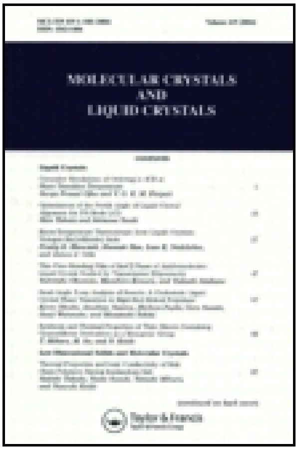

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Temperature-Induced Phase Separation of Side-Chain LCP/LMWLC Blends

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A blend of side-chain liquid crystal polymer (SCLCP) and low molecular weight liquid crystal (LMWLC) was used to investigate a phase separation behavior induced by temperature. Phase separation at room temperature was observed only for the compositions higher than 60 wt% LMWLC because of good miscibility between two components. An interesting phenomenon was observed when the film transmittance for a phase-separated sample as a function of temperature was measured under cross-polarizer. That is, transmittance below T_{NI} of LMWLC was observed lower than that below T_{SI} of SCLCP, which was not expected initially. The fact was considered as a micro-phase separation induced by an interfacial effect between SCLCP and LMWLC phase.

Keywords: 7CB; low molecular weight liquid crystal (LMWLC); phase separation; side-chain liquid crystal polymer (SCLCP); temperature-induced

INTRODUCTION

To use as an information display material, polymer-dispersed liquid crystal (PDLC) composites were intensively studied in recent years [1–3]. Several problems, however, have not been solved such as stability of internal structure of materials, contrast ratio, wide viewing

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angle, on-state haze, and so on. Among them, the on-state haze phenomenon occurs because of the refractive index mismatching between LMWLC and polymer matrix when the viewing direction is different from the orthogonal. This on-state haze is an inevitable problem as long as an isotropic polymer is used as matrix of PDLC system, because matching the exact refractive index between the phase-separated LMWLC and the polymer matrix is possible only at one fixed temperature [4].

Several efforts to overcome this problem were made, involving the use of a birefringent liquid crystalline polymer as matrix instead of conventional isotropic polymer [5–7]. If both the polymer matrix and LMWLC droplet are birefringent, as in the case of SCLCP and LMWLC, it is possible to match the refractive indices for all directions in the on-state, making it possible for a haze-free film.

Mixing a SCLCP with LMWLC, however, may bring about some undesirable effects from the application view-point of PDLC film, such as difficult phase separation between SCLCP and LMWLC, or lowering glass transition of the resulting PDLC materials. We investigated the phase behavior and interfacial phenomena, using the mixture of a side-chain liquid crystal polymer (SCLCP) and a LMWLC, 4-cyano-n-heptyl biphenyl (7CB). Mesogen unit in the matrix SCLCP was chosen as similar chemical structure with 7CB. Phase separation for the blend system at room temperature was observed for compositions higher than 60 wt% LMWLC because of good compatibility between SCLCP and LMWLC. An interesting phenomenon in film transmittance was observed at the transition temperature of the liquid crystalline SCLCP/isotropic LMWLC phase into the liquid crystalline SCLCP/liquid crystalline LMWLC phase for a 2/8 SCLCP/LMWLC film, which was considered as the result of micro-phase interfacial interactions between SCLCP and LC phase.

EXPERIMENTAL

Materials

A side-chain liquid crystal polymer (SCLCP), having poly(methyl methacrylate) back bone, was synthesized with side-chain mesogen unit similar to 7CB (Fig. 1). Number average molecular weight (Mn) and weight average molecular weight (Mw) of SCLCP were determined as 1,400 and 10,000 from Gel Permeation Chromatography (GPC), respectively. 4-cyano-n-heptyl biphenyl (7CB) was obtained from E. Merck and used without further purification.

