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Phase behavior of electron beam cured and uncured propoxylated glyceroltriacrylate/E7 mixtures

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Summary

The phase properties of uncured and electron beam cured propoxylated Glyceroltriacrylate (GPTA)/E7 mixtures are investigated using polarized optical microscopy and differential scanning calorimetry. The cured samples were prepared by polymerization/crosslinking reactions with controlled dose and dose rate by means of electron beam irradiation. The experimental phase diagram of cured GPTA/E7 mixtures was successfully analyzed using a model based on the Flory-Rehner elastic free energy supplemented with the Maier-Saupe free energy of nematic order. The data corresponding to the uncured samples were successfully interpreted combining the Flory-Huggins theory of isotropic mixing and the Maier-Saupe theory of nematic order.

Introduction

The phase properties of mixtures of polymers and liquid crystals (LCs) have been investigated particularly due to their importance for numerous applications. For example, Polymer Dispersed Liquid Crystals (PDLCs) are used for light control devices like optical shutters (1,2). PDLC films can be electrically switched from a cloudy light scattering off-state to an activated transparent on-state. They consist commonly of micron-sized dispersions of low molecular weight LC (LMWLC) within a solid polymer matrix. The electro-optical characteristics of these materials are governed by the thermodynamical properties and therefore, it is important to understand their phase behavior.

Recently, theoretical phase diagrams of mixtures of crosslinked polymers and (LMWLC) were reported (3,4). A formalism combining the Flory-Rehner (5) theory of rubber elasticity for the isotropic free energy and the Maier-Saupe (6,7) theory for the nematic free energy has been applied. Using a similar formalism, Nwabunma et al. (8,9) were able to analyze the experimental phase diagram of a LMWLC and the photopolymerizable multicomponent polymer precursor NOA65. The phase diagram of the ultraviolet cured system was also investigated. The nematic LMWLC used by Nwabunma et al. was 4-cyano-4'-*n*-heptyl-biphenyl (7CB). Recently (10), we reported a study of the phase behavior of uncured and electron beam (EB) cured propoxylated Glyceroltriacrylate (GPTA)/ 4-cyano-4'-*n*-octyl-biphenyl (8CB) mixtures. The cured samples were prepared by crosslinking polymerization of the GPTA/8CB blends under EB exposure. The EB

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curing of acrylates has the advantage of not requiring a photoinitiator as in the UV method. This technique has been used as a powerful tool to obtain well defined PDLC films (11-13).

The present work goes along the same lines and considers a similar investigation of the phase behavior of uncured and EB cured GPTA/E7 mixtures. There is however a substantial difference between the two systems since E7 is an eutectic mixture of four cyanobiphenyls while 8CB considered in reference (10) was a single cyanobiphenyl LC component. Moreover, E7 has a single nematic-isotropic transition temperature and no crystalline phase in the whole range of temperature considered while 8CB is characterized by three different transition temperatures as explained in reference (10). The phase behavior for both cured and uncured samples is studied experimentally by polarized optical microscopy (POM). Differential scanning calorimetry (DSC) measurements were performed for the uncured GPTA/E7 mixtures. The experimental data of this system are analyzed theoretically combining the Flory-Huggins (14) model of isotropic mixing and the Maier-Saupe model of nematic order (6,7). Theoretical modelling for cured samples was made using the Flory-Rehner theory of rubber elasticity (5) and the Maier-Saupe theory.

Experimental

Materials

Monomeric propoxylated Glyceroltriacrylate (GPTA) was obtained as a donation from Cray Valley (France) and used without purification. The eutectic LC mixture E7 was purchased from Merck Ltd (GB), containing 51 weight percent (wt%) of 4-cyano-4'-*n*-pentyl-biphenyl (5CB), 25wt% of 7CB, 16wt% of 4-cyano-4'-*n*-oxyoctyl-biphenyl (80CB), and 8wt% of 4-cyano-4"-*n*-pentyl-p-terphenyl (5CT). E7 exhibits a single nematic-isotropic transition temperature at T_{NI}=60°C (15).

Sample preparation - uncured state

Blends of x wt% of E7 and (100 - x) wt% of GPTA (x=10, 20,..., 90) were prepared at room temperature and stirred mechanically overnight. Afterwards, these mixtures were coated on round glass slides particularly adapted for microscopy observations. The thickness and the uniform application of the reactive films on the glass slides were controlled by using a bar-coater of 10 µm (Braive, Belgium). The same procedure was repeated to obtain several samples for each composition. For the DSC measurements, the samples were prepared by introducing approximately 3mg of the initial mixture into aluminum DSC pans.

