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Equilibrium phase diagrams of mixtures of propoxylated glyceroltriacrylate (GPTA) and low molecular weight liquid crystals (LMWLCs) are investigated. The experimental phase diagrams of monomeric and electron beam (EB) cured GPTA/LMWLC blends are established by polarized optical microscopy (POM). Three LMWLC are used exhibiting different nematic-isotropic transition temperatures. One is the single component LMWLC 4-cyano-4′-*n*-pentyl-biphenyl (5CB), another one is the eutectic mixture known as E7, and the third one is the single component 4-cyano-4′-*n*-octyl-biphenyl (8CB) exhibiting both nematic and smectic A orders. The experimental data are successfully analyzed within a unified theoretical treatment based on mean field approximations.

Keywords: Liquid crystal; monomer; phase diagram; electron beam curing; network; microscopy

INTRODUCTION

The phase diagrams of monomeric and electron beam (EB) cured

propoxylated glyceroltriacrylate (GPTA) in mixtures with different LMWLCs are investigated. The cured samples were prepared by exposing the GPTA/LMWLC mixture to EB irradiation. This technique gives well-defined samples[1] with a high conversion ratio of the monomer. Compared with curing by ultraviolet exposure, EB-curing of acrylates has the advantage of not using a photoinitiator that could reduce substantially the performance of such materials.

Three LMWLCs are used in this investigation. These are the single components 4-cyano-4′-*n*-pentyl-biphenyl (5CB) and 4-cyano-4′-*n*-octyl-biphenyl (8CB), and the eutectic mixture of four cyanoparaphenylene derivatives known as E7.

The experimental diagrams are established using polarized optical microscopy (POM) and the data analyzed with classical theories. In the case of linear polymers, the free energy of isotropic mixing is described by the Flory-Huggins[2] lattice model. The Flory-Rehner[3] elasticity theory is used for systems involving crosslinked polymers. In order to include the effects of nematic and smectic-A interactions, the model of Maier-Saupe[4] for nematic ordering is supplemented with the MacMillan[5] theory of smectic-A order.

The systems investigated here allow us to assess the effect of curing on the phase behavior of polymer/LMWLC mixtures and consequently to estimate the miscibility depression due to the size and elasticity of the polymer network. By considering three different LMWLCs with well known properties, we are able to identify the changes in the phase behavior due to the nature of LMWLC.

EXPERIMENTAL PART

Materials

Propoxylated glyceroltriacrylate (GPTA) as monomer was obtained from Cray Valley (France). The LMWLC 5CB and E7 were purchased from Merck Encolab GmbH (Germany). 5CB can be characterized by the following characteristic transition temperatures: T_{KN}=23°C, and T_{NI}=35.3°C[6]. E7 exhibits a single nematic-isotropic transition temperature at T_{NI}=61°C. The LMWLC 8CB was purchased from Frinton Laboratories (New Jersey, USA) and presents in the pure state characteristic transition temperatures : T_{KS}=21.5°C, T_{SN}=33.5°C, and T_{NI}=40.5°C.

Sample preparation

x weight-percent (wt%) of LMWLC (x=10, 20, ..., 90) and (100-x)wt% of GPTA were mixed together at room temperature for several hours. Samples including the reactive initial mixtures only and a second series consisting of the same blends but in the cured state were prepared.

Reactive blends in the uncured state

The reactive initial mixtures were sandwiched between two round glass slides. Several samples at the same composition were prepared independently to check the reproducibility of the results.

EB curing of GPTA/LMWLC samples

An Electrocurtain Model CB 150 (Energy Sciences Inc.) with an operating high voltage of 175kV was used as generator. The samples prepared as mentioned above were placed in a tray which was passed in a nitrogen atmosphere under the electron-curtain on a conveyor belt. A beam current of 7mA and a constant conveyor speed of 0.19ms^{-1}

allowed to achieve a dose of 104kGy. For each composition, several samples have been prepared and exposed to the EB radiation to cure the polymerizable mixture.

POM measurements

A Leica DMRXP equipped with a heating-cooling stage Linkam THMSE 600 was employed as POM. First, the samples prepared as mentioned earlier were submitted to a heating rate of 2°C/min from room temperature to 15 degrees above the transition temperature leading to the isotropic phase. Then samples were left approximately 5min in the isotropic state. The samples corresponding to approximately 30wt% LMWLC or higher were then cooled to room temperature at a rate of -2°C/min. The same rate was used for samples with lower concentration of LMWLC but cooling was performed to lower temperatures. This procedure was followed after 5min by a heating ramp at a rate of 2°C/min. Transition temperatures were recorded during this heating ramp.