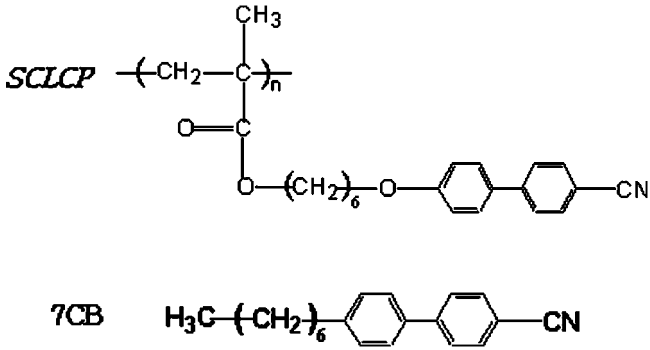

FIGURE 1 Chemical structures and characteristics of matrix SCLCP and 7CB.

Experimental Procedure

Predetermined ratio of SCLCP and 7CB was dissolved in co-solvent, methylene chloride. The solution was poured into petridish to remove the solvent at room temperature. Remained solvent was thoroughly removed on the hot plate set at ca. 120°C. Perkin Elmer DSC-7 differential scanning calorimeter was utilized under nitrogen atmosphere for thermal analysis of the blends. Typically, 10 mg of the mixture was used for the thermal analysis. For the light transmittance experiment with temperature, the mixture was sandwiched between two glass plates and, then, set in a Mettler FP80 hot stage equipped with temperature controller. The hot stage was mounted on a Zeiss Jenalab Pol-D polarizing optical microscope. One of the eyepieces of the microscope was replaced with photosensor conneced to a New Port 1830C optical power meter. The outline of the experimental set-up was shown in Figure 2.

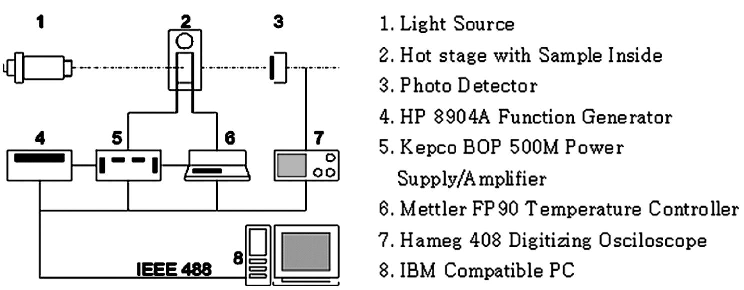

FIGURE 2 Schematic diagram of experimental set-up.

RESULTS AND DISCUSSION

As is well known, a low molecular weight liquid crystal such as 7CB may act as plasticizer in a most amorphous polymer matrix. Our previous work shows that, when 7CB concentration is above 40% in poly (methy methacrylate) (PMMA) matrix, phase separation occurs at room temperature for the 7CB/PMMA blend [8]. By the time, if a SCLCP having a 7CB-like side-chain mesogen is utilized as matrix instead of an usual PMMA, much more plasticizing effect of 7CB in the matrix SCLCP can be expected because of similar chemical structure of side-chain mesogen of SCLCP.

This expectation is clearly shown in Figure 3 of DSC thermograms for the SCLCP/7CB blends which have several different 7CB compositions of 20, 40, 60, 80, and 90 wt%. Though not shown in the figure, smectic-to-isotropic transition temperature (T_{SI}) of pure SCLCP was observed at about 100°C and similar values could be found elsewhere [9]. As is clearly seen in this figure, phase separation phenomena cannot be found for the blends having compositions lower than 60 wt% of 7CB. Instead, only down-shift of T_{SI} of SCLCP to about 70°C can be observed. Very weak signal for the phase separation, however, can be found at about 40°C in the thermogram of 4/6 SCLCP/7CB blend. This signal can be found more clearly in the thermogram of cooling scan. After then, T_{NI} of 7CB can be clearly observed as is seen in the thermogram of 2/8 SCLCP/7CB sample. From this result, one can conclude that the phase separation between SCLCP and 7CB may occur when 7CB concentration is higher than ca. 60 wt% in the blend. On the other hand, once phase separation occurs, T_{SI} of SCLCP is stabilized and fixed at a temperature of ca. 60°C.

