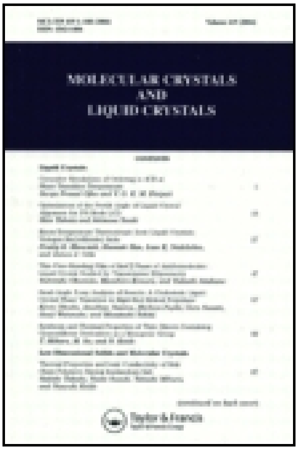

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

A Study of Reflectivity on the Liquid Crystal/Polymer Composite Films

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A Study of Reflectivity on the Liquid Crystal/Polymer Composite Films

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We have studied the reflectivity on the liquid crystal/polymer composite films. The reflectivity is remarkably affected by the morphology and the birefringence of liquid crystals. It is expected that paper-like displays are realized by the controlling morphology and using higher birefringence liquid crystals.

Keywords: phase separation; liquid crystal/polymer composite films

INTRODUCTION

In attempting of activities for the reflective displays without a polarizer [1, 2, 3], the liquid crystal/polymer composite films have a attracted much attentions due to the reflective direct view displays, because of the considerable decrease in light loss compared with the commonly used TN-LCDs which have a polarizer. In this device prepared by the photopolymerization induced phase separation process, several factors such as the morphology of the composite films, and physical properties in both liquid crystals and polymers play an important role to determine the reflectance on their devices. It is expected that the control of phase separated structure in the films and using the higher birefringence in liquid crystals are one of the key technology to realize a paper-like display with the reflectance more than 50%.

In this paper, we describe the influence of morphology in the composite films on their reflectance, and some factors including the birefringence of liquid crystals and the thickness in the films.

EXPERIMENT

To examine the factors concerning reflectance, the liquid crystal mixture KT10-9 (Δn: 0.291) manufactured by Dainippon Ink & Chemicals Inc. composed of the pyridine based liquid crystals and the diacrylate HX-220 (Nippon Kayaku Inc.) is used. To analyze morphology in liquid crystal/polymer composite films, the fluorinated tolane based liquid crystal mixture of PAL-746 (Dainippon Ink & Chemicals Inc.) with 0.266 of birefringence and various diacrylates having the different methylene groups in the main chain or having the different alkyl side chain as shown in Figure 1 were used. HDDA and C2000 was manufactured by Sartomer Inc.. AE-67 was synthesized by esterification between epichlorohydrin modified 1,6-hexanediol-diacrylate and lauric acid using dicyclohexyl carbodiimide. A 4 mol% of photoinitiatore (Irg-651 manufactured by Chiba-Geigy) was added in the total diacrylate. After filling materials in a LC cell with a 10 μm to a 50 μm cell gap, 20 to 400 W/m^2 of UV light at 365nm was irradiated to a homogeneous solution containing liquid crystals and diacrylates through UV-35 optical sharp-cut edge filter (HOYA Inc.) using a high pressure mercury lamp at a 2 °C above isotropic-nematic transition temperature to induce the polymerization for 60 seconds.

The phase transition temperatures in the homogeneous solution were observed by cross-polarized and phase-contrast optical microscopy equipped with a hot stage (METTLER, FP-82HT) controlling a temperature .

The field emission scanning electron microscope (SEM) S-800 (HITACHI Inc.) was used in order to identify morphology in the films. After a curing, the sample was braked under the liquid-nitrogen, and then extract liquid crystals from the films with methanol. The size in liquid crystalline domains in the films was evaluated with SEM photograph and the laser diffraction particle size analyzer SALD-2000J (SHIMADZU Inc.). This apparatus is that the distribution of size in liquid crystal domains in the films can be obtained from the spatial diffraction laser light pattern depending on the size.

Leica's confocal laser scanning microscope is used to capture the time resolved microscopic image at 0.5 seconds intervals. The objective lens in this experiment have a resolution of 300 nm horizontal. The two beams of Kr laser at 473nm and 488nm are employed to increase contrast.

The reflectance was measured with the integrating sphere (labsphere Inc.) equipped with luminance meter BM-7 (TOPCON Inc.).