Sample preparation - cured state

For our experiments, an Electrocurtain Model CB 150 (Energy Sciences Inc.) with an operating high voltage of 175 kV was used. The samples prepared as mentioned above were placed on a tray which was exposed to the EB radiation under a nitrogen atmosphere on a conveyor belt. The applied dose of 104 kGy (i.e. 104 J/g) was achieved by using a conveyor speed of 0.19 $\mathrm{m \cdot s^{-1}}$ and a beam current of 7 mA. The temperature during EB exposure was not controlled. Since the thickness of all samples did not exceed 10µm, uniform and total penetration could be obtained.

POM measurements

The polarized optical microscope (POM) employed in this work was a Leica DMRXP, equipped with a heating-cooling stage Linkam THMSE 600. Samples were submitted to the following thermal treatment : They were first heated at a 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. Afterwards, the samples with concentrations lower than 50wt% in LC were cooled down to T=-10°C at a rate of -2°C/min in order to be able to detect phase separation. For the other samples possessing higher LC compositions, the same heating/cooling ramps were applied but cooling was performed to room temperature only. This procedure was followed after 5min by a heating ramp at a rate of 2°C/min. Transition temperatures were recorded during the heating ramp.

DSC measurements

DSC measurements were performed on an apparatus of the type SEIKO DSC 220C equipped with a liquid nitrogen system. The apparatus cell was purged with nitrogen at a rate of 50ml/min. The same heating/cooling ramps were used as for the microscopy measurements in the temperature range from -100°C to 100°C. Data were recorded systematically on the second heating ramp.

Theoretical modeling

The formalism for calculating the phase diagram of linear polymers and nematic LMWLC has been layed down by Kyu et al. (16) using the Flory-Huggins lattice model for isotropic mixing and the Maier-Saupe model for nematic order. A similar calculation is made here to mimic the phase diagram of uncured samples. Extension of this calculation to systems involving crosslinked networks is straightforward starting from the Flory-Rehner theory of rubber elasticity which takes into account the forces opposing the network swelling at the crosslinks. In general, the free energy density is a sum of two terms

$$f = f^{(i)} + f^{(n)} \tag{1}$$

The first term is the isotropic free energy density

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

where k_B is the Boltzmann constant, T is the absolute temperature, φ_r is the reference state polymer volume fraction, N_c is the mean number of repeat units between consecutive crosslinks, α and β are the model dependent rubber elasticity parameters, and χ is the Flory-Huggins interaction parameter. φ_1 and φ_2 are the volume fractions of LC and polymer, respectively, assuming that $\varphi_2 = 1 - \varphi_1$. N_1 represents the number of repeat units of the LC which is considered to be equal to 1. For uncured GPTA/E7 samples, the isotropic free energy is (14)

$$\frac{f^{(i)}}{k_B T} = \frac{\varphi_1}{N_1}\ln\varphi_1 + \frac{\varphi_2}{N_2}\ln\varphi_2 + \chi\varphi_1\varphi_2 \tag{3}$$

N_2 is the number of repeat units of the uncured GPTA. Since the molecular weight of GPTA is nearly 50% higher than that of E7, one would expect N_2 to be either 1 or 2. We have chosen N_2=2 to obtain reasonable values of the intercation parameter χ in the range of temperature explored experimentally. The second term on the right hand side of equation 1 represents the nematic free energy according to the Maier-Saupe theory (6,7)

$$\frac{f^{(n)}}{k_B T} = \frac{\varphi_1}{N_1}\left[-\ln Z + \frac{1}{2}\nu\varphi_1 s^2\right] \tag{4}$$

where Z is the nematic partition function

$$Z = \int d(\cos\theta)\,\exp\left[\frac{m_n}{2}\left(3\cos^2\theta\ -1\right)\right] \tag{5}$$

and s is the orientation order parameter

$$s\ =\ \frac{1}{2}\left[3\langle\cos^2\theta\rangle\ -\ 1\right] \tag{6}$$

θ is the angle between the nematic director and a reference axis and <...> designates the average with respect to the orientation distribution function, $\nu = 4.54T_{NI}\ /\ T$ is the Maier-Saupe quadrupole interaction parameter and m_n is a mean field parameter expressed in terms of ν, s and φ_1 from minimization of $f^{(n)}$ with respect to s as $m_n\ =\ \nu\ s\ \varphi_1$. Details for the construction of the theoretical phase diagram may be found in references (3,4,9).