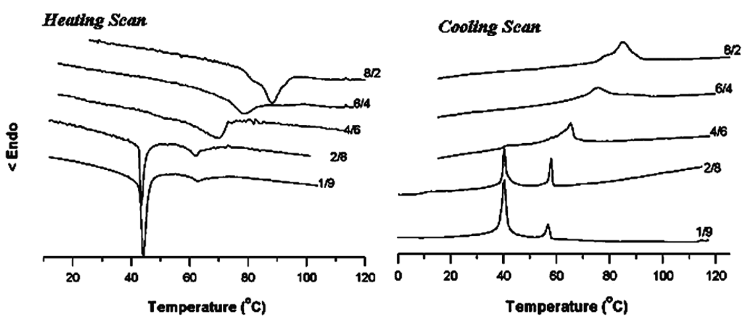

FIGURE 3 Heating- and cooling-scan DSC thermograms of SCLCP/7CB blends having several different concentrations of 7CB: 20, 40, 60, 80, and 90 wt%.

One can easily expect from DSC results that the blends of SCLCP/7CB with higher than 60 wt% of 7CB concentration may exist as two different liquid crystalline phases at temperature below than about 43°C, i.e., the 7CB-rich low molecular weight liquid crystalline phase and the SCLCP-rich liquid crystalline polymer (LCP) phase, respectively. Furthermore, in the temperature range from 43 up to 60°C, there will exist another two phases, 7CB-rich isotropic phase and SCLCP-rich LCP phase, respectively. As temperature increases higher than 60°C, two isotropic phases will finally transformed into the one single phase. This fact is expected more clearly from the cooling-scan thermograms (Fig. 3b). Some lower-shifts of transition peaks in the thermograms were induced by super-cooling effect.

Optical light transmittance of a 20 μm-thick film of 2/8 SCLCP/7CB blend is shown in Figure 4. Measurement was performed as function of temperature under the cross-polarized light. As expected in Figure 3, clear and dramatic changes in transmittance were seen at two different temperatures, i.e., 43 and 60°C, respectively. A noticeable phenomenon, however, could be observed in the figure. In the temperature range between T_{NI} and T_{SI} than that below T_{NI}, much higher transmittance through the cross-polarizer was observed. When considering larger amount of liquid crystalline phase below T_{NI} (two liquid crystalline phases) than that in the range between T_{NI} and T_{SI} (one isotropic and the other liquid crystalline phase), this fact is an unexpected result. When a sample film composed of two different liquid crystalline

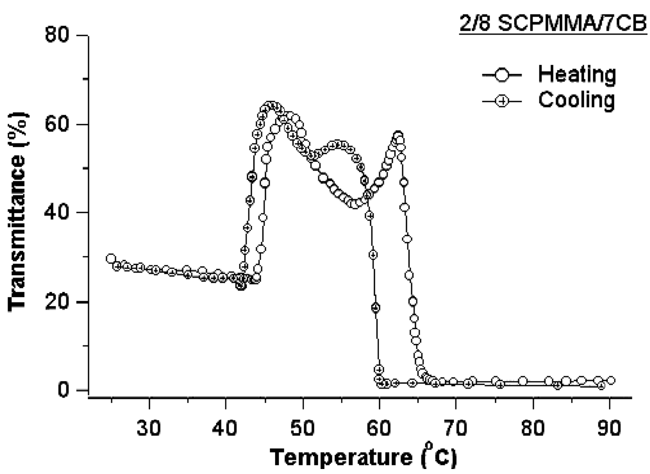

FIGURE 4 Optical light transmittance as function of temperature for a 20 μm-thick film of 2/8 SCLCP/7CB blend under cross-polarized light.

phases is exposed between the cross-polarized light, total amount of transmittance is expected much larger than that with two phases of one isotropic and the other liquid crystalline phase. In the present case, there will exist two different liquid crystalline phases below T_{NI}, i.e., 7CB-rich LC phase and SCLCP-rich LCP phase, respectively.

