spinodal decomposition. Observation under the microscope or the light-scattering experiment in this work seems to have gathered data for the later stage of the phase separation, for which the mechanism is different from its early stage.[43,44] Further cooling of the system in a certain time interval may increase the difference in the refractive indices between the two domains,[33] whence the observed scattering intensity increases without changing the scattering angle at the maximum intensity. The domain sizes in the polymer/isotropic two-phase system will eventually become bigger due to the coarsening effect or Ostwald ripening if the system is maintained at the temperature for a long time. When the temperature reaches T_{NI}, 43 °C, a drastic increase of the scattering intensity at low angles is observed and the intensity diminishes with an increase of the scattering angle, as shown in the inset of Figure 4. This is due to the multiple scattering effect by LC domains where LC molecules are transformed into a nematic state from an isotropic one. Multiple light scatterings result from a large refractive index difference between the polymer matrix and nematic LC droplets of which optic axes are randomly oriented in the matrix.[28-35]

With the data obtained by DSC analysis and the optical microscopic measurements for several different PMMA/7CB compositions, a phase diagram of the PMMA/7CB system was made, as shown in Figure 5. The unfilled squares indicating T_{cloud} at the given concentrations were obtained by phase-contrast light microscopy as well as the light-scattering measurement while the filled squares showing T_{NI} were done by cross-polarized light microscopy and DSC. Data obtained by DSC produced both the filled triangles representing T_g of the blends and the unfilled

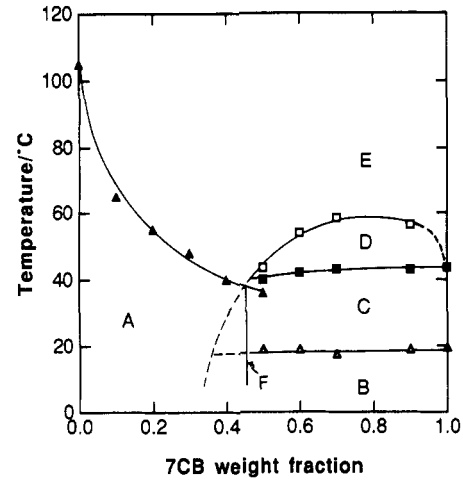

Figure 5. Phase diagram of the binary PMMA/7CB blend with LC concentrations of 0–0.9 weight fraction: (A) glassy single-phase state; (B) PMMA/solid crystalline 7CB two-phase state; (C) PMMA/nematic 7CB two-phase state; (D) PMMA/isotropic 7CB two-phase state; (E) homogeneous single-phase state.

triangles describing the phase boundary between the PMMA/nematic LC two-phase state and the PMMA/solid crystal LC two-phase state. LC up to about 45 wt % in the blend is molecularly mixed with PMMA above T_g and thus cannot form its own nematic LC domains. 7CB simply acts as a plasticizer in the concentration range so that T_g of PMMA shifts from 105 to 40 °C as the LC concentration increases.[40] The line F at the concentration of 45 wt % is the boundary of the phase separation below T_g. The blend in the concentration range of about 35–45 wt % LC must be homogeneous below T_g because of poor mobility of the polymer, although the phase separation is expected as drawn by the thin dotted line.[45] When the LC concentration becomes 50 wt % or higher, the two-phase state begins to appear below T_{cloud} where some of the LC molecules aggregate to form dispersed LC domains in the PMMA matrix. The phase diagram strongly suggests that there is a region around the concentration of LC with 45 wt % in the blend where the polymer/LC single-phase state may transform directly to the polymer/nematic LC two-phase state without going through the polymer/isotropic LC two-phase state. This phenomenon is clearly observed with the PS/7CB system described later.

