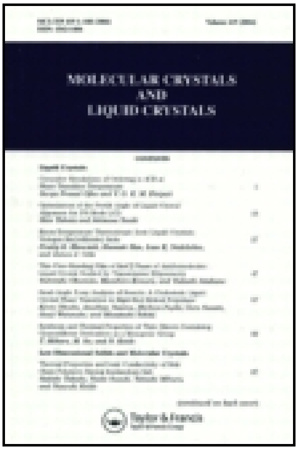

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thermo-Optical Investigations of Polysiloxane/Liquid Crystal Mixtures

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To cite this article: N. Gogibus, U. Maschke, F. Benmouna, B. Ewen, X. Coqueret & M. Benmouna (2001): Thermo-Optical Investigations of Polysiloxane/Liquid Crystal Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 675-683

To link to this article: http://dx.doi.org/10.1080/10587250108025346

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 675-683
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Gordon and Breach Science Publishers imprint,
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Printed in the USA

Thermo-Optical Investigations of Polysiloxane/Liquid Crystal Mixtures

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Thermo-optical properties of poly(dimethylsiloxane)/liquid crystal and poly(methylphenylsiloxane)/liquid crystal blends are investigated. Two low molecular weight liquid crystals are considered: 4-cyano-4′-*n*-pentyl-biphenyl or 5CB and the eutectic mixture of cyanoparaphenylene derivatives known as E7. Equilibrium phase diagrams are established by polarized optical microscopy and analyzed within mean field theories of isotropic mixing and nematic order. Effects of the methyl-phenyl substitution, the nature of liquid crystal and the polymer molecular weight on the phase diagram are discussed.

Keywords: Liquid crystal; monomer; phase diagram; Flory-Huggins; Maier-Saupe; microscopy

INTRODUCTION

Blends of polymers and low molecular weight liquid crystals (LMWLCs) consist of micron-sized droplets dispersed in a polymer matrix. They are useful in a number of applications making use of electro-optical properties[1,2]. They can be switched from opaque to translucid films by applying an electric field. The electro-optical response of these systems is tightly correlated with their thermophysical properties. The purpose of this paper is to see how the nature and molecular weight of the polymer and the nature of the LMWLC affect the phase behavior of the mixture. In particular, the loss of miscibility of the polymer/LC system is evaluated when a phenyl group is changed into a methyl group in the monomer. The miscibility also depends on the molecular weight of polymer and the nature of LC. Equilibrium phase diagrams are established by polarized optical microscopy (POM) and analyzed using a combination of the Flory-Huggins[3] theory of isotropic mixing and the Maier-Saupe[4] theory of nematic order.

EXPERIMENTAL PART

Materials

PDMS and PMPS were prepared by anionic living polymerization using n-butyllithium as initiating species and trimethylchlorosilane as end-capper. The obtained products were purified and characterized by gel permeation chromatography (GPC). The molecular weight and the degree of polydispersity (M_w/M_n) are obtained from toluene solutions at 25°C giving M_w=5500g/mol (PDMS) with M_w/M_n=1.3, M_w=45000g/mol (PDMS) with M_w/M_n=1.1, and M_w=26000g/mol with M_w/M_n=1.3 (PMPS). These polymers will be referred to as PDMS5500, PDMS45000, and PMPS26000, respectively. The LMWLC 4-cyano-4′-*n*-pentyl-biphenyl (5CB) and E7 were purchased from Merck Encolab GmbH (Germany). 5CB can be characterized by the following transition temperatures: T_{KN}=23°C, and T_{NI}=35.3°C. E7 exhibits a single nematic-isotropic transition temperature at T_{NI}=61°C.

Sample preparation

The sample preparation was made with a combination of the solvent induced phase separation (SIPS) and the thermal induced phase separation (TIPS)[1,2] methods. The polymer and the LC were dissolved in a common organic solvent THF at 55 weight-percent (wt%) for PDMS5500 and PMPS26000 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.

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 approximately 15 degrees above the transition temperature leading to the isotropic phase. The samples were left for about 15 min in the isotropic state. The subsequent thermal processes applied to the samples depend on the kinetics of reaching the thermodynamic equilibrium state. Further details on the experimental procedure and data recording can be found elsewhere[5-7]. At least two samples were prepared independently with the same composition to check reproducibility of the results.

RESULTS AND DISCUSSION

In this section, we discuss the results of POM measurements on PDMS/5CB and PDMS/E7 for the two systems with M_w=5500g/mol and 45000g/mol of PDMS. These results allow us to assess the effect of LC and polymer molecular weight on the phase diagrams. Then we discuss the results of PMPS/5CB and PMPS/E7 with M_w (PMPS)=

26000g/mol. An induced miscibility of the blend following a substitution of a methyl group into a phenyl group in the monomer is shown. Before discussing the results, we briefly present the theoretical formalism used to analyze the phase diagrams.