To study this phenomenon in more detail, we observed the morphology changes with temperature for the same film under the polarized optical microscope (POM). POM micrographs of 2/8 SCLCP/7CB blend at several different temperatures are shown in Figure 5. Films with 20 μm-thickness was used. As well seen in the figure, liquid crystalline phase starts to occur at about 62°C in the sample during cooling and increases as temperature reaches T_{NI}. Furthermore, it is noticeable that another liquid crystalline phase starts to occur below T_{NI} within existing liquid crystalline phase, which is considered as the 7CB-rich liquid crystalline phase. Though total amount of liquid crystalline phase, however, seemed to be increased, brightness of the phase through the polarizer seems to be weaker than that above T_{NI}. As the temperature goes down to 22°C, darkness of the film increases much more. Considering this observations and DSC thermograms altogether, this phenomenon was considered as the results from the micro-phase separation and transformation into isotropic state

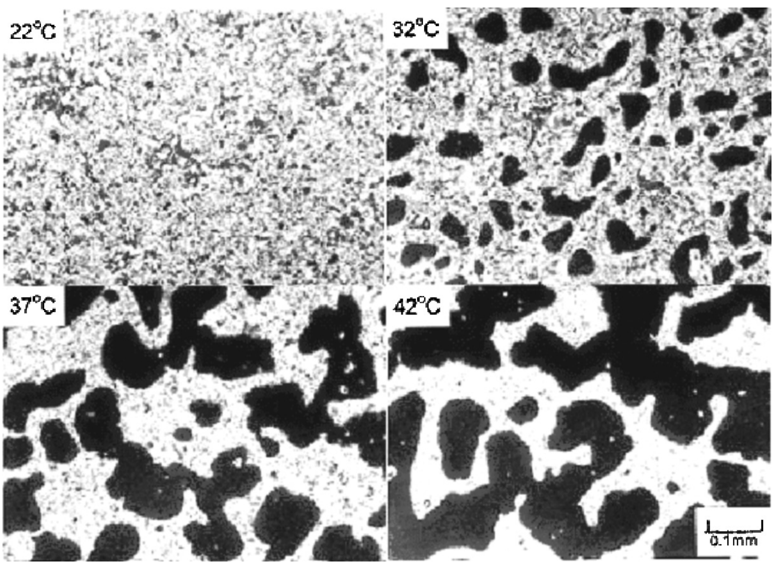

FIGURE 5 POM micrographs for a 20 μm-thick film of 2/8 SCLCP/7CB blend at several different temperatures.

within the sample. This isotropic transformation, even though in temperature region of LMWLC phase, is considered as due to the severe interfacial molecular interactions between SCLCP and LMWLC phase. More works are being done for this speculation.

CONCLUSIONS

A blend of side-chain liquid crystal polymer (SCLCP) and low molecular weight liquid crystal (LMWLC) was used to investigate a phase separation behavior induced by temperature. Phase separation between SCLCP and 7CB may occur when 7CB concentration is higher than ca. 60 wt% in the blend. Once phase separation occurs, T_{SI} of SCLCP is stabilized and fixed at a temperature of ca. 60°C. An interesting phenomenon was observed when the film transmittance for a phase-separated sample as a function of temperature was measured under cross-polarizer. That is, transmittance below T_{NI} of LMWLC was observed lower than that below T_{SI} of SCLCP, which was not expected initially. This phenomenon was considered as the results from the micro-phase separation and transformation into isotropic state within the sample. This isotropic transformation, even though in temperature region of LMWLC phase, is considered as due to the severe interfacial molecular interactions between SCLCP and LMWLC phase. More works are being done for this speculation will be reported sooner.

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