Phase diagrams with concentrations higher than 90 wt % LC, i.e. the solution with a small amount of the polymer as the solute, are drawn easily for T_{NI} and T_{CN} based on DSC data showing the phase boundaries of the phases D and C, and C and B in Figure 5. However, it was difficult to observe the phase separation temperature, T_{cloud}, of the boundary of phases E and D since the LC-rich domains are predominant over the polymer-rich domains to be regarded as a single phase. The LC mixture with less than 5 vol % low molecular-weight polymer has been characterized to show that the phase transition from an isotropic state to a nematic state was observed before the phase separation was detected.[18,19] However, the blend with more than 50 wt % LC shows that the phase separation occurs before isotropic LC turns into the nematic state when the temperature is lowered. A dilute polymer solution has the maximum in the phase separation curve at a decidedly low polymer concentration[46] and the same is expected in a polymer/LC blend. An attempt was made to complete the boundary of the phases between E and D in Figure 5 for the mixture with less than 10 wt % polymer by drawing the bold dotted line based on the works of Flory.[46]

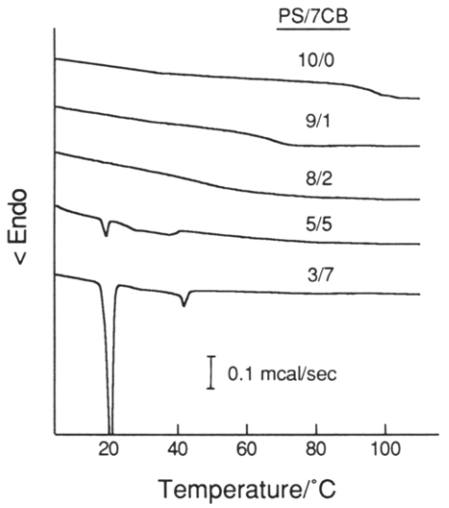

Figure 6. DSC thermograms of the binary PS/7CB blends.

Patwardhan and Belfiore[9] and Huh et al.[10] reported the phase diagrams of EBBA and TBBA/PS blends and blends of PEG/6OBA and BPAPC/5OCA, respectively, but they did not observe the existence of the polymer/isotropic LC two-phase state. Several other research groups[30-37] have described an electrooptical display technique based on polymer-dispersed liquid crystals (PDLC) for the phase separation. Their works have been oriented more toward the applications, but the accurate phase diagrams have not been presented. Extending the Flory lattice model, Ballauff[20-23] has predicted the existence of a polymer/isotropic LC two-phase state and interpreted rationally the experimental data of Dubault et al.[8] based on the theory, and more recently Orendi and Ballauff[38] have used a blend of PAA and tetracosane ($C_{24}H_{50}$) to prove the existence of an isotropic two-phase state. However, the system was not exactly a polymer/LC blend but rather a oligomer/LC blend. As far as we know, our results present the first accurate phase diagram observed experimentally to support Ballauff's prediction in terms of the existence of a polymer/isotropic LC two-phase state using a polymer/LC system. Turning to T_{NI} and T_{CN}, one may notice that T_{NI} and T_{CN} of blends with over 50 wt % 7CB do not change very much compared with those of the pure 7CB. This indicates that the crystalline domains in the LC-rich phase are perturbed little by PMMA molecules. The polymer molecules in the LC-rich phase must be separated from the LC clusters in order not to disturb the solid crystal structure of the LC.

PS/7CB Blends. In order to examine our observation further, we chose the PS/7CB blend as another system in which the phase separation could be easily detected due to a relatively large refractive index difference between the components compared with that in the PMMA/7CB blend. As shown in Figure 6, DSC thermograms of the PS/7CB blends are similar to those of the PMMA/7CB system. A small amount of LC is completely miscible with PS and acts as a plasticizer, lowering T_g of the blend down to approximately 30 °C from 95 °C, which is T_g of the pure PS. For the blend with larger than 30 wt % 7CB, the characteristic transition peaks of the LC begin to appear like the PMMA/7CB system. In addition, T_g of the PS-rich phase in 5/5 or 3/7 composition is observed at around 26 °C, which indicates that the phase separation at temperatures below 26 °C is stopped due to the vitrification of the PS-rich phase. Optical micrographs of the mixture with a composition of PS/7CB 4/6 by weight are shown in Figure 7. They are similar to those in Figures 2 and 3 for the PMMA/7CB 3/7 blend. Figure 7B-2 observed with

