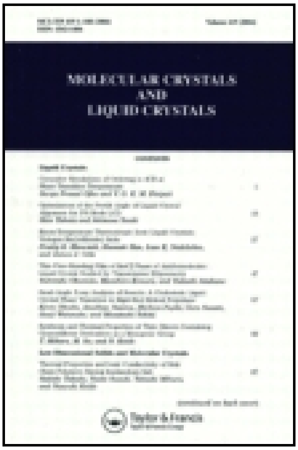

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AN ANALYSIS OF PHOTO-POLYMERIZATION INDUCED PHASE SEPARATION PROCESS IN LIQUID CRYSTAL/POLYMER COMPOSITE FILMS

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An Analysis of Photo-Polymerization Induced Phase Separation Process in Liquid Crystal/Polymer Composite Films

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The various diacrylates having different alkyl side-chain are systematically synthesized to investigate the relation between solubility in diacrylates for liquid crystals and phase separation process. In order to analyze the kinetics in photo-polymerization induced phase separation for a homogeneous mixture consisted of liquid crystals and monomers, time resolved confocal laser scanning microscopy with a high resolution is used. The difference between binodal decomposition and spinodal decomposition can be observed for the first time in the system of LC/monomer mixture. The occurring either spinodal or binodal decomposition in the phase separation process depends on the number of methylen in side-chains in diacrylates.

Keywords: Phase separation; Liquid crystal/polymer composite films; Spinodal decomposition; Binodal decomposition

INTRODUCTION

Liquid crystal/polymer composite films have a profound interest because oftheir potential in various electro-optical applications such as direct view displays. These composite films have been prepared from a phase separation process induced by a thermal quenching, or by a solvent evaporation, or by polymerization through thermal initiation or photo initiation. In general, time-resolved light scattering profiles, low angle X-ray scattering, electron microscopes, and optical microscopes are widely used to clarify factors dominating the phase separation process or determining the morphology in polymer-polymer systems.

We focus attention on the films fabricated by photo-polymerization induced phase separation process in the system composed of liquid crystals and photo curable two functional monomers. Since the electro-optical properties are strongly affected by the final morphology in the films depending on the kinetics on the phase separation process [1], an investigation of kinetics in the phase separation process is a very important with a view to controlling morphology in the films. Considering the kinetics, there is necessity to prove into whether the phase separation based on spinodal decomposition or binodal decomposition is occurred, because these two differences concerning phase separation process lead to the formation of complete distinct morphology in the films. Time resolved confocal laser microscopic images with high resolutions (xy: 260nm, xz: 648nm) are used to understand the kinetics, because various uncertain factors exist in photo induced phase separation process of liquid crystal/polymer composite systems. The confocal laser microscope has advantages that the selectivity of taking images in the only focal plane allows us to yield high-resolution images due to elimination of origin to deteriorate the resolution affected by images in out of focal plane. In this paper, we describe the kinetics based on observation of confocal laser microscope during photo polymerization. Moreover, phase separation process is systematically compared with molecular structure in two functional monomers to elucidate the influence of qualitative properties in the monomers.

EXPERIMENT

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 number of methylene either in the main chain or in alkyl side chain as shown in Figure 1 were used. Experimental monomers are synthesized by esterification between epichlorohydrin modified 1,6-hexanediol-diacrylate and fatty acids using dicyclohexyl carbodiimide. A 4 mol% of photoinitiatore (Irg-651 manufactured by Chiba-Geigy) was added in the total amount of diacrylate. After capillary filling above mixtures into a LC cell with 50μm cell gap, 20 or 200W/m^2 of UV light at 365nm was irradiated to a homogeneous solution consisted of liquid crystals and diacrylates using a high pressure mercury lamp at a 2°C above isotropic-nematic transition temperature to induce the polymerization. The phase transition temperatures in the homogeneous solution were observed by cross-polarized optical microscopy equipped with a hot stage (METTLER, FP-82HT) controlling a temperature to establish phase diagrams. Solubility parameter is calculated with the base of Hilldebrand-Scatchard theory to estimate miscibility. The confocal laser-scanning microscope (Leica) is captured with the microscopic image at 0.35 seconds intervals. Spectroscope is placed between objective lens and detector establishing microscopic images in order to avoid a detection of UV. This configuration on the optical system leads

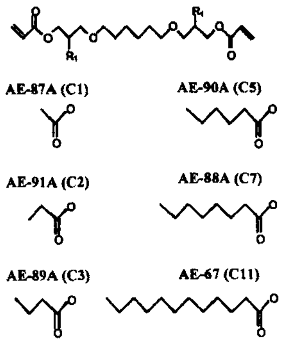

FIGURE 1. Molecular structure in synthesized diacrylates

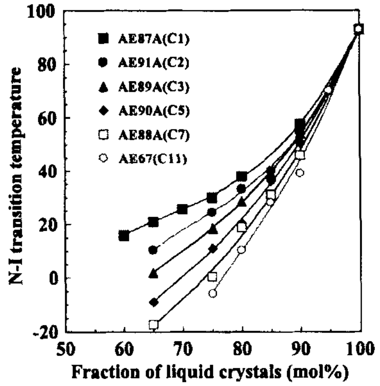

FIGURE 2. Phase diagram depending on various synthesized monomers

to be able to observe the photo-induced phase separation process under the microscope. The objective lens in this experiment has a resolution of 260nm horizontal and 648nm vertical. The two beams of Kr laser at 473nm and 488nm are employed to increase contrast of images.

