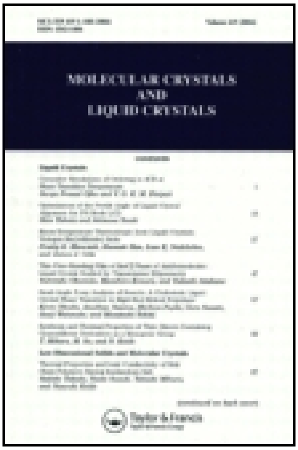

Molecular Crystals and Liquid Crystals

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Phase Diagrams and Thermophysical Properties of Polysiloxane and E7 Systems

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PHASE DIAGRAMS AND THERMOPHYSICAL PROPERTIES OF POLYSILOXANE AND E7 SYSTEMS

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Phase diagrams of various polysiloxanes and the eutectic liquid cristalline mixture of cyanoparaphenylenes E7 are established. Thermophysical properties are investigated considering the case of Poly(dimethylsiloxane) and Poly(methylphenylsiloxane) with different molecular weights. Differential Scanning Calorimetry and Polarized Optical Microscopy are used to construct the phase diagrams and obtain thermophysical data that are rationalized using a combination of the Flory-Huggins theory of isotropic mixing and the Maier-Saupe theory of nematic order. The glass transition temperature versus composition of the blends investigated yields information of the plasticising effect of the small liquid crystal molecules.

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INTRODUCTION

Polymer Dispersed Liquid Crystals are composite materials made of polymers and low molecular weight liquid crystals (LMWLCs). They consist generally of micron-sized droplets dispersed in a solid polymer matrix and are used in a number of applications using their special electro-optical behaviour [1,2]. This behaviour is directly related to thermo-physical properties and miscibility parameters. In a search for the best systems in terms of electro-optic performance, mechanical strength, ageing, availability and cost, we performed a systematic study using a variety of molecular species and experimental techniques. The present contribution is an effort along these lines aiming at the investigation of the effects of the chemical nature of compounds and molecular weight of polymer on thermophysical properties. Several systems are considered involving 2 polysiloxanes and the eutectic mixture of cyanoparaphenylenes E7. The polymers are linear poly(dimethylsiloxane) (PDMS) and poly(methylphenylsiloxane) (PMPS) characterized by different molecular weights. Equilibrium phase diagrams are established by Polarized Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC) and analyzed theoretically 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 for PDMS $M_w = 45000\,\text{g/mol}$ with $M_w/M_n = 1.1$, and for PMPS $M_w = 60000\,\text{g/mol}$ with $M_w/M_n = 1.3$. These polymers will be referred to as PDMS45000 and PMPS60000, respectively. The LC E7 was purchased from Merck Eurolab (Germany). It exhibits a single nematic-isotropic transition temperature at $T_{NI} = 61°\text{C}$.

Sample Preparation

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

PMPS60000 and 70 wt.-% 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.

Polarized Optical Microscopy (POM)

The thermo-optical studies were performed on a POM ZEISS equipped with a Linkham heating/cooling stage and a 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.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed on a Mettler 30 calorimeter equipped with a liquid nitrogen system allowing cooling experiments. A rate of 2°C/min (heating and cooling) was used in the temperature range −170 to +150°C. The program consists first in cooling the sample followed by two heating and cooling cycles as indicated in Figure 1. Data analysis was carried out on the first heating ramp. The peaks of the clearing points were used to determine the nematic-isotropic transition temperature. Further details on the experimental procedure and data recording for POM and DSC techniques can be found elsewhere [5–7]. Protocoles of

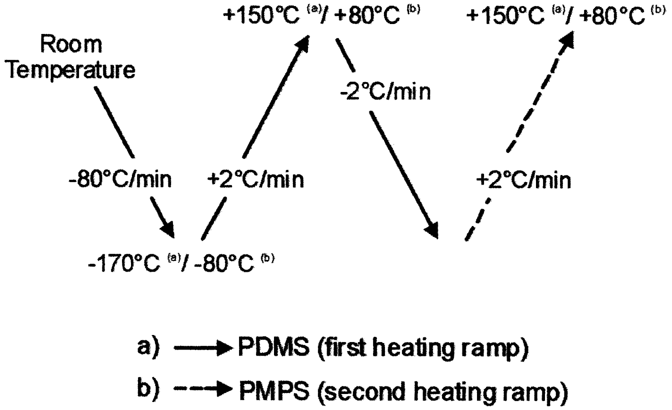

FIGURE 1 Thermal treatment adopted to obtain DSC thermograms.

the thermal treatments for POM and DSC are roughly the same (see illustration in Figure 1). In each case, at least two duplicate samples were used independently to check the reproducibility of results.

