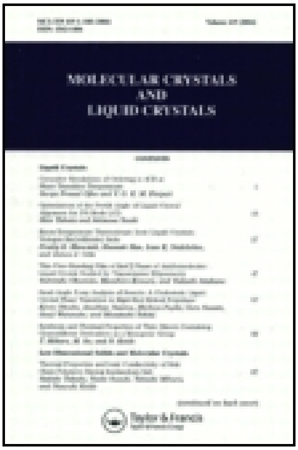

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Equilibrium phase diagrams of uncured and UV-cured difunctional hexanedioldiacrylate and the eutectic mixture of low molecular weight liquid crystals E7 are established by polarized optical microscopy and differential scanning calorimetry. Data are analyzed using the Maier-Saupe model of nematic order. In the case of the uncured system the Flory-Huggins free energy of isotropic mixing is applied while for the cured system, the Flory-Rehner elastic free energy model is used. A good correlation between experimental and theoretical phase diagrams is found in both systems.

Keywords: Polymer; monomer; liquid crystal; phase diagrams; Flory-Huggins; Maier-Saupe; Flory-Rehner; microscopy; DSC

INTRODUCTION

The phase behavior of blends of difunctional monomeric hexanedioldiacrylate (HDDA) and ultra-violet (UV) cured HDDA with the eutectic mixture of low molecular weight liquid crystals (LMWLCs) E7 is studied. E7 exhibits a single nematic-isotropic transition temperature T_{NI} at 61°C. The phase diagrams are established by polarized optical microscopy (POM) and differential scanning calorimetry (DSC) and analyzed by the Maier-Saupe theory[1] for nematic order. In the case of the monomeric HDDA/E7 mixture, the Flory-Huggins[2] free energy of isotropic mixing is used to calculate the phase diagram while for UV-cured samples, the elastic free energy is described by the Flory-Rehner[3] theory of rubber elasticity.

EXPERIMENTAL PART

Materials

The monomer hexanedioldiacrylate (HDDA) was purchased from UCB Chemicals (Drogenbos, Belgium) and used without purification. HDDA presents a crystalline to isotropic transition at T_{KI}=0.2°C with an enthalpy change of ΔH_{NI}=139J/g. The LMWLC purchased from Merck-Clévenot (Sainte Geneviève des Bois, France) is the eutectic mixture E7 exhibiting a glass transition at T_g=-62°C and a nematic to isotropic transition at T_{NI}=61°C with ΔH_{NI}=4.5J/g. The UV-polymerization process was induced by 2 weight% (wt-%) of Darocur 1173 (Ciba, Rueil Malmaison, France) with respect to the amount of monomer used.

Sample preparation

HDDA/E7 mixtures were prepared with various LMWLC contents and stirred mechanically until they became homogeneous. Samples for calorimetric measurements were prepared by introducing approximately 3mg 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 λ=365nm with a beam intensity of 17.5mW/cm^2. The UV-exposure time was fixed at three minutes.

Characterization methods

The Polarized Optical Microscopy (POM) measurements were performed on a Leica DMRXP microscope equipped with a heating/cooling stage Chaixmeca. Samples were first heated from room temperature to a temperature located 15°C above the isotropic phase limit then quenched at 100°C/min to -80°C for the uncured mixtures and to 20°C for the cured mixtures. 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. For both uncured and cured mixtures, two independent samples of the same composition were analyzed.

Differential Scanning Calorimetry (DSC) measurements were performed on a Seiko DSC 220C calorimeter. The DSC cell was purged with 50ml/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.

RESULTS AND DISCUSSION

Uncured HDDA/E7 system

The phase behavior of the uncured HDDA/E7 system is quite rich if one looks at a large domain of temperature as revealed by the DSC thermograms. An example of these thermograms is given in Figure 1 for various systems including pure HDDA, pure E7 and several mixtures. The curve at the bottom corresponding to the pure E7 clearly