Theoretical formalism

The data are analyzed using a formalism starting from a free energy that is a sum of two terms. One is the Flory-Huggins[3] free energy of isotropic mixing $f^{(i)}$ and the other is the Maier-Saupe[4] free energy of nematic order $f^{(n)}$

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

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

$k_B T$ is the thermal energy, $\varphi_1=1-\varphi_2$ the volume fraction of LC, $N_1=1$ and N_2 is the number of polymer repeat units, χ is the Flory-Huggins[3] interaction parameter, Z is the nematic partition function, $v=4.54T_{NI}/T$, T_{NI} represents the nematic-isotropic transiton temperature of the pure LMWLC, s is the nematic order parameter. Both quantities s and Z depend on temperature and composition while the isotropic parameter χ is function of temperature only according to $\chi=A+B/T$ where A and B are constants. The binodal is calculated following the standard procedure[5-9] of equating the chemical potential of liquid crystal and polymer in the two coexisting phases (α) and (β) $\Delta\mu_1^{(\alpha)}=\Delta\mu_1^{(\beta)}$ and $\Delta\mu_2^{(\alpha)}=\Delta\mu_2^{(\beta)}$ with $\Delta\mu_1=\left(\partial \Delta F/\partial n_1\right)_{T,n_2}$, ΔF being the total free energy of the blend, n_1 the number of LC molecules, n_2 the number of polymer molecules. The spinodal curve is plotted by solving the equation $\partial^2 f/\partial\varphi_2^2 = 0$ while the critical point is obtained by solving the set of equations $\partial^2 f/\partial\varphi_2^2 = 0$ and $\partial^3 f/\partial\varphi_2^3 = 0$. These calculations lead to the phase diagrams represented in the figures below where solid lines are binodals and dashed lines are spinodals.

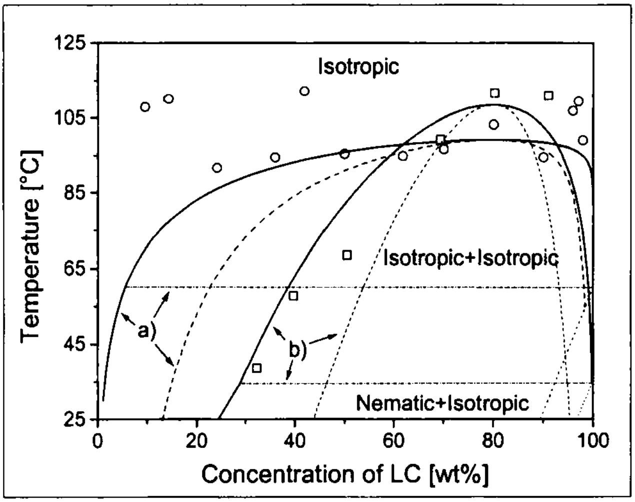

FIGURE 1 The phase diagram of PDMS with M_w=5500g/mol and E7 (a) or 5CB (b). The symbols represent POM data. The solid (binodal) and dashed (spinodal) curves are calculated using $N_1=1$, $N_2=16$ and for E7, $\chi=-11.63+4619/T$; $T_{NI}=61$°C and for 5CB $\chi=-0.7+565/T$; $T_{NI}=35.3$°C.

PDMS/LC blends

Figure 1 shows the (T,φ_1) phase diagram of PDMS5500/5CB and PDMS5500/E7[5,6]. A substantial loss of miscibility of PDMS in E7 is obtained as compared to 5CB. The critical point is approximately the same in both diagrams since they correspond to the same polymer. Away from this point however, the miscibility is different. For example, the solubility limit of 5CB at 25°C is nearly 25wt% but less than 2wt% for E7. Hence, the nature of the low molecular weight LC has an important impact on the miscibility of the PDMS/LC systems. On the other hand, investigation of PDMS45000/E7 and PDMS45000/5CB systems allows us to give an estimate of the miscibility loss for a relatively high polymer molecular weight but Figure 2 shows that only a small difference is found between the two systems corresponding to E7 and 5CB. For example, at 25°C the solubility limit of PDMS45000 in both E7 and 5CB is few percents. A slight miscibility enhancement in 5CB is seen instead of a factor 10 obtained previously in the case of

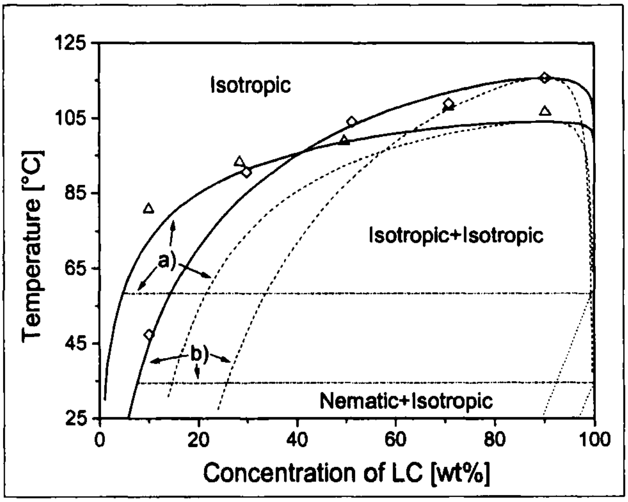

FIGURE 2 The same as in Figure 1 with M_w=45000 and N_2=80. For E7 χ=-11.63+4619/T (a), and for 5CB χ=-4.4+1950/T (b) For high M_w the nature of LC is not very important.