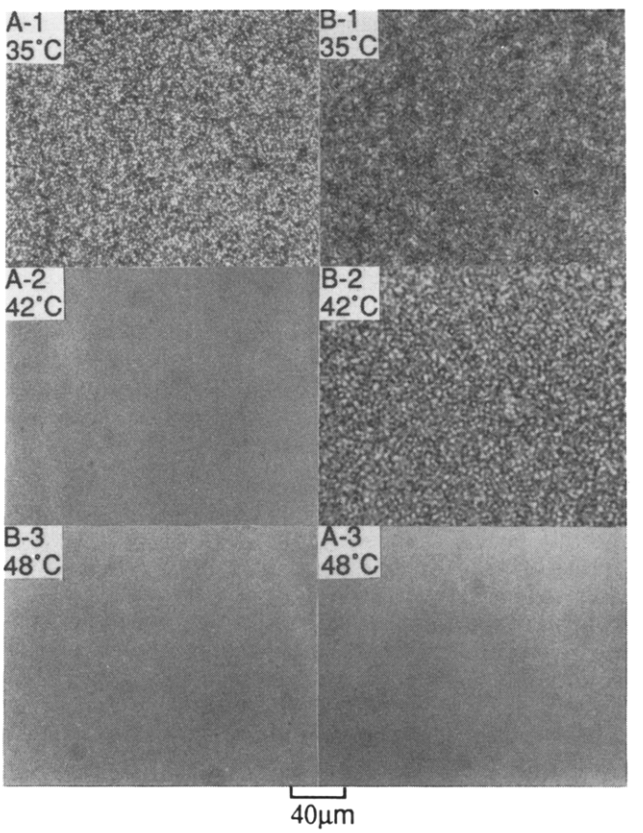

Figure 7. Optical micrographs of the PS/7CB 4/6 blend at fixed temperatures during heating with a rate of 1 °C/min: series A, by the cross-polarized mode; series B, by the phase-contrast mode with polarizer only.

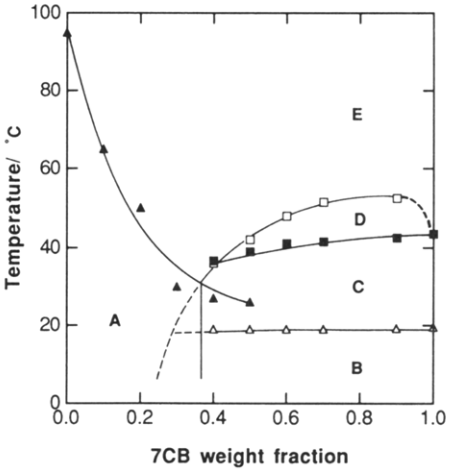

Figure 8. Phase diagram of the binary PS/7CB blend with LC concentrations of 0–0.9 weight fraction: (A) glassy single-phase state; (B) PS/solid crystalline 7CB two-phase state; (C) PS/nematic 7CB two-phase state; (D) PS/isotropic 7CB two-phase state; (E) homogeneous single-phase state.

the phase-contrast optical microscope clearly shows the PS/7CB isotropic two-phase morphology at 42 °C whereas the cross-polarized optical microscope fails to detect it at the same temperature. A phase diagram of the PS/7CB mixture is constructed as shown in Figure 8 using DSC and optical microscopic data as before. For the LC concentrations higher than 90 wt % a tentative drawing was done as the same in Figure 5. With these results, we can conclude that the polymer/LC blend generally has a polymer/isotropic two-phase state when the critical temperature is higher than T_{NI} of the LC component.