RESULTS AND DISCUSSION

Figure 2a and 2b give thermograms for PDMS/E7 and PMPS/E7 systems, respectively. These spectra cover the whole range of composition from bulk polymer to pure LC by increments of 20 wt.-%. They show the characteristic transitions and their changes with the blend composition. In particular a drop in the polymer glass transition is clearly seen in Figure 2b as the concentration of small liquid crystal molecules acting as a plasticiser increases. The other observation concerns the variation of nematic → isotropic transition temperature with the polymer concentration. For the PDMS system, this transition takes place at a constant temperature (i.e., 61°C) indicating that the LC phase in the droplets is pure E7. However, in the case of PMPS/E7, an anomalous phenomenon emerges in the sense that the temperature at which the nematic → isotropic transition takes place increases sensitively when polymer is added to bulk LC. This is not expected and a tentative explanation invokes preferential solvation of some constituants of E7 towards the polysiloxanes. This effect was already observed in poly(n-butylacrylate)/E7 system [8]. In order to illustrate this phenomenon, we plot in Figure 3a an amplification of the phase diagram near the bulk liquid crystal point. This amplification shows clearly the anomalous increase of T_{NI} in the PMPS/E7 system with increasing polymer concentration. In the case of PDMS/E7 blend, the expected behavior whereby T_{NI} remains equal to T_{NI} for the bulk liquid crystal is found. This is so even in the presence of a significant amount of polymer. The entire phase diagram is shown in Figure 3b where we include the results for 45000 PDMS/E7 system for completeness. These data are obtained by POM while those of Figure 3a were extracted from DSC thermograms. The consistency of these 2 sets of data is rather gratifying. In addition to confirming the DSC results, the latter figure carries another message telling us that even though the molar mass of PMPS is much higher, its compatibility with the LC E7 is larger than that of PDMS.

The curves in Figure 3b are obtained from theoretical calculations based on a model that combines the Flory-Huggins theory of isotropic mixing and Maier-Saupe theory of nematic order [9]. The solid lines are binodals whereas dashed lines are spinodals. The calculations are made according to the standard procedure of chemical potentials equalities in coexisting phases. Other investigations were reported in the literature addressing a variety of questions [10–15]. The models used were more or less different

