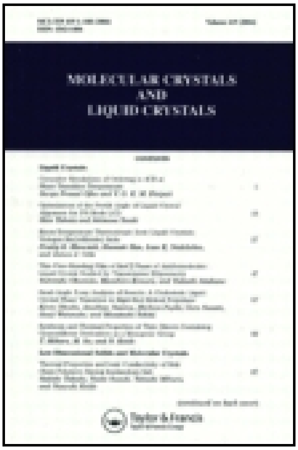

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Phase Behaviour of Uncured and UV-cured (2-ethylhexylacrylate-1,6-hexanedioldiacrylate)/E7 Mixtures

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PHASE BEHAVIOUR OF UNCURED AND UV-CURED (2-ETHYLHEXYLACRYLATE-1,6-HEXANEDIOLDIACRYLATE)/E7 MIXTURES

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The equilibrium phase diagram of UV-cured (2-ethylhexylacrylate-1,6-hexanedioldiacrylate) and the multicomponent nematic fluid E7 is established by polarized optical microscopy and differential scanning calorimetry. The enthalpy changes at the nematic-isotropic transition for both uncured and UV-cured samples are used to determine the liquid crystal (LC) solubility limit in the acrylate rich phase and to estimate the fractional amount of phase separated LC.

Keywords: DSC; monomer; nematic liquid crystal; optical microscopy; phase diagram; polymer

INTRODUCTION

The phase behaviour and the phase separation processes are among the main parameters governing the morphology and the electro-optical performances of Polymer-Dispersed Liquid Crystals (PDLC) films [1]. It has been demonstrated that uncured and UV-cured monofunctional monomer/liquid crystal (LC) systems exhibit a UCST shape phase diagram [2,3]. In the case

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of difunctional monomer/LC mixtures, the phase diagram of the unreacted initial blend are of the UCST type whereas after UV-curing an isotropic miscibility gap (Isotropic + Isotropic) has been clearly evidenced even at high temperature [4,5]. In the present paper the phase behaviour of mixtures containing a monofunctional monomer (2-ethylhexylacrylate; EHA) and a difunctional monomer (1,6-hexanedioldiacrylate; HDDA) in the (50:50) weight.% ratio and the eutectic mixture of low molecular weight liquid crystals (LMWLCs) E7 is studied in both uncured and UV-cured states. The multicomponent fluid E7 exhibits a wide nematic phase with a nematic-isotropic transition temperature T_{NI} at 61°C. The phase diagram of the UV-cured system ([EHA-HDDA]/E7) is established by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The enthalpy changes at the nematic-isotropic transition for both uncured and UV-cured samples are used to determine the liquid crystal solubility limit in the acrylate rich phase and to estimate the fractional amount of phase separated LC.

EXPERIMENTAL PART

Materials

The monofunctional acrylate monomer 2-ethylhexylacrylate (EHA) was supplied from Aldrich (Saint Quentin Fallavier, France). The difunctional monomer hexanedioldiacrylate (HDDA) was purchased from UCB Chemicals (Drogenbos, Belgium). Both monomers were used without further purification. EHA is fully isotropic in the temperature range of interest (-100 to $+100$°C) whereas HDDA presents a crystalline to isotropic transition at $T_{\mathrm{CI}} = 0.2$°C with an enthalpy change of $\Delta H_{\mathrm{CI}} = 139\,\mathrm{J/g}$. The initial reactive monomer mixture was prepared by mixture EHA and HDDA at room temperature in the (50:50) weight.% (wt.%) ratio. The LMWLC purchased from Merck-Clévenot (Sainte Geneviève des Bois, France) is the eutectic mixture E7 exhibiting a glass transition at $T_{\mathrm{g}} = -62$°C with $\Delta C_{\mathrm{p}} = 0.48\,\mathrm{J/(g.^{\circ})}$ and a nematic to isotropic transition at $T_{\mathrm{NI}} = 61$°C with $\Delta H_{\mathrm{NI}} = 4.5\,\mathrm{J/g}$. The UV-polymerization process was induced by 2 wt.% of Darocur 1173 (Ciba, Rueil Malmaison, France) with respect to the amount of monomer used.

Sample Preparation

EHA–HDDA/E7 mixtures were prepared with various LMWLC contents and are stirred mechanically until they became homogeneous. Samples for calorimetric measurements were prepared by introducing approximately 3 mg of the initial mixture into aluminium DSC pans, which have been sealed to avoid evaporation effects during the temperature treatment. Samples for microscopy observations were prepared by placing one drop of the reactive mixture between standard glass slides. The UV-curing was performed using a Seiko-UV 1 Unit. The wavelength of the UV radiation was set at $\lambda = 365\,\text{nm}$ with a beam intensity of $17.5\,\text{mW/cm}^2$. The UV-exposure time was fixed at three minutes.

Characterization Methods

Differential Scanning Calorimetry (DSC) measurements were performed on a Seiko DSC 220C calorimeter. The DSC cell was purged with 50 ml/min of nitrogen. Rates of 10°C/min (heating) and 30°C/min (cooling) were used in the temperature range -100 to $+100$°C. The program consists first in cooling the sample followed by several heating and cooling cycles. Data analysis have been carried out on the second heating ramp.