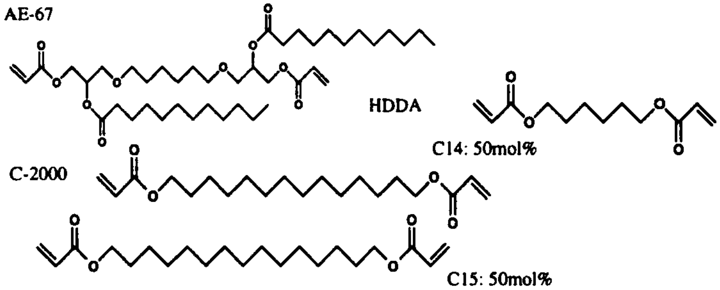


FIGURE 1. Molecular structure of diacrylates

A halogen lamp is used as the light source. The sample attached to the black back plate is placed at the center of the integrating sphere so that an uniform light scattering by the effect of internal integrating sphere is illuminated to the surface of sample. BM-7 is positioned to normal direction of the sample surface. The luminance at the surface of the white standard (labspherte Inc.) is defined as 100 % of reflectance. The total flux incident on each the froward scattering light and the backward scattering light in the films is measured with the integrating sphere equipped with the photometer. A sample mounted at the entrance port of the sphere is illuminated with He-Ne laser positioned out side of the sphere to normal direction of the sample in the case of the measurement on the forward scattering light. In the case of backward scattering light, a sample is mounted at a port on the opposite side of the entrance port on the sphere.

RESULTS AND DISCUSSION

Phase diagram

The phase diagram in the homogeneous solution was established to identify the regions occurring two phase separations. Figure 2 depicts the phase diagram with the observation of the polarized microscopy. The nematic-isotropic transition temperature T_{ni} is gradually decreased with the decrease of molar fraction in liquid crystals. No Upper Critical Solution Temperature (UCST) behavior can be seen due to the crystallization of monomer. In the AE-67 diacrylates, the nematic-isotropic transition temperature as a function of liquid crystal fraction is different from other diacrylates. The degree of changes in T_{ni} decreased with the decrease of liquid crystal fraction is greater than both C2000 and HDDA showing an

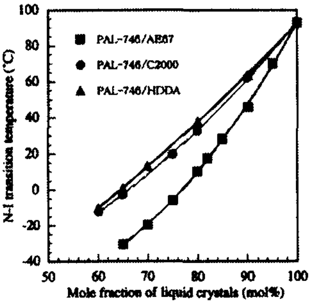


FIGURE 2 Phase diagrams in the homogeneous solution

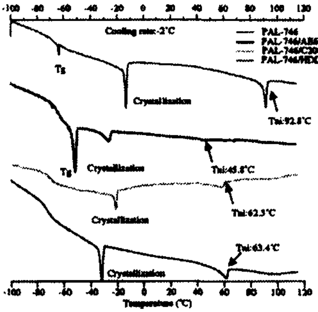


FIGURE 3 DSC chart

analogous phase diagram. In differential scanning calorimetry (DSC) as shown in Figure 3, although a peak with regard to the nematic-isotropic transition appears in the C-2000 and HDDA, no peak in the AE-67 system at 90 mol% of liquid crystals is observed. It is suggested that the thermal behavior in the AE-67 system is distinct from other diacrylates without side chains.

The morphology of Liquid crystal/polymer composite films

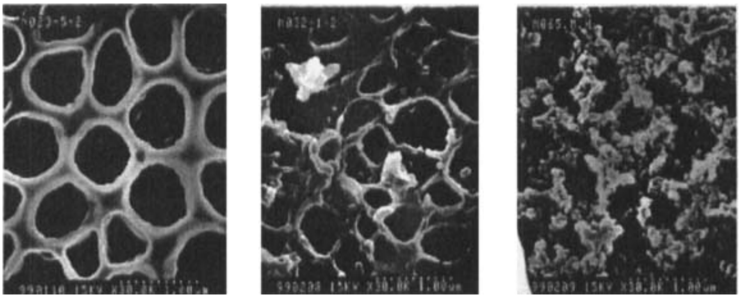
The photographs with scanning electron microscope are shown in Figure 4. Liquid crystalline phase is observed as a cavity of black area in the photographs. A white area represents the cured polymer phase in the films. A mesh-like polymer phase is obtained. This structure of polymer phase can be confirmed by a substitution of air, after a liquid crystal phase formed in the films is extracted by methanol. These photographs show the differences of morphology depending on the type of diacrylate. HDDA in which the number of methylene groups in the main chain is 6 exhibits interconnected spherical particles on the polymer-phase. As the number of methylene groups increase, the shape of surface changes from interconnected spherical particles into smooth surface which is seen in C-2000 and AE-67 of diacrylate.