Direct transformation from a polymer/nematic LC two-phase state into a homogeneous mixture without going

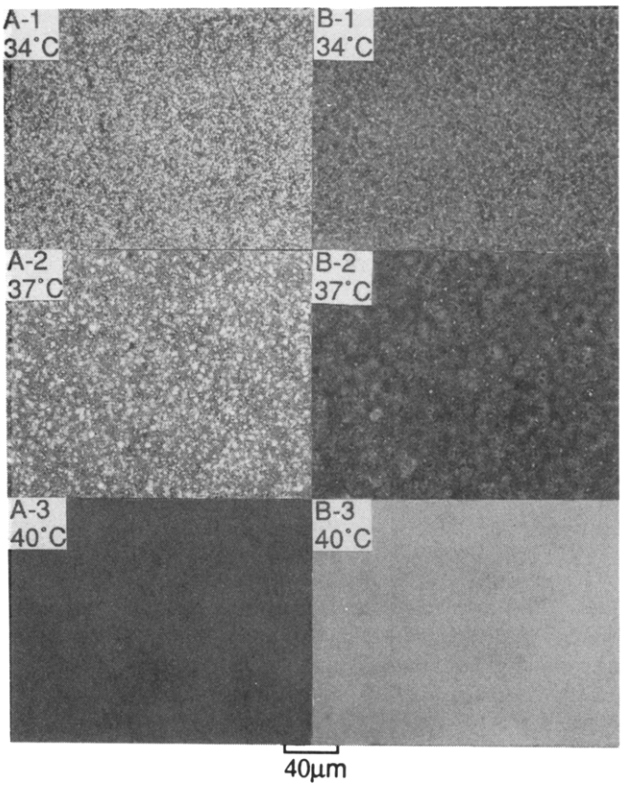

Figure 9. Optical micrographs of the PS/7CB 6/4 blend at fixed temperatures during heating with a rate of 0.5 °C/min: series A, by the cross-polarized mode; series B, by the phase-contrast mode with polarizer only.

through the isotropic two-phase state was observed in the concentration range 35–40 wt % LC. Optical micrographs in Figure 9 show such a process for the blend of PS/7CB 6/4 by weight. Below T_{NI}, as shown in Figure 9A-1, the optical characteristics observed in the cross-polarized mode appear to be the same as in Figure 7 for the PS/7CB 4/6 blend or in Figure 2 for the PMMA/7CB 3/7 blend. However, upon heating to 37 °C, the irregular aggregates of the LC domains grow slightly bigger. These aggregates are formed when the LC-rich domains become mobile above T_g of the polymer-rich domains and tend to coalesce or do Ostwald ripening. The blend finally becomes a homogeneous single-phase state when the temperature increases over 40 °C, as shown in Figure 9A-3,B-3.

Conclusions

Phase behavior of polymer/low molecular-weight LC blends were studied by DSC, optical microscopy, and a light-scattering method. Phase diagrams of both the PMMA/7CB and PS/7CB blends were constructed from the results. The low molecular-weight LC, 7CB, showed partial miscibility with PMMA or PS and acted as a plasticizer judging from the T_g depression of the blends.

DSC thermograms indicate that the phase separation of polymer/LC blends occurred over 40 wt % 7CB in PMMA and over 30 wt % in PS, showing the characteristic peaks of LC itself. It is important to point out that the existence of the polymer/isotropic LC two-phase state, undetectable by either DSC or cross-polarized optical microscopy, was obseved by an optical microscope with the phase-contrast mode above T_{NI} and was reconfirmed by the light-scattering experiments. It is concluded that the polymer/LC system with certain compositions shows states of homogeneous single-phase, polymer/isotropic LC two-phase, polymer/nematic LC two-phase, and polymer/crystalline LC two-phase depending on temperature.

For a mixture of the polymers and 7CB with a certain ratio, it was observed by an optical microscope that the direct transformation from the polymer/nematic LC two-phase state into the homogeneous single-phase state occurred without going through the nematic-to-isotropic transition of LC-rich domains.

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