The Polarized Optical Microscopy (POM) measurements were performed on a Leica DMRXP microscope equipped with a heating/cooling stage Linkam THMSE600. Samples were first heated from room temperature to a temperature located 15°C above the isotropic phase limit then quenched at 30°C/min to 20°C. Subsequently another heating cycle with a rate of 5°C/min up to the isotropic state was carried out. The whole procedure was repeated twice. Two independent samples of the same composition were analyzed.

RESULTS AND DISCUSSION

Morphology and Phase Diagram

Figures 1a and 1b are optical micrographs taken at $T = 25$°C on the uncured and UV-cured samples prepared with the same LC content (90 wt.% E7). The comparison between these two textures is interesting because it gives an indication of the drastic changes of the morphology before and after UV-curing. Figure 1a shows a Schlieren texture characteristic of the nematic phase whereas Figure 1b displays clearly two coexisting phases with numerous small birefringent microdomains dispersed in the polymer matrix and large nematic defects indicating a macrophase separation. These morphology changes illustrate unambiguously the miscibility loss of the LC with a polymer network compared to the acrylate monomer mixture.

Figure 2 gives the equilibrium phase diagram of the UV-cured [EHA–HDDA]/E7 system obtained by POM and DSC measurements. The closed symbols represent POM data and the x-symbols are the DSC data while the solid and dashed lines are guides to the eyes. Three distinct regions

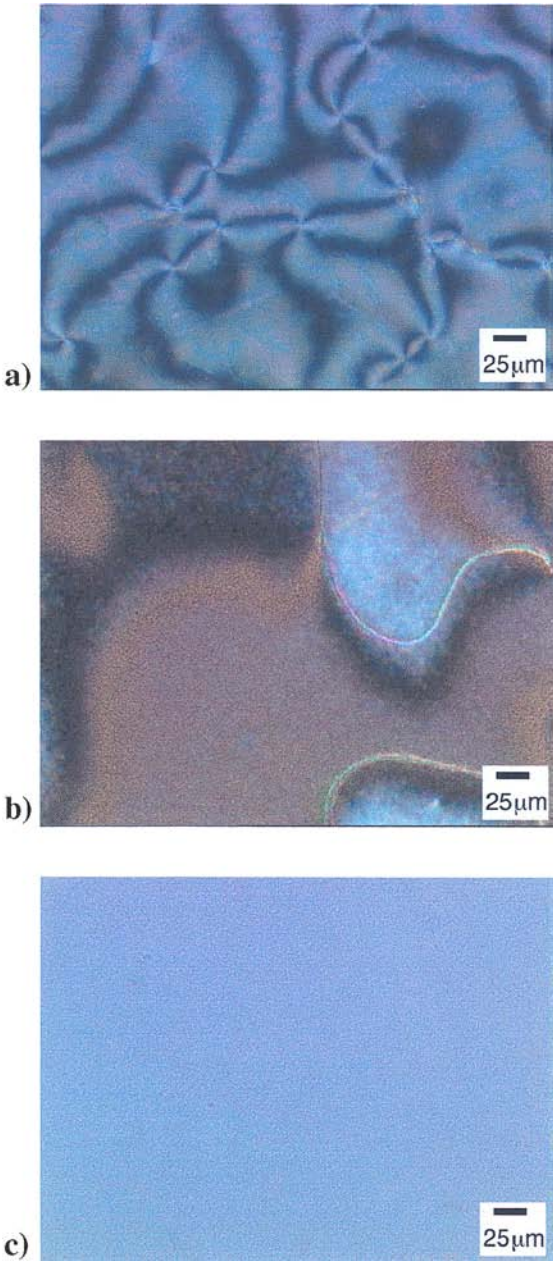

FIGURE 1 Optical micrographs of [EHA–HDDA]/E7 (10/90) mixtures: a) uncured state, $T = 25°\text{C}$ (N); b) cured state, $T = 25°\text{C}$ (N + I), and c) UV-cured state $T = 65°\text{C}$ (I + I). (See COLOR PLATE VI)

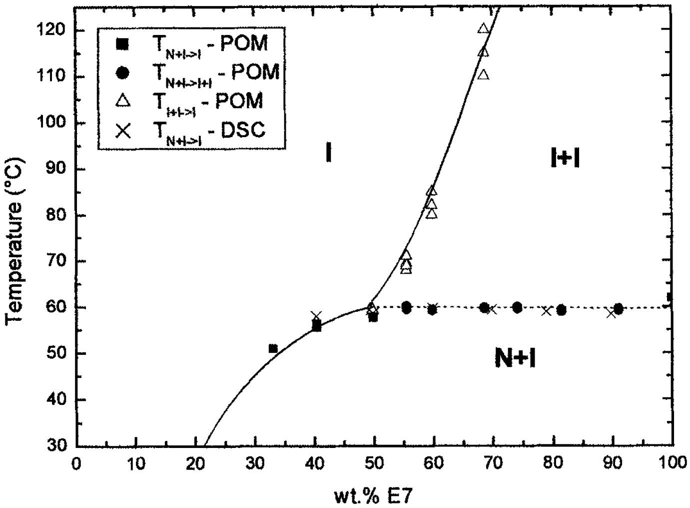

FIGURE 2 Equilibrium phase diagram of UV-cured [EHA–HDDA]/E7 system. The closed symbols represent POM data and the x-symbols are DSC data. The solid and dashed lines are guides for the eyes.

can be distinguished. At lower temperatures the diagram exhibits a wide biphasic (N + I) domain where a pure nematic phase (E7) is in equilibrium with a swollen isotropic network.