RESULTS AND DISCUSSION

Phase diagram

The phase diagram in the homogeneous solution was established to identify the regions occurring either two-phase separations or one phase. Figure 2 depicts the phase diagram with the observation of the polarized microscopy. The nematic-isotropic transition temperature (T_{ni}) is gradually decreased as the molar fraction in liquid crystals decreases. Although photo polymerization induced phase separation systems typically show Upper Critical Solution Temperature (UCST) behavior[2], no UCST behavior can be seen in the experimental systems. Changes on T_{ni} as a function of the molar fraction in liquid crystals become high as number of methylen in the side-chain increases. These trend of changes imply that the molecular structure on the side-chain in two functional monomers has an influence of solubility for liquid crystals. In fact, when the various slopes indicated in the phase diagram in Figure 2 are compared with solubility parameter as shown in Table 1, there are relations that solubility parameter is inversely proportional to the number of methylen in side-chain. The solubility parameter close to that of liquid crystals shows a higher miscibility. In the AE-67, the large change of T_{ni} as a function of liquid crystal fraction on the phase diagram is observed.

Name of monomers	Number of methylen in side chain	Solubility paramer
AE-67	11	9.35
AE-88A	7	9.51
AE-90A	5	9.63
AE-89A	3	9.77
AE-91A	2	9.86
AE-87A	1	9.95
PAL-746	Liquid crystals	9.17

TABLE 1. Solubility parameter in synthesized monomers and LC

Time resolved confocal laser microscopic images

Figure 3 (a) shows the time-resolved confocal laser microscopic images on UV-exposure with 65mol% of liquid crystal fraction in the composition of the AE-87. The confocal laser microscopic images indicate two-dimensional distributions of reflective intensity in laser from objects. It is estimated that the reflective intensity come from differences on refractive index between liquid crystal rich phase and monomer rich phase, because anisotropy of refractive index in liquid crystals depends on concentration of residual monomers in liquid crystal rich phase, which is changed in the course of the phase separation process. A white area on the images represents the shape of liquid crystal domains. A complicated pattern on liquid crystal domain is observed as shown in Figure 3 (a). It is considered that the formation of these patterns with regard to liquid crystal domains is attributed to spinodal decomposition that concentration fluctuations develop and are

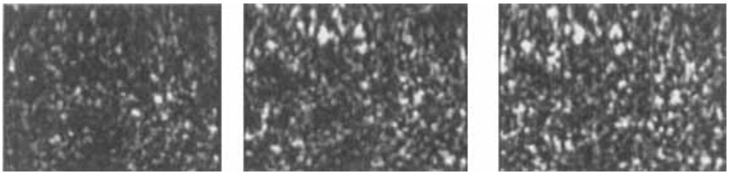
At 2.8 seconds of UV-exposure   3.15 sec.   3.2 sec

FIGURE 3. (a) 65mol% of LC fraction in the composition containing AE-87

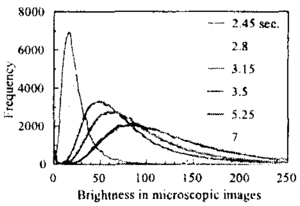

FIGURE 3 (b)
Histogram of brightness in microscopic images

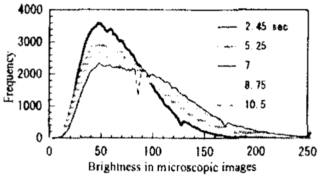

FIGURE 4(a)
Histogram of brightness in microscopic images for binodal decomposition

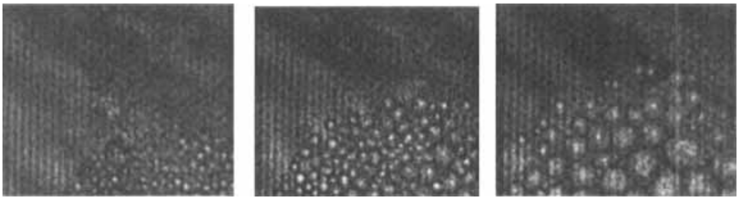
At 8.4 seconds of UV-exposure   11.76 sec.   15.12 sec.

