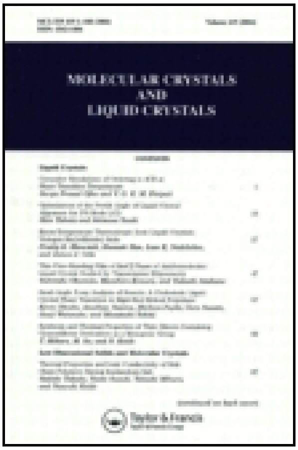

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N. Gogibus [a] [b], U. Maschke [a], F. Benmouna [c], F. Roussel [d], B. Ewen [b], X. Coqueret [a], J.-M. Buisine [d] & M. Benmouna [c]

[a] Laboratoire de Chimie Macromoléculaire (UPRESA CNRS N° 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, F-59655, Villeneuve d'Ascq Cedex, France

[b] Max-Planck-Institut für Polymer-forschung, Postfach 3148, D-55121, Mainz, Germany

[c] Faculté des Sciences, Université Aboubakr Belkaïd, BP119, 13000, Tlemcen, Algeria

[d] Laboratoire de Thermophysique de la Matière Condensée (Equipe de l'UPRESA N° 8024 du CNRS), Université du Littoral, MREID, F-59140, Dunkerque, France

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Effects of Polymer Architecture on the Phase Properties of Polymethylsiloxane/Liquid Crystal Blends

N. GOGIBUS[ab], U. MASCHKE[a], F. BENMOUNA[c], F. ROUSSEL[d],
B. EWEN[b], X. COQUERET[a], J.-M. BUISINE[d] and M. BENMOUNA[c]

[a]*Laboratoire de Chimie Macromoléculaire (UPRESA CNRS N° 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cedex, France,* [b]*Max-Planck-Institut für Polymer-forschung, Postfach 3148, D-55121 Mainz, Germany,* [c]*Faculté des Sciences, Université Aboubakr Belkaïd, BP119, 13000 Tlemcen, Algeria and* [d]*Laboratoire de Thermophysique de la Matière Condensée (Equipe de l'UPRESA N° 8024 du CNRS), Université du Littoral, MREID, F-59140 Dunkerque, France*

The phase properties of polydimethylsiloxane (PDMS) and low molecular weight liquid crystals (LMWLCs) with different size and architecture of the polymer are investigated. An oligomer of molecular weight 800 g/mol and two linear polymers of molecular weight 5500 and 45000 g/mol are considered. Electron beam cured PDMS/4-cyano-4′-*n*-pentyl-biphenyl (5CB) mixtures in which the polymer is a crosslinked network are also investigated. Experimental phase diagrams are established using polarized optical microscopy (POM) and analyzed using classical theories for the free energy of isotropic mixing, network elasticity and nematic order.

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

INTRODUCTION

The equilibrium phase behavior of mixtures of polymers and low molecular weight liquid crystals (LMWLCs) are the subject of a particular attention from a fundamental and a practical point of view[1]. These are heterogeneous mixtures consisting of micron-sized ordered domains dispersed in a solid polymer matrix. As such, their phase properties and morphologies are of particular interest and were reported in several recent studies[2,3]. It was observed that the nature of molecular species, polymer size and architecture govern substantially the compound morphology and the blend miscibility. In the present paper, a study of the equilibrium phase diagrams of several mixtures made of polydimethylsiloxane (PDMS) and LMWLCs (5CB and E7) is reported. Linear PDMS with different molecular weights are considered together with the electron beam cured PDMS/5CB system[4-6].

EXPERIMENTAL PART

Materials

PDMS of molecular weight M_w=5500g/mol (M_w/M_n=1.3) and M_w=45000g/mol (M_w/M_n=1.1) were prepared by an anionic living polymerization method using n-butyllithium as initiating species and trimethylchlorosilane as end-capper. A PDMS diacrylate of molecular weight 800g/mol was obtained from ABCR (Karlsruhe, Germany). These polymers will be referred to as PDMS800, PDMS5500 and PDMS45000, respectively. The LC 5CB was purchased from Merck Encolab GmbH (Darmstadt, Germany) which provides a nematic-isotropic transition temperature of T_{NI}=35.3°C.

Sample preparation

PDMS5500/5CB and PDMS45000/5CB

The polymer and the LC were dissolved in a common organic solvent THF at 55 weight-percent (wt%) for PDMS5500 and 70wt% for

PDMS45000 at room temperature. These mixtures were stirred mechanically for two hours before a small quantity was cast on a clean glass slide. Then THF was evaporated completely at room temperature for 24 hours.