The morphology in the films and their reflectance

The influence of mole fraction of liquid crystals on the reflectance is shown in Figure 5. The maximum reflectance in HDDA having the interconnected spherical polymer surface shows 16.5 % of reflectance at a 13 μm of cell gap. The higher reflectance more than 20% at 13 μm can be attained in the composite films having a smooth polymer surface using C-2000 and AE-67. 24.1% of the most high reflectance is obtained in AE-67 at 80 mol% of LC fraction. The inflection points indicating the maximum reflectance on the curve of AE-67 and HDDA predicts the existence of a peak on the curve in the C-2000 at less than 65 mol% of liquid crystals. These inflection points on the each curve imply that a certain optimum morphology is required to obtain the higher reflectance. Figure 6 shows the relation between the reflectance and the mesh size determined from the SEM photograph in each film. The maximum reflectance in each film is obtained at the appropriate mesh size from 0.5 μm to 0.65 μm in which corresponds to the wavelength of visible light. However, there are the differences of the maximum reflectance between diacrylates.

It is considered that these differences derive from the orientation of liquid crystalline molecules at the surface of polymer phase, because the shape of the surface on polymer phase in the HDDA is different from other diacrylates as shown in Figure 4.

In order to evaluate the mesh size in the wider area than the SEM observation, the distribution of mesh size was measured with the laser diffraction particle size analyzer using the laser beam at 1 mm in diameter. The results in the case at 80 mol% of liquid crystal fraction are shown in Figure 7 as a representative example. When the distribution in the mesh size as shown in Figure 7 are compared with the reflectance as a function of liquid crystal fraction as shown in Figure 5, the narrow distributions in the mesh size can be observed in the AE-67 of the films indicating a higher reflectance. On the other hand, the HDDA and C-2000 having the broader



(a) PAL746 80mol%/AE67 (b)PAL746 65mol%/C2000 (c)PAL746 65mol%/HDDA

FIGURE 4 Photographs with scanning electron microscope

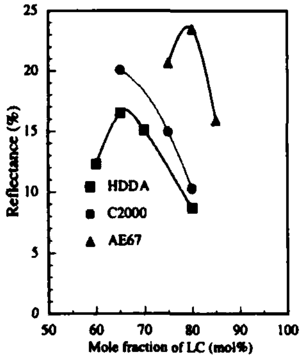


FIGURE 5 The reflectance as a function of LC fractions

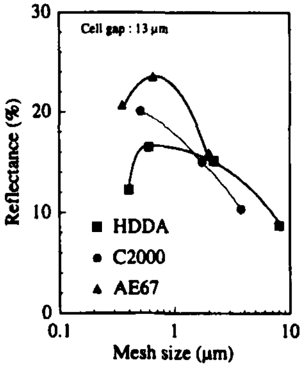


FIGURE 6 The reflectance as a function of the mesh size

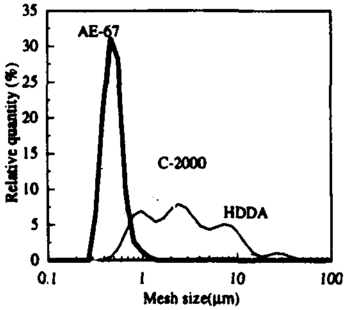


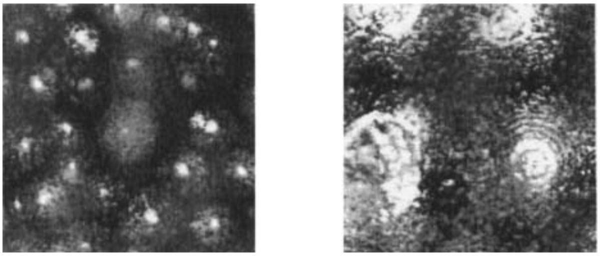
FIGURE 7 The distribution of the mesh size with various diacrylates at 80 mol% of LC fraction using the diffraction particle size analyzer