RESULTS AND DISCUSSION

Figure 1 shows three diagrams corresponding to mixtures of the monomeric GPTA and E7, 8CB and 5CB in the descending order. The shape of these diagrams is similar except a shift in the temperature scale. This shift is due to the fact that transition temperatures of the LMWLCs considered are widely different. These diagrams exhibit two regions. A wide isotropic phase in the upper part of the figure expresses the relatively high miscibility of GPTA and the LMWLCs. This miscibility explains the absence of an isotropic+ isotropic (I+I) gap in the figure. The biphasic region nematic + isotropic designed by (N+I)

shows that an isotropic GPTA rich phase is in equilibrium with a polymer free LMWLC nematic phase. A rapid depression of the

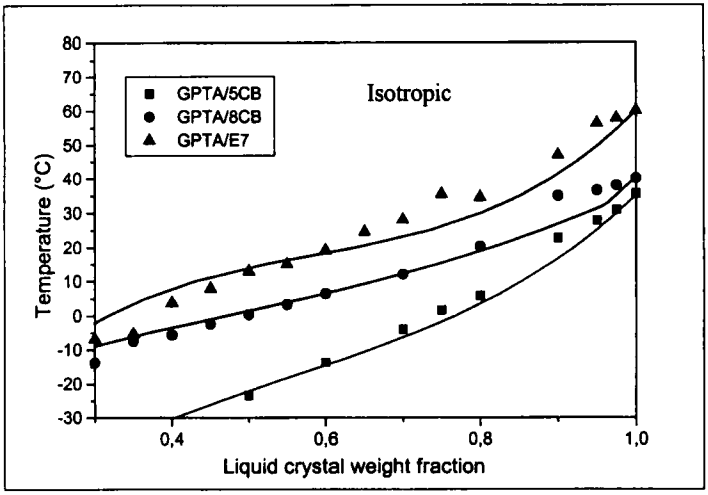

FIGURE 1 Equilibrium phase diagrams of mixtures of the monomeric GPTA/LMWLC with 5CB, 8 CB, and E7. The symbols represent averaged experimental data obtained by POM. The solid lines are the calculated curves using the parameters : N_1=1; N_2=2; 5CB: T_{NI}=35.3°C, χ=-0.596+ 392/T; 8CB: T_{NI}=40.5°C, χ=-6.075+1861/T; and E7: T_{NI}=61°C, χ=-0.152+403/T.

temperature is observed when concentration of LMWLC decreases from 1. This behavior is characteristic of oligomer/LMWLC mixtures[7]. The diagram corresponding to 8CB exhibits an additional region that corresponds to a smectic-A nematic below 33.5°C. In this case, a smectic-A pure LMWLC phase coexists with a monomer rich phase in the isotropic state. The eutectic mixture E7 has the lowest

miscibility with regards to the uncured GPTA while 5CB is the most compatible among the three LMWLCs considered.

The solid lines in Figure 1 are the calculated curves starting from a free energy that is the sum of two terms $f=f^{(i)}+f^{(a)}$. The first term is the Flory-Huggins[2] free energy for isotropic mixing

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

where k_B is the Boltzmann constant, T is the absolute temperature, N_1 and N_2 are the numbers of repeat units of LMWLC and GPTA, respectively, and χ is the Flory-Huggins interaction parameter; φ_1 and φ_2 are the volume fractions of LMWLC and polymer, respectively, assuming incompressibility $\varphi_2=1-\varphi_1$.

The second term is the anisotropic free energy which can be modeled according to the Maier-Saupe-McMillan[4,5] theories of nematic and smectic-A orders

$$\frac{f^{(a)}}{k_B T}=\frac{\varphi_1}{N_1}\left[-\ln Z+\frac{1}{2}\nu \varphi_1 (s^2+\zeta \sigma^2)\right] \tag{2}$$

s and σ are the nematic and smectic order parameters, respectively, ν is the so-called quadrupole Maier-Saupe parameter, ζ is another parameter that depends upon the ratio of nematic-isotropic (T_{NI}) and smectic-A-nematic (T_{SN})[4,5] transition temperatures, Z represents the anisotropic partition function. In the case of a nematic LMWLC, it is sufficient to let the order parameter σ be 0. The details describing the procedure for calculating the coexistence curves were given elsewhere[8].