PDMS800/5CB

(100 - x) wt% of PDMS800 (x=10, 20, ...,90) and x wt% of 5CB 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.

PDMS800/5CB - Uncured samples

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

PDMS800/5CB - Cured samples

An Electrocurtain Model CB 150 (Energy Sciences Inc.) with an operating high voltage of 175kV was used as generator. Thin films of the PDMS800/5CB mixtures were prepared on round glass slides which were then placed in a tray passing 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 electron beam radiation to cure the polymerizable mixture.

POM measurements

The thermo-optical studies were performed on a POM ZEISS equipped with a heating/cooling stage Linkam temperature control unit. Samples were heated from room temperature to 15 degrees above the transition temperature leading to the isotropic phase. Then samples were left approximately 15 min in the isotropic state. The following thermal processes applied on the samples depend on the kinetics of reaching the thermodynamic equilibrium state. Further details can be found in references[5-7]. At least two samples were prepared independently with the same composition to check reproducibility of the results.

RESULTS AND DISCUSSION

Figure 1 represents the diagram of PDMS44000/5CB (□,upper diagram), PDMS5500/5CB (○, middle diagram) and PDMS800/5CB (*, lower diagram). The latter polymer is rather a short oligomer dissolving 5CB with a relatively high degree of compatibility. This figure gives a measure of the loss of miscibility of PDMS in 5CB as the polymer molecular weight increases. At room temperature (20°C), 5CB phase separates in the highest molecular weight PDMS as soon as φ_l exceeds 5wt% while the oligomer is completely miscible at all compositions. For the intermediate molecular weight PDMS, 5CB presents a limit of solubility near 15wt%. The three diagrams are put together to show differences in the phase properties of the systems. The upper two diagrams were discussed previously[5]. They exhibit both (I+I) and (N+I) miscibility gaps in addition to a single isotropic phase. The case of oligomer has not been reported before. It gives a different phase behavior as compared to higher molecular weight systems. In particular, it does not exhibit the (I+I) region reminiscent of the low miscibility of the high molecular weight polymers. The phase diagram of the oligomer system exhibits only an (N+I) gap and a single (I) region. The solid line represent calculated binodals using a combination of the

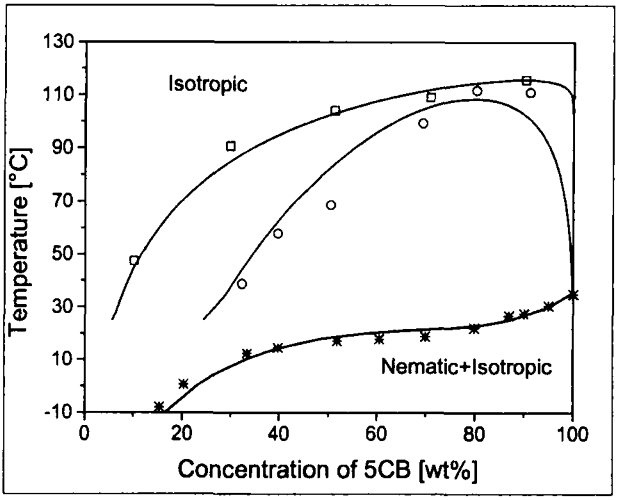

FIGURE 1 Equilibrium phase diagrams of three PDMS/5CB systems with linear polymers having the molecular weight M_W=44000, 5500 and 800 g/mol in the descending order. The solid curves are the binodal calculated using the following parameters $N_1=1$, $T_{NI}=35.3°C$ and in the descending order ($N_2=80$, $\chi=-4.4+1950/T$), ($N_2=16$, $\chi=-0.7+565/T$) and ($N_2=5$, $\chi=-2.65+1073/T$).

Flory-Huggins[8] theory of isotropic mixing and the Maier-Saupe[9] theory of nematic order.

The free energy has an isotropic part $f^{(i)}$

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

where N_1 and φ_1 are the number of repeat units and volume fraction of LC; N_2 and φ_2 represent similar quantities for the polymer; χ is the temperature dependent interaction parameter. We assume that

$\chi=A+B/T$, where A and B are constant parameters. The nematic free energy contribution is $f^{(n)}$