M_w=5500g/mol. Hence, if the polymer molecular weight is high, the choice of LC is irrelevent and has a little impact on the equilibrium phase diagram.

PMPS/LC blends

Figure 3 shows the phase diagrams of PMPS/5CB and PMPS/E7 with M_w(PMPS)=26000g/mol that is intermediate between the molecular weights of PDMS considered before[5,6]. One observes that the miscibility of PMPS in E7 is much lower than in 5CB. At room temperature, the limit of solubility of E7 in PMPS is about 10wt%

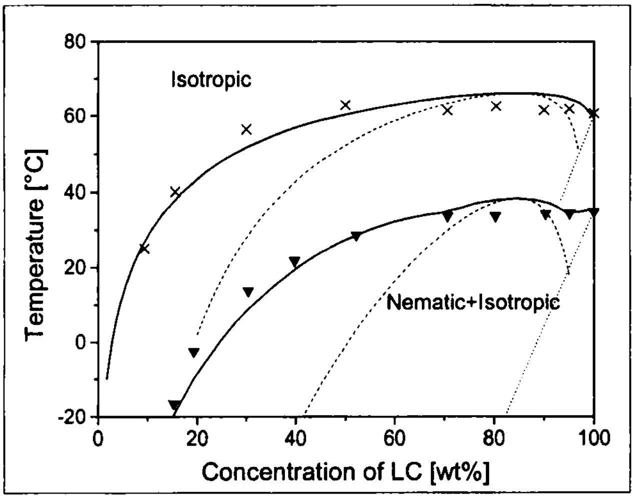

FIGURE 3 Phase diagrams of PMPS/E7 (upper curves) and PMPS/5CB (lower curves) with M_w of PMPS=26000g/mol. The theoretical curves are calculated using $N_1=1$; $N_2=30$; for E7 : T_{NI}(E7)=61°C; $\chi=-7.23+2618/T$ (upper diagram), and for 5CB T_{NI}=35.3°C; $\chi=-1.6+713/T$ (lower diagram). The nature of LC is important in mixtures involving PMPS.

while that of 5CB is 40wt%. At 40°C, the solubility of E7 is less than 20wt% while 5CB is soluble in PMPS at any composition. Note that PMPS and PDMS differ via a methyl/phenyl group substitution and it is interesting to compare the phase diagrams of these two systems and to see the changes in the solubility of LC as a result of this substitution.

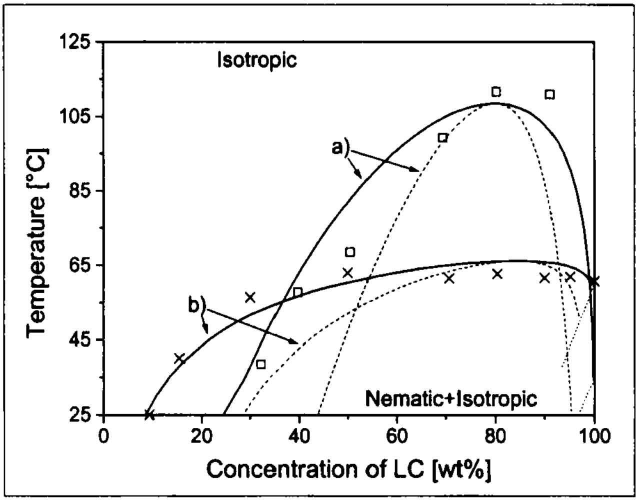

FIGURE 4 Phase diagrams of a) PDMS5500/5CB and b) PMPS26000/E7. The theoretical curves are obtained using the same parameters as in the previous figures.

Comparing Figures 1 and 3 shows that the miscibility of 5CB is much higher in PMPS than in PDMS even with M_w(PDMS)=5500g/mol. Interestingly, Figure 4 shows that the phase diagrams of PMPS26000/E7 and PDMS5500/5CB are different in the whole (T, φ_l) frame. Below 50°C, PMPS is only slightly miscible in E7 while above 50°C, an inversion takes place whereby the miscibility of PMPS in E7 is much higher than PDMS5500 in 5CB.

CONCLUSIONS

The phase diagrams studied here call for at least three remarks. 1) Miscibility of PDMS/E7 is not very sensitive to M_w of the polymer. 2) Miscibility of PDMS/5CB is significantly reduced when M_w of PDMS increases. 3) Miscibility is significantly enhanced for PMPS in both liquid crystals as compared to PDMS, namely when a methyl is changed into a phenyl group.

Acknowledgements
N. Gogibus thanks Professor H. W. Spiess for his interest in this work and the Max-Planck-Institut für Polymerforschung for financial support.

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