Results and discussion

The results for the uncured GPTA/E7 mixtures are shown in figure 1.

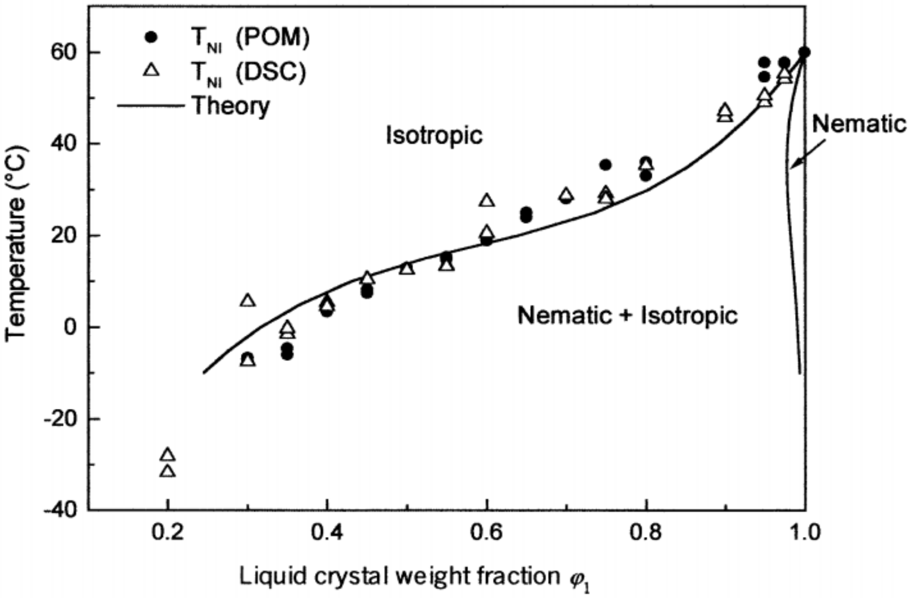


Figure1 : Temperature/composition diagram of the uncured GPTA/E7 system. The symbols represent experimental data obtained by POM and DSC. The solid line is the theoretical curve obtained using the following parameters : N_1=1, N_2=2, χ=-0.152+403/T, and T_{NI}=60°C

The symbols are POM and DSC data and the solid line represents the calculated curve. Three regions can be distinguished. There is a wide region showing a single isotropic phase in the upper part of the diagram. This region covers a large domain in the temperature/composition diagram and expresses the high miscibility of uncured GPTA and E7. A nematic + isotropic (N+I) miscibility gap is found at lower temperatures, where a GPTA rich phase in the isotropic state coexists with a practically pure nematic E7 phase. A good agreement between the experimental results obtained by DSC and POM is observed. The (N+I) transition temperature decreases rapidly upon addition of GPTA to a E7 pure phase. For example, at φ_1=0.9 the (N+I)/I transition takes place almost at T=45°C which means that there is a drop of 15°C below the N/I transition temperature for pure E7. A similar decrease of the transition temperature is observed for systems with linear polymers (17) with a more pronounced decrease for a lower molecular weight polymer.

The temperature/composition diagram obtained for EB cured GPTA/E7 samples is shown on figure 2. The filled circles represent the POM data while the solid line is the theoretical binodal. At lower temperatures, the diagram exhibits a wide biphasic region where a pure nematic E7 phase is in equilibrium with a swollen isotropic network. In the upper part of the diagram and on the left hand side of the solid curve, a single isotropic phase of cured GPTA and E7 is observed. With the POM technique used here, it was possible to observe clearly the transition from the (N+I) region to the isotropic single phase from φ_1=0.35 to nearly φ_1=1. Below φ_1=0.35 the measurement shows no evidence of phase separation upon cooling the samples far below 0°C and slow heating.