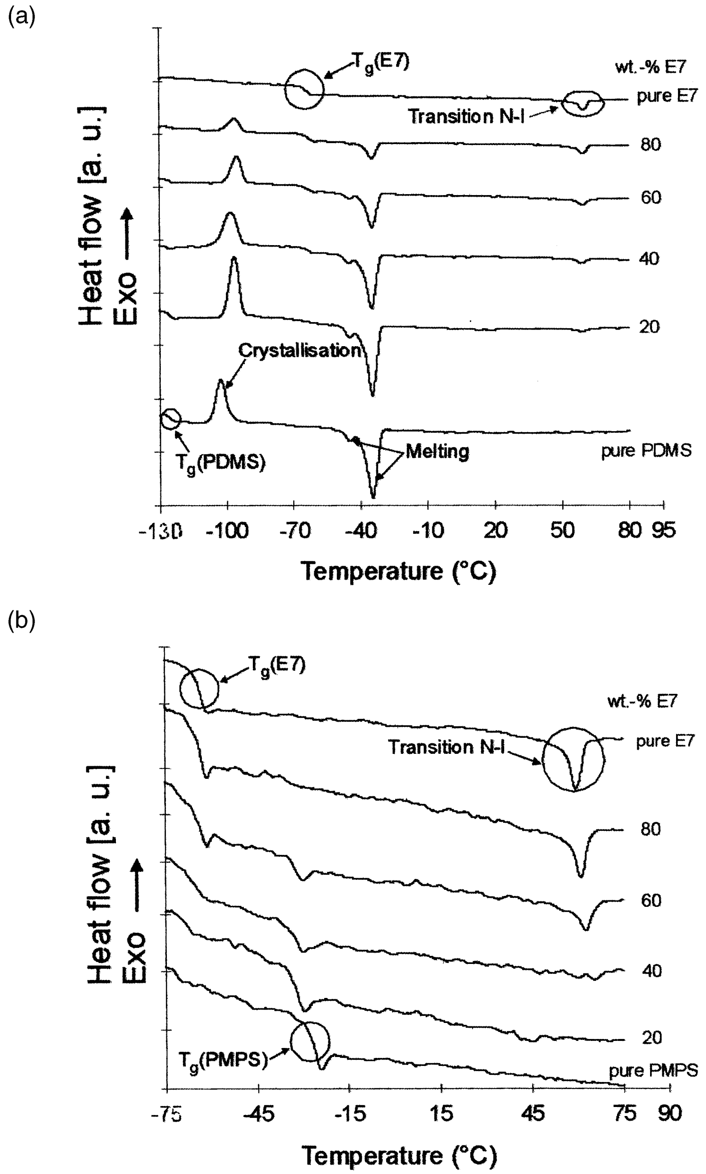

FIGURE 2 a) DSC thermograms of PDMS45000/E7 systems at different compositions. b) DSC thermograms of PMPS60000/E7 systems at different compositions. All the transitions are identified in this figure.

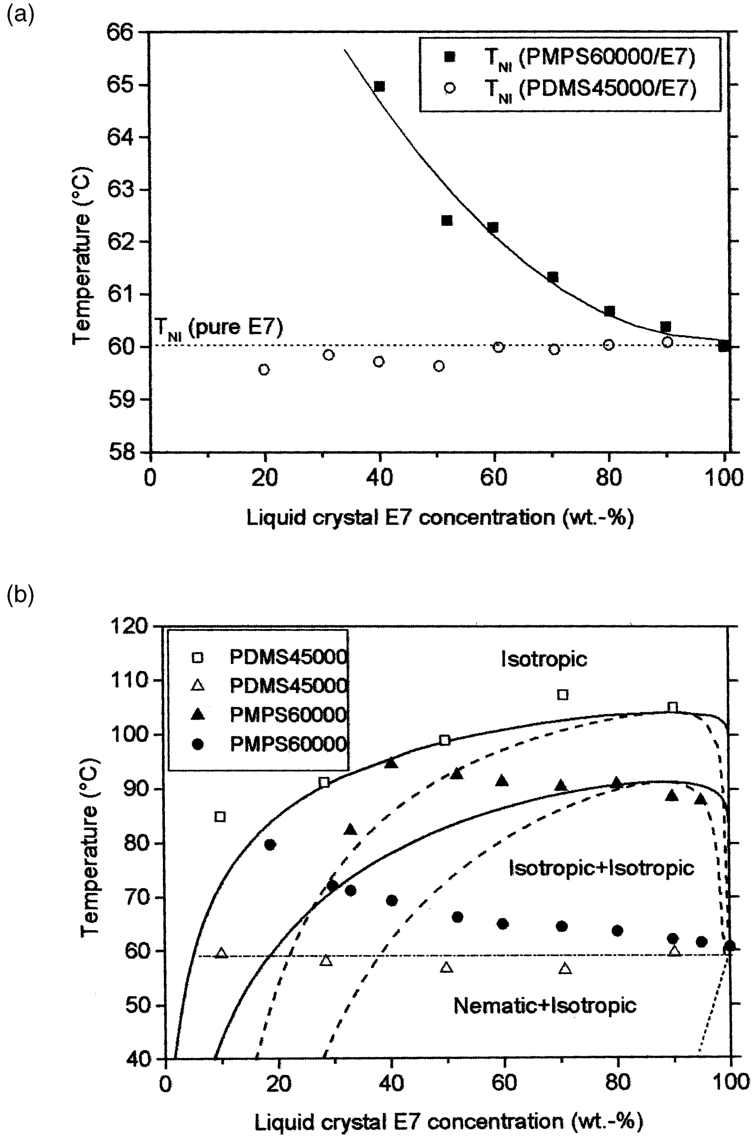

FIGURE 3 a) DSC data showing an amplified view of the phase diagram near bulk E7 point for both PDMS45000/E7 and PMPS60000/E7 systems. b) The phase diagrams of PDMS45000/E7 and PMPS60000/E7 systems as obtained from POM observations.

depending on the points under focus. Obviously the anomalous increase of T_{NI} when polymer is added to LC cannot be accounted for by these simple theories unless one includes the preferential solvation aspect into the picture.

CONCLUSIONS

Variations of the nematic → isotropic and glass transition temperatures for PDMS/E7 and PMPS/E7 systems are investigated using POM and DSC measurements. Both techniques give consistent results showing a peculiar behaviour of the nematic → isotropic transition in the case of PMPS/E7 system. The observed nematic → isotropic transition at a temperature above 61°C is attributed to a preferential solvation phenomenon emerging in the PMPS. Such pecularities are not found in the present PDMS/E7 system. Another finding here is that changes of methyl groups into phenyl groups in the monomer siloxane leads to a significant miscibility enhancement.

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