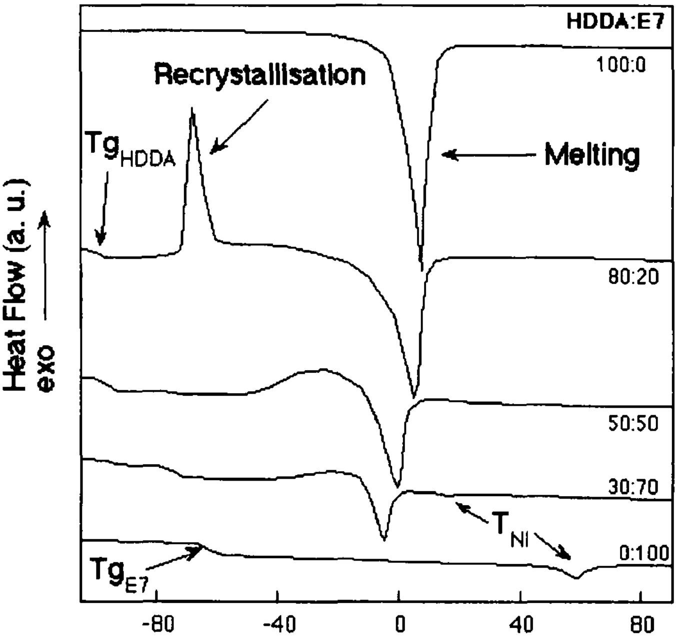

FIGURE 1 DSC thermograms of the monomeric HDDA/E7 system with the compositions indicated on the figure. The thermograms of the pure compounds are also shown. T_g represents the glass transition temperature and T_{NI} is the nematic-isotropic transition temperature observed by DSC.

exhibits a glass transition at T_g=-62°C and a nematic-isotropic transition at T_{NI}=61°C. The thermograms above show that by adding monomeric HDDA, both transitions shift to lower temperatures. At a certain concentration of HDDA, crystalline and melting transitions appear. For the system of 50wt% HDDA, a large melting peak appears at –5°C and a distinct bump of crystallisation of HDDA at –30°C. The melting peak widens and shifts to higher temperatures when HDDA concentration increases. For pure HDDA, the crystallisation peak is found near 0°C. In the temperature/E7 volume fraction (T, φ_1) frame, these transitions lead to a complicated phase diagram whose description is the subject of a separate work. Here, we limit ourselves to the temperature range where the system exhibits isotropic and nematic phases only. Figure 2 gives the (T, φ_1) equilibrium phase diagram for the uncured HDDA/E7 mixture. The symbols represent POM and DSC data while the solid curve is the theoretical binodal. Calculations are made assuming that the free energy is a sum of two terms. One is the Flory-Huggins[2] free energy of isotropic mixing $f^{(i)}$

$$\frac{f^{(i)}}{k_B T} = \frac{\varphi_1}{N_1}\ln\varphi_1 + \frac{\varphi_2}{N_2}\ln\varphi_2 + \chi\varphi_1\varphi_2 \tag{1}$$

where φ_1 and φ_2 are the volume fractions of E7 and monomeric HDDA, respectively; N_1=1 assuming that the LMWLC has a single repeat unit and N_2 is the number of repeat units of HDDA; the interaction parameter χ is function of temperature. According to Maier-Saupe theory[1] the nematic free energy is

$$\frac{f^{(n)}}{k_B T} = \frac{\varphi_1}{N_1}\left[-\ln Z + \frac{\nu\varphi_1 s^2}{2}\right] \tag{2}$$

where s is the nematic order parameter and ν the so-called quadrupole interaction parameter; Z represents the nematic partition function. The details of the calculation of the coexistence curve are described elsewhere[4] and will not be reproduced here.

Figure 2 shows a good correlation between POM and DSC data and between these data and the calculated curve. Two distinct regions are found. In the upper part, a single isotropic phase is obtained.

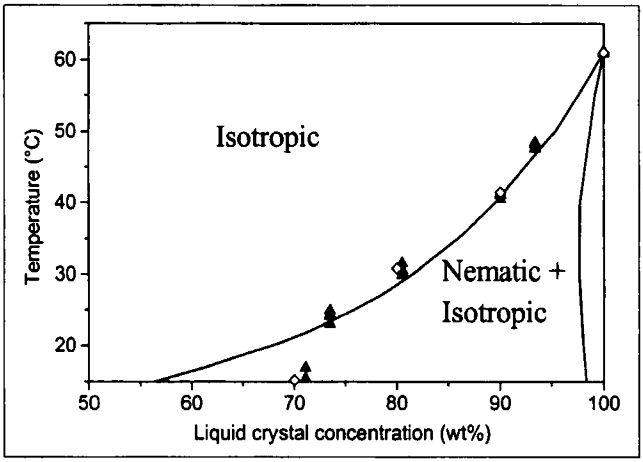

FIGURE 2 Equilibrium phase diagram of uncured HDDA/E7 system. The open diamonds represent DSC data whereas the closed triangles are POM data. The solid line represents the theoretical curve calculated using $N_1=1$, $N_2=2$, $\chi = -1.88 + 887/T$, and $T_{NI}=61°C$.

In the lower part, a biphasic region shows that an isotropic monomer rich phase coexists with a practically pure nematic LMWLC phase. No isotropic miscibility gap (I+I) is observed, indicating a relatively high miscibility of HDDA and E7. The diagram does not exhibit a single nematic phase as one would expect for compatible mixtures. Consistent tendencies between measurements and calculated curves are found. The (N+I)/I transition temperature undergoes a sharp depression when HDDA is added to the LMWLC. When only 10wt% monomer is added to the LMWLC, the transition from (N+I) to I takes place at 43°C implying a depression by approximately 20°C. Adding 30wt% HDDA yields even a sharper decrease from 61°C to 20°C showing the increasing immiscibility HDDA/E7.