The theoretical curves of Figure 1 fit quite well with the experimental data for the three LMWLCs considered here. Figure 2

represents the phase diagrams of EB-cured GPTA and the same LMWLCs. Similar symbols are used to represent POM data as in

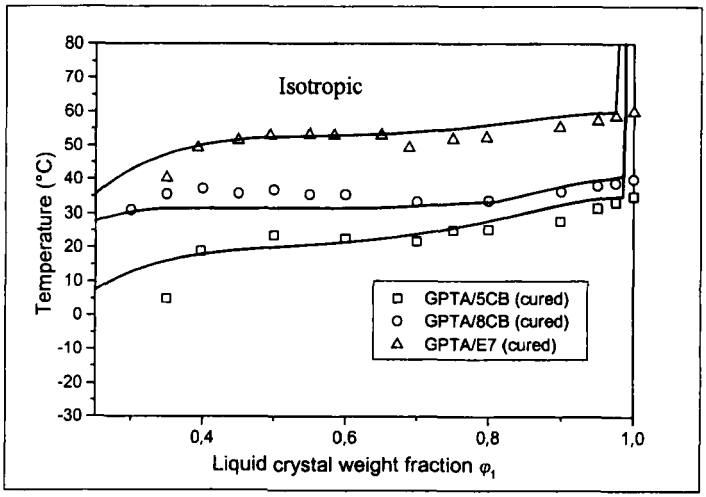

FIGURE 2 The same as Figure 1 for the EB-cured GPTA/LMWLC mixtures. The model parameters employed in this case are N_1=1; N_c=50; 5CB: T_{NI}=35.3°C, χ=-0.52+342/T+0.6φ_2+ 0.03φ_2^2; 8CB: T_{NI}=40.5°C, χ=-0.32+ 320/T+0.7φ_2+ 0.03φ_2^2; E7: T_{NI}=61°C, χ=-0.35+ 348/T+0.5φ_2+0.03φ_2^2.

Figure 1. Qualitatively the three diagrams have a similar shape and are shifted to a higher temperature range as compared to monomeric GPTA systems. Unlike Figure 1, these diagrams exhibit large miscibility gaps whereby a pure LMWLC ordered phase is in equilibrium with an isotropic polymer rich phase. With the POM technique, it was possible to observe clearly the transition from (S+I) to (N+I) for the GPTA/8CB system and from (N+I) to (I+I) and I for all the systems investigated. The thermal treatment described in the experimental procedure was chosen in such a way to avoid crystallization of 5CB and 8CB. This

figure confirms the decreasing extend of miscibility in going from 5CB to 8CB and to E7 as observed in the monomeric case.

The solid lines are the binodals calculated using a similar formalism in which the isotropic energy is modified to account for the elasticity of the crosslinked polymer network. This is made according to the Flory-Rehner[3] theory of rubber elasticity

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

where N_c is the number of monomers between consecutive crosslinks, α and β are the rubber elasticity parameters, and φ_r is the initial polymer volume fraction. The parameters α and β are chosen according to the model of Flory-Erman[9] and Petrovic[10]. This choice is not crucial but allows us to improve the fit between theory and experiments. The polymer volume fraction at crosslinking φ_r is identified with φ_2 since polymerization and crosslinking reactions are made in situ by the EB-curing method. The isotropic interaction parameter χ is considered to be function of temperature and composition[11] in order to capture the plateau shown by the three diagrams of Figure 2 while the phase diagrams of uncured systems require that χ is function of temperature only. The theoretical model considers ideal networks and does not take into account possible heterogeneities and defects that would lead to a different value of N_c.

CONCLUSIONS

The phase properties of uncured and EB-cured GPTA systems with 5CB, 8CB and E7 are investigated. The experimental diagrams are established by the POM technique and analyzed using appropriate

models for the isotropic and anisotropic free energies. The shapes of phase diagrams are not affected by the nature of LMWLC but very sensitive to the EB-curing process. E7 exhibits the lowest miscibility while 5CB is the most compatible among the three LMWLCs with both monomeric and EB- cured GPTA system. The effect of EB curing reduces significantly the miscibility of GPTA and LCs and lead to wide (I+I) miscibility gaps.

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