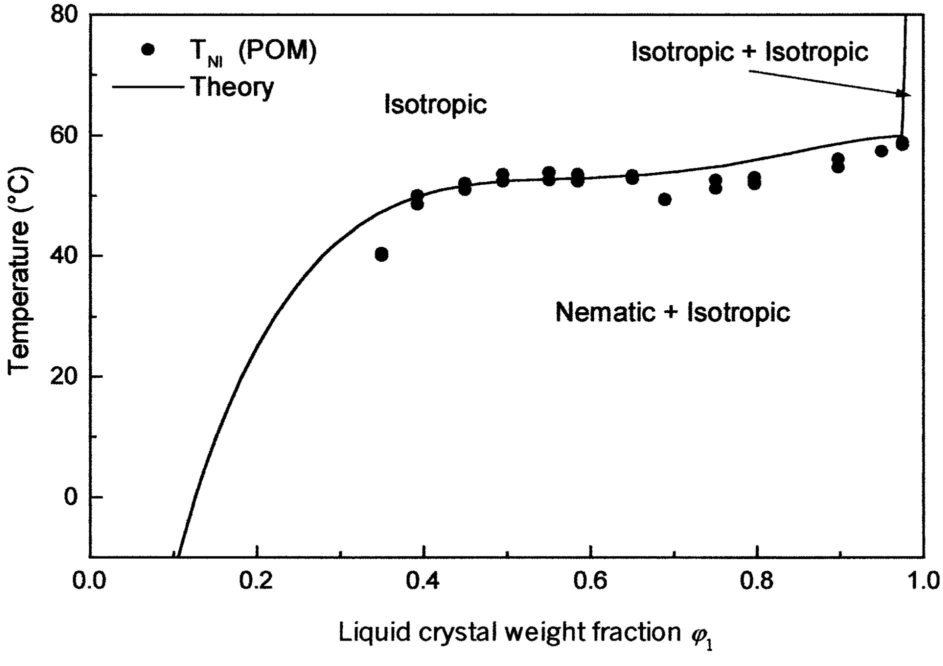
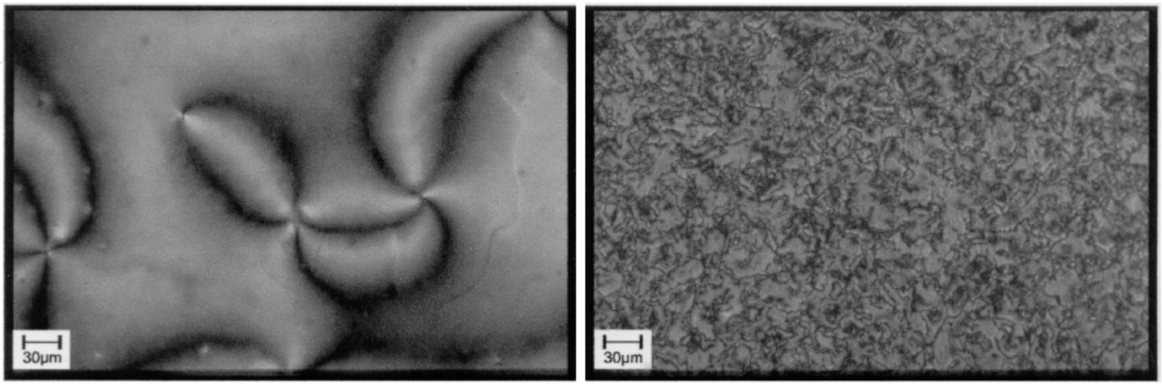


Figure 2 : Diagram as in figure 1 for the EB cured system. The model parameters employed are N_1=1, N_c=50, $\alpha = (f - 2 + 2\varphi_2)/f$; $\beta = 2\varphi_2 / f$; f represents the functionality of the monomer, f=3; χ=-0.35+348/T+0.5φ_2+0.03φ_2^2, and T_{NI}=60°C

Comparison between the diagrams of cured and uncured samples illustrates unambiguously the high miscibility of the uncured system. To see how the ordered domains look like inside the (N+I) regions, figures 3a and 3b show micrographs corresponding to the point φ_1=0.9 and T=20°C for uncured and cured systems, respectively. Figure 3a shows clearly the Schlieren texture characteristic of the nematic order but the isotropic phase is not seen. The micrograph of the cured GPTA/E7 system (figure 3b) shows clearly the two coexisting phases. The dark regions represent the isotropic phase while the bright domains represent the nematic droplets dispersed in the polymer network.