UV cured HDDA/E7 system

Figure 3 gives the equilibrium phase diagram of the UV-cured HDDA/E7 system obtained by POM and DSC measurements. The theoretical diagram is established using the same procedure as in Figure 2 except that the isotropic free energy is modified to take into account the size and architecture of the UV-cured polymer network. Since one deals with a crosslinked polymer, the free energy should account for the presence of crosslinks that put an upper bound to the network swelling. Therefore, equation 1 should be modified accordingly Using the rubber elasticity theory of Flory-Rehner[3], one has

$$\frac{f^{(i)}}{k_B T} = \frac{3\alpha\varphi_r{}^{2/3}}{2N_c}\left(\varphi_2^{1/3} - \varphi_2\right) + \frac{\beta\varphi_2}{N_c} ln\varphi_2 + \frac{\varphi_1}{N_1} ln\varphi_1 + \chi\varphi_1\varphi_2 \qquad (3)$$

where N_c is the mean number of repeat units between consecutive crosslinks, φ_r is the initial polymer volume fraction at crosslinking, α and β are rubber elasticity parameters. Polymerization/crosslinking under UV-curing takes place in-situ meaning that $\varphi_r = \varphi_2$. The rubber elasticity parameters α and β may depend upon the functionality f of monomers at crosslinks and the polymer volume fraction. Figure 3 shows that the equilibrium phase diagram is quite different from that of the uncured system. UV-curing leads to a drastic loss of miscibility with the LMWLC. The isotropic region is much narrower than in Figure 2 and a wide (I+I) miscibility gap emerges. This gap consists of a swollen isotropic network coexisting with a pure isotropic LMWLC phase. Note that the monomeric HDDA/E7 system did not show such a gap. Below 61°C, there is an (N+I) region where an isotropic polymer rich phase coexists with a pure LMWLC nematic phase. Unlike uncured

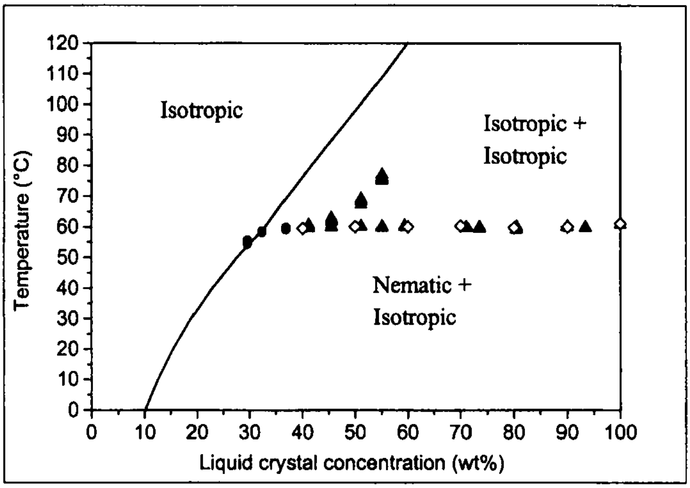

FIGURE 3 Equilibrium phase diagram of UV-cured HDDA/E7 system. The closed symbols represent POM data and the open diamonds are DSC data. The solid line is the theoretical curve calculated using $N_1=1$, $N_c=5$, $\chi=-1.6+823/T$, $\alpha=(f-2(1-\varphi_2))/f$, $\beta=2\varphi_2/f$, f=3 and $T_{NI}=61°C$.

systems, the (N+I) to (I+I) transition takes place at the transition temperature of pure E7. The rapid turn over of the data above 61°C is due to a saturation of the network for the small value of N_c characterizing a densely crosslinked network.

CONCLUSIONS

The phase properties of difunctional monomeric and UV-cured HDDA/E7 mixtures are investigated. Thermograms of the uncured systems show a variety of phase transitions. The glass transition temperature of the LMWLC decreases substantially as the monomer concentration increases and the relatively high miscibility of HDDA and E7 induces a plasticizing effect. The equilibrium phase diagrams of uncured and UV-cured systems are quite different due to the high elastic forces at the crosslinks. Addition of a small amount of E7 leads to the emergence of a pure LMWLC phase. The saturation limit is related to N_c or the average chain length between consecutive crosslinks. Experimental data are analyzed successfully using the Maier-Saupe theory of nematic order, the Flory-Huggins theory for the uncured system or the Flory-Rehner theory for the crosslinked polymer.

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