On the left hand side of the diagram a single isotropic (I) phase of UV-cured [EHA–HDDA] and E7 is observed. The third region on the upright hand side of the diagram shows the emergence of a wide (I + I) miscibility gap. This gap consists of a swollen isotropic network coexisting with a pure isotropic LC phase even at high temperatures. A typical texture of the (I + I) morphology is displayed in Figure 1c.

This miscibility gap is characteristic of the phase behaviour of crosslinked polymers where elastic forces at the crosslinks oppose stretching beyond the saturation limit. At this limit any additional amount of LC forms an excess pure LC macrophase in contrast with linear polymers and monomers where the LC phase is in principle never entirely pure [5]. Theoretical investigations based on a combination of the Flory-Rehner [6] and the Maier-Saupe [7] theories are underway to confirm with a thermodynamic model the position of the solid and dashed lines.

Thermophysical Characteristics

Figure 3 shows the variations of ΔH_{NI} and ΔC_{p} vs LC content for monomer and UV-cured [EHA–HDDA]/E7 systems. ΔC_{p} and ΔH_{NI} are inferred from

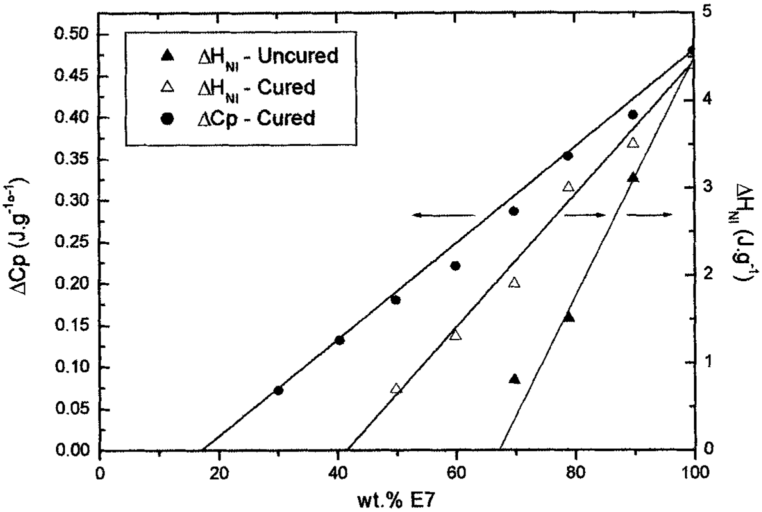

FIGURE 3 Variation of the enthalpy ΔH_{NI} at the NI transition T_{NI} (right y axis) and the heat capacity ΔC_p at T_g (left y axis) versus LC content. Both monomer and UV-cured systems are represented for comparison.

the heat capacity change at $Tg = -62°C$ and from the enthalpy change at the nematic-isotropic transition $T_{NI} = 61°C$, respectively. Both quantities were deduced from DSC measurements. ΔH_{NI} and ΔC_p increase linearly with the LC concentration. The variation of ΔH_{NI} vs LC content for the monomer system is also linear and lies below that of the UV-cured sample especially at low LC compositions, showing the increased miscibility of the monomer and the LC before polymerization. In order to estimate quantitatively these results, the LC solubility limit β has been determined by linear regression of the experimental data sets, followed by calculating the x axis intercepts. In the case of the uncured mixture, the value of β was 67%, whereas in the case of polymerized samples a value of 42% was found. For the cured system, the value of β extracted from ΔC_p ($\beta = 18\%$) is lower than that from ΔH_{NI} ($\beta = 42\%$). This can be explained by the fact that the solubility of LC molecules in the polymer network at T_g (−62°C) is lower than that at T_{NI} (+61°C) [8].

CONCLUSIONS

The phase properties of uncured and UV-cured [EHA–HDDA]/E7 mixtures have been investigated. It has been shown that the UV-curing process induces drastic changes of the sample morphology illustrating the miscibility loss of the LC with a polymer network compared with a monomer mixture. The equilibrium phase diagram of UV-cured systems exhibits a wide miscibility gap (I + I) due to the elastic forces at the crosslinks. Addition of a small amount of E7 leads to the emergence of a pure LMWLC phase. The LC solubility limit β has been determined from the enthalpy changes at T_{NI} and from the heat capacity change at T_{g}. The miscibility of the LC with [EHA–HDDA] decreases drastically after UV-curing. It was also found that β decreases with decreasing temperature.

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