The solid line in figure 2 represents the calculated curve using the Flory-Rehner elastic free energy and the Maier-Saupe nematic free energy. The parameters α and β are chosen according to the Flory-Erman (18) model while the polymer volume fraction at crosslinking is $\varphi_r=\varphi_2$, since the polymerization/crosslinking reactions are made in situ. To fit the data, it was necessary to assume that the isotropic interaction parameter varies both with temperature and composition (19). This enables us to capture the plateau-like of the temperature versus composition curve in the intermediate composition range. N_c is a characteristic parameter of an idealized network in which one can define an average chemical length of the chain section between consecutive crosslinks. An accurate estimate of N_c is quite difficult and it is not only dependent upon the elastic free energy model used but also its value is affected by unavoidable defects in the network such as heterogenities, loops, pendant chains and entanglements. In reference (3), it was shown that for a given interaction parameter χ, increasing N_c enhances miscibility of LC in the polymer matrix and the domain of single isotropic phase on the left hand side of the diagram becomes wider. The value of N_c=50 is chosen to fit best with the data above 60°C designating the degree of compatibility of E7 and the polymer network. Note that in the case of GPTA/8CB, the properties of the elastic free energy of the polymer network are the same and in particular, experimental data above 60°C were successfully fitted with the same value N_c=50. In references (8-9) a similar theory was used to analyze the phase diagram of uncured and UV-cured NOA65/7CB systems with N_c=150.



a) **b)**

Figure 3 : Optical micrographs of films taken at φ_1=0.9 and T=20°C a) for the uncured sample showing the Schlieren texture and b) for the cured sample showing the morphology in the (N+I) phase

The diagram of the uncured system is much simpler and requires only N_2, the number of repeat units of GPTA and the variation of χ with temperature.

Conclusion

The phase behavior of EB cured and uncured GPTA/E7 mixtures is studied. The temperature/composition diagrams are established by POM supplemented by DSC and the data are analyzed either by the Flory-Huggins or the Flory-Rehner theories for the isotropic free energy and the Maier-Saupe theory of nematic order. The experimental data have been successfully analyzed within mean field theories using a reasonable choice of parameters. Both diagrams exhibit an (N+I) miscibility gap and a single isotropic region. The uncured system has enhanced miscibility and its (N+I)/I transition temperature drops suddenly when a small amount of GPTA is added to pure E7. Textures of the two systems can be unambiguously distinguished since the size of ordered domains are much larger for uncured samples.

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References

1. Doane JW (1990) Polymer Dispersed Liquid Crystal Displays. In: Bahadur B (ed) Liquid Crystals: Their Applications and Uses. World Scientific, Singapore
2. Drzaic PS (1995) Liquid Crystal Dispersions. World Scientific, Singapore
3. Benmouna F, Bedjaoui L, Maschke U, Coqueret X, Benmouna M (1998) Macromol Theory Simul 7:599
4. Benmouna, F, Coqueret X, Maschke U, Benmouna M (1998) Macromolecules 31:4879
5. Flory PJ, Rehner J (1944) J Chem Phys 12:412
6. Maier W, Saupe A (1959) Z Naturforschung 14a:882
7. Maier W, Saupe A (1960) Z Naturforschung 15a:287
8. Nwabunma D, Kyu T (1999) Macromolecules 32:664
9. Nwabunma D, Kim KJ, Chien LC, Kyu T (1998) Macromolecules 31:6806
10. Maschke U, Benmouna F, Roussel F, Daoudi A, Gyselinck F, Buisine JM, Coqueret X, Benmouna M (1999) Macromolecules: 32:8866
11. Gyselinck F, Maschke U, Traisnel A, Coqueret X (1999) Mol Cryst Liq Cryst 329:569
12. Maschke U, Traisnel A, Turgis JD, Coqueret X (1997) Mol Cryst Liq Cryst 299:371
13. Maschke U, Coqueret X, Loucheux C (1995) J Appl Polym Sci 56:1547
14. Flory PJ (1965) Principles of Polymer Chemistry. Cornell University Press, Ithaca, USA
15. Value given by Merck Ltd, GB
16. Shen C, Kyu T (1995) J Chem Phys 102:556
17. Benmouna F, Daoudi A, Roussel F, Leclercq L, Buisine JM, Coqueret X, Benmouna M, Ewen B, Maschke U (2000) Macromolecules: 33:960

18. Flory PJ, Erman B (1982) Macromolecules 15:800
19. Koningsveld R, Kleintjens LA, Shultz A (1970) J Polym Sci Part A2 8:1261