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

where Z is the nematic partition function, s is the nematic order parameter and ν is the quadrupole Maier-Saupe parameter

$$\nu \;=\; 4.54\frac{T_{NI}}{T} \tag{3}$$

T_{NI} is the nematic/isotropic transition temperature of the LC. The binodal is obtained by solving the set of equations

$$\mu_1^{(')} \;=\; \mu_1^{('')};\qquad \mu_2^{(')} \;=\; \mu_2^{('')} \tag{4}$$

where (') and ('') designates the coexisting phases, μ_1 and μ_2 are the chemical potentials of LC and polymer, respectively. It is easy to verify that

$$\mu_1=N_1\left[f-\varphi_2\frac{\partial f}{\partial\varphi_2}\right]\qquad \mu_2=N_2\left[f-\varphi_1\frac{\partial f}{\partial\varphi_1}\right] \tag{5}$$

This equation is valid for the isotropic, nematic chemical potentials and their sum. The phase behavior in the case of EB-cured systems is quite different from that of Figure 1. Indeed, as one can see from Figure 2, the diagram of EB-cured PDMS/5CB exhibits three distinct regions. On the left hand side, a single isotropic phase emerges. On the right hand side, below 35.5°C, the diagram exhibits an (N+I) region consisting of an isotropic swollen network coexisting with a pure nematic LC phase. Above 35.5°C, a miscibility gap (I+I) is found whereby a swollen isotropic network coexists with a pure isotropic LC phase. This region is quite extended expressing the relatively high incompatibility of 5CB with the crosslinked PDMS network. The transition temperature from

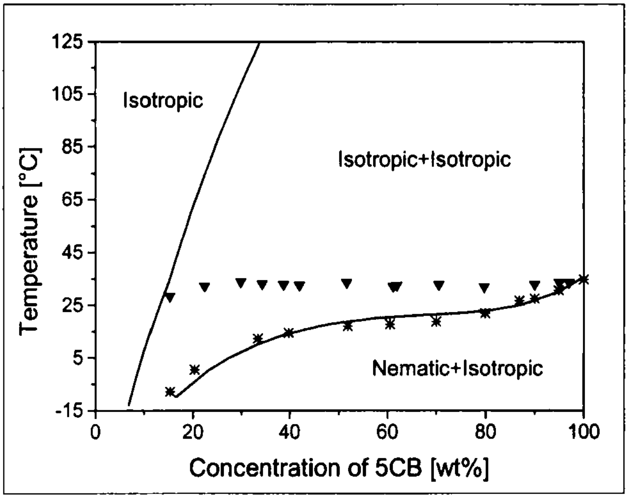

FIGURE 2 The equilibrium phase diagram of the EB cured PDMS/5CB (upper diagram) and PDMS oligomer/5CB (lower diagram) systems. The symbols represent POM data while the solid line are the calculated diagrams using the following parameters for the cured system $N_\mathrm{I}=1$, $N_\mathrm{C}=5$, $\chi= -0.87+687/T$, $f=3$ and $T_\mathrm{NI}=35.5°\mathrm{C}$. The diagram of the oligomer/5CB system is the same as in Figure 1. It is included here for comparison only.

(N+I) to (I+I) is practically constant indicating that the LC rich phase is pure. This is a known consequence of the presence of crosslinks in the polymer network. The solid lines are the theoretical curves calculated with a similar procedure except that the isotropic free energy is modified to include the effects of elastic forces opposing swelling beyond a certain limit. Here, the isotropic energy is modelled according to the rubber elasticity theory of Flory-Rehner[10]

$$\frac{f^{(i)}}{k_B T} = \frac{3\alpha\varphi_0^{2/3}}{2N_c}\left[\varphi_2^{1/3} - \varphi_2\right] + \frac{\beta\varphi_2}{N_c}\ln\varphi_2 + \frac{\varphi_1\ln\varphi_1}{N_1} + \chi\varphi_1\varphi_2 \qquad (6)$$

where N_C is the number of repeat units between consecutive crosslinks, φ_0 is the volume fraction at crosslinking. In the present EB-curing method, crosslinking reaction takes place in situ and hence φ_0=φ_2. The rubber elasticity parameters α and β are model dependent and the following expressions are found useful for fitting the calculated diagram with the experimental data[11]

$$\alpha = \frac{\mathrm{f} - 2 + 2\varphi_2}{\mathrm{f}}, \quad \beta = \frac{2\varphi_2}{\mathrm{f}} \qquad (7)$$

where f is the functionality of monomers at the crosslinks.

CONCLUSIONS

The equilibrium phase diagrams of PDMS/5CB systems with linear polymers and EB-cured systems are established by POM. The data are analyzed using a combination of mean field approximations distinguishing the free energies of linear and crosslinked polymers. In the latter case, a particular attention is given to the elastic forces at the crosslinks of the network that oppose swelling beyond a certain limit. This allows us to assess the effects of the polymer size and architecture on the equilibrium phase diagrams.

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