distribution in the mesh size indicates a lower reflectance. It is estimated that these distribution in the size influences the reflectance in the films.

Phase separation process during photopolymerization

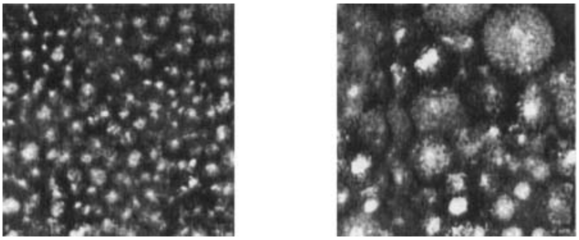
We have investigated the behavior of liquid crystalline domains during photopolymerization to understand the phase separation kinetics because the morphology in the films play one of important role to determine the reflectance. The time resolved confocal laser scanning microscopy [4] was carried out with 20 W/m^2 of UV-exposure to suppress the rate of evolution on the phase separation. The Hg lamp is equipped for the microscope so that the sample placed on the stage is irradiated over a limited area through the objective lens. The image is recorded at 0.5 seconds intervals for 50 seconds with the micro computer. Figure 8 (a)-

(c) shows the time resolved microscopic photographs at 0.5-1 seconds and 2 seconds for each diacrylate mixed with PAL-746 at 80-82 mol% of LC fraction. A white area on the photograph represents the nematic phase. A black area indicates either monomer-rich phase or isotropic phase contained liquid crystals and monomers. We first observe the nucleation of the nematic domains which suggests the occurrence of binodal decomposition. As photopolymerization goes on, the nuclear growth and coalescence of spherical nematic domains is observed. Moreover, the behavior on the nematic domains in the kinetics of phase separation can be distinguished by the type of diacrylate as shown in Figure 8 (a)-(c) and Figure 8. In the HDDA, the size at around 3 μm at 0.5 seconds in nematic domains come from the nucleation rapidly becomes the larger size at more than 8 μm within 2 seconds, because the coalescence of neighboring nematic domains frequently occurs. In the C-2000, the smaller size of nematic domains at nearly 1.6 μm than the HDDA forms at the first stage of phase separation. The nematic domains slightly growing without coalescence suddenly become a larger with the coalescence after 1 second of UV-exposure. In the AE-67, the spherical nematic domains at 1 μm continue to gradually grow with a slight coalescence. The interconnected spherical domains forms at the final stage of the phase separation process. It is suggested that the uniform size in the nematic domains from 0.5 μm to 0.65 μm is readily obtained with the AE-67 because the coalescence of nematic domains rarely occurs. The differences in the kinetics of phase separation depending on the diacrylates can be proved from the time resolved confocal laser microscopy. It is presumed that the numerous factors including mobility of both molecule, solubility and viscosity participate in the kinetics of the phase separation.



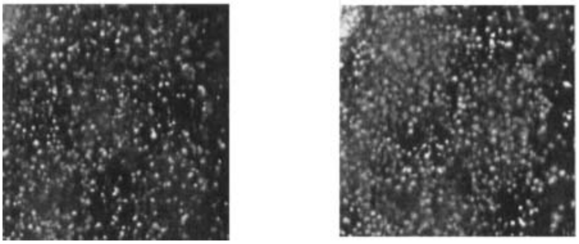
0.5 seconds 2 seconds

FIGURE 8 (a) HDDA 20mol%/ PAL 746 80 mol% with 20 W/m^2 UV-exposure



0.5 seconds 2 seconds

FIGURE 8 (b) C2000 20 mol%/ PAL746 80% with 20 W/m^2 UV-exposure



1 second 2 seconds

FIGURE 8(c) AE67 18 mol%/PAL 746 82 mol% with 20W/m^2 UV-expopsure

Influence of birefringence

The reflectance dependence of birefringence Δn on liquid crystals is depicted in Figure 9. In this comparison, the composite films having a similar morphology with the different birefringence of liquid crystals is used to eliminate the influence of morphology. The reflectance is logarithmically proportional to the birefringence. To achieve the reflectance more than 50% at 13 μm of cell gap, the requirement of birefringence more than 0.41 is estimated by extrapolation.