FIGURE 4 (b) 90 mol% of LC fraction in the AE-87 system amplified simultaneously, because the complicated pattern is not a deformation but an increase of brightness related with the concentration fluctuations in liquid crystal rich phase as the phase separation goes on. Figure 3 (b) shows histogram on frequency as a function of gray scale corresponding to brightness in the images. A position of peak on the curve in the histogram shifts toward brighter images along with the evolution of phase separation. The changes in this histogram illustrate one of the evidence that spinodal decomposition characterized by the amplifying concentration fluctuations occurs during the phase separation process [3].

On the other hand, the phase separation process differed from spinodal decomposition is observed in 90 mol% of liquid crystal fraction shown in Figure 4(b) due to an occurrence of liquid crystal droplets accompanying with binodal decomposition characterized by a nucleation and nuclear growth. We first observe the nucleation of the nematic domains. As photo polymerization goes on, by the nuclear growth and coalescence of spherical nematic domains, the size on liquid crystal domains as shown in Figure 4(b) increases as an elapsed time in UV-exposure proceeds. Figure 4(a) shows typical histogram in binodal decomposition. A position of peak representing maximum brightness in the histogram is independent of the evolution of phase separation. This tendency suggests typical binodal decomposition that the concentration of liquid crystals in liquid crystal rich phase at the initial stage is

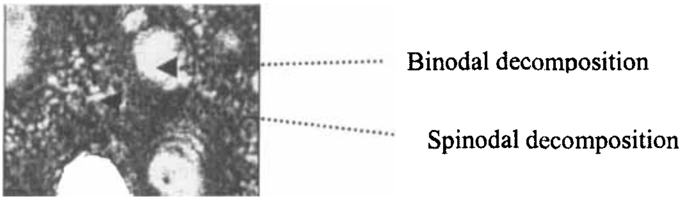

FIGURE 5. Phase separation transferring from binodal to spinodal decomposition

maintained in the course of the phase separation.

Other than typical evolution in either binodal decomposition or spinodal decomposition described above, the kinetics in phase separation transferring from occurrence of binodal decomposition at the initial stage into spinodal decomposition can be observed as shown Figure 5. Numerous liquid crystal domains as a nucleation with coalescence occur at the beginning. Later, spinodal decomposition immediately occurs at the monomer rich phase where is surroundings of liquid crystal droplets. This sequence in the phase separation is qualitatively consistent with the Flory-Huggins theory that predict the occurrence of spinodal decomposition after binodal decomposition when the phase separation curve in theoretic phase diagram on UCST behavior shifts toward a higher temperature as polymerization proceeds [4].

Influence of monomers on Kinetics in phase separation process

Figure 6 depicts the classification on phase separation process with various alkyl side-chains in two-functional monomers. In the AE-87A having C1 of side-chain, typical spinodal decomposition is observed in the range of liquid crystal fraction from 65 mol% to 80 mol%. The transferring phase separation process occurs in the range from nearly 85 mol% to 90 mol%. When number of methylen in the side-chain became two, the range in binodal decomposition appears only at over 90 mol% of liquid crystal fraction. In addition, the range of liquid cryasral fraction occurring binodal decomposition is expanded at a higher liquid crystal fraction as the number of methylen in the side-chain increases. The range of transferring phase separation is expanded less than C5. On the contrary, the range occurring binodal decomposition is broadened more than C7 of the side-chain. Since the AE-87, which has the most wide range occurring spinodal decomposition, is a lower solubility parameter compared with other synthesized monomers, it is estimated that a lower miscibility readily lead to develop an unstable phase separation as spinodal decomposition.

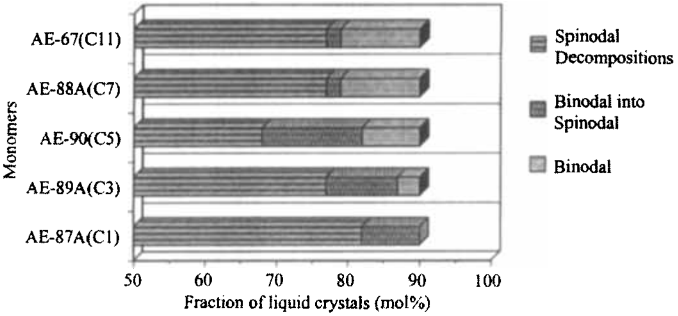

FIGURE 6. Classification of phase separation

CONCLUSION

In this paper, we have shown the kinetics in the photo-induced phase separation process on the system consisted of liquid crystals and diacrylates. In time resolved confocal microscopy, the differences of kinetics between binodal decompositon and spinodal decomposition can be distinguished by either the formation of complicated image pattern with regard to concentration fluctuations in liquid crystal rich phase or the images in the formation of liquid crystal droplets accompanying nucleation and nuclear growth. It is turned out that the kinetics of phase separation depends on the length of alkyl side-chain in diacrylates.

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