Effect of thickness in the films

We have examined the influence of thickness in the films on the reflectance. Figure 10 shows the forward and backward light scattering intensity as a function of thickness in the films. The backward light scattering intensity related the reflectance increases as the thickness increases. On the other hand, the forward light scattering intensity decrease as the backward light scattering increase. This trend suggests one of evidence that the forward light scattering is influenced by the backward light scattering behavior. However, the sum of both the forward and backward light scattering intensity is not reached at 100 %. It is presumed that the residual component of light intensity is composed of the sideward light scattering and a few percentage of the surface reflection on a glass substrate. Figure 11 shows the sideward light scattering intensity versus thickness in the films, where the sideward light scattering represents the differences between 100 % and the sum of forward and backward light scattering. The sideward light scattering intensity is saturated at more than 10 μm of the thickness. When the total reflection occurs at the boundary between a glass substrate and the air, the light scattering angle over 34° against normal to the glass substrate reflects toward the side of cell. Consequently, since the saturation is observed in spite of the continuous increase of the backward light scattering intensity, it is estimated that this effect of total reflection contributes to the sideward light scattering intensity.

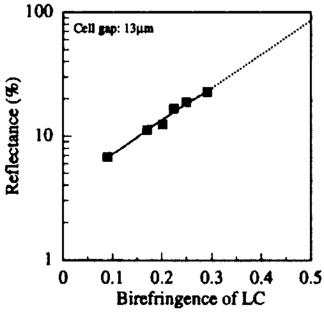
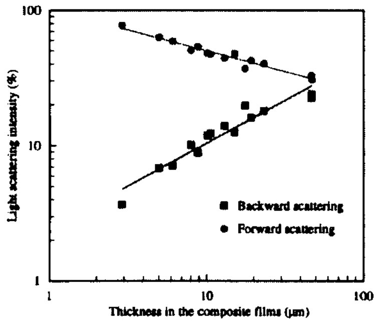


FIGURE 9 The reflectance dependence of birefringence on LC



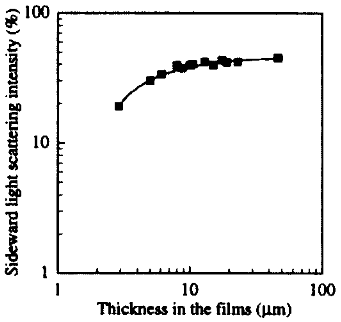


FIGURE 10 Forward and backward light scattering intensity vs. thickness in the films

FIGURE 11 Sideward light scattering intensity vs. thickness in the films

CONCLUSION

We have investigated numerous factors to determine the reflectance in liquid crystals/polymer composite films prepared by the photopolymerization induced phase separation process. It is illustrated that the reflectance is affected by the morphology of films represented by the size in liquid crystal domains and their distribution. The size in the liquid crystal domains corresponded to the wavelength of visible light is required to attain the higher reflectance. Since the morphology is sensitive to the kinetics of phase separation, the kinetics have been examined with the time resolved image by the confocal laser scanning microscopy. It is turned out that the process on growing nematic domains in the kinetics of phase separation depends on the type of diacrylate. When the coalescence of neighboring spherical nematic domains rarely occurs at the first stage of phase separation process, the uniform size in the nematic domains is readily obtained. It is considered that the occurrence of coalescence is related by the rate of diffusion for the molecules dissolved in both two separated phase. In addition to improve the reflectance over 50 %, the higher birefringence on liquid crystals more than 0.41 is needed.

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