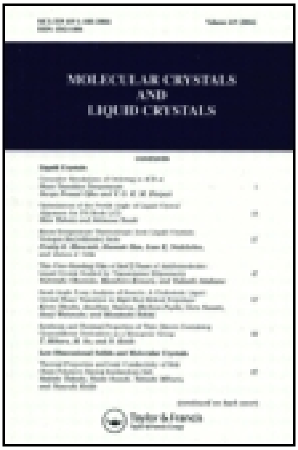

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POLYMER DISPERSED LIQUID CRYSTALS MADE OF DEUTERIATED POLYSTYRENE AND 8CB BLENDS: A SMALL ANGLE NEUTRON SCATTERING STUDY

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Structural properties of Polymer Dispersed Liquid Crystals made of mixtures of deuteriated polystyrene (dPS) and 4-cyano-4′-n-octylbiphenyl (8CB) are studied by Small Angle Neutron Scattering (SANS). Two distinct blends are considered with a polymer dPS molar mass M_w equal to 49500 g/mol and liquid crystal concentration 60 and 75 weight% (wt.-%). Data covering the range

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of temperature from 30°C to 75°C are discussed. In this temperature domain, 8CB exhibits a variety of orderings such as smectic-A (21.5°C–33.5°C), nematic (33.5°C–40.5°C) or simply an isotropic state above 40.5°C. The results are rationalized in terms of the Random Phase Approximation (RPA) invoking the temperature dependence of the Flory-Huggins interaction parameter and the correlation length of fluctuations at the interface of polymer and liquid crystal.

Keywords: liquid crystal; neutron scattering; phase behavior; polymer

INTRODUCTION

Structural and phase properties of Polymer Dispersed Liquid Crystals are accessible by the Small Angle Neutron Scattering (SANS) technique. This technique is powerful in probing the conformation of chains in such systems in terms of temperature and composition [1–7]. It gives a high contrast of the coherent signal via deuterium labelling, contrast that leads to a coherent signal orders of magnitude larger than the incoherent component. By deuterium labelling the polymer, one is able to explore long range composition fluctuations and changes of chain conformation with temperature [8,9]. Application of neutron scattering to polymer blends takes a particular advantage of the recent advances in modelling using analytical calculations and computer simulations [10–12]. For example, de Gennes [13] Random Phase Approximation (RPA) can be used to extract the Flory-Huggins [14] interaction parameter χ_{AB} describing the extend of miscibility of polymer and LC. In the zero angle of scattering limit, one can relate the RPA result to the free energy in the Flory-Huggins model f_{FH} as follows [1,13,14]

$$S^{-1}(q=0) = \frac{\partial^2 f_{FH}}{k_B T \partial^2 \varphi_B^2} = \frac{1}{N_A \varphi_A} + \frac{1}{N_B \varphi_B} - 2\chi_{AB} \tag{1}$$

where the subscripts FH, A and B refer to Flory-Huggins, LC, and polymer, respectively; k_B is the Boltzmann constant and T is the absolute temperature. The letter q represents the amplitude of the scattering wave vector and $S(q=0)$ is the zero q limit of the structure factor; N_A and N_B are the numbers of repeat units of the LC and the polymer while ϕ_A and ϕ_B represent their volume fractions. Following the standard procedure, one obtains the inverse structure factor at finite scattering angle

$$S^{-1}(q) = \frac{1}{N_A \varphi_A} + \frac{1}{N_B \varphi_B} - 2\chi_{AB} + q^2 \xi^2 \tag{2}$$

This result provides a direct connection between the thermodynamic properties at $q = 0$ given by the first 3 terms on the right hand side and the structural properties at finite q.

Recently we reported a detailed study of the phase diagram of blends made PS and 8CB [6,7] in the temperature, composition frame. Various systems characterized by different polymer (PS) molar masses were examined using polarized optical microscopy (POM), differential scanning calorimetry (DSC) and light scattering. Data were rationalized in terms of a combination of the Flory-Huggins [14] theory of isotropic mixing and the Maier-Saupe-McMillan [15–17] theory of nematic and smectic-A order. In view of the encouraging results obtained from the thermophysical study and the consistency observed between data and theoretical formalism, we report here the results of an investigation of the structural properties by performing SANS measurements of PDLC films made of deuteriated polystyrene (dPS) and 8CB mixtures. A deuterated sample of PS with molar mass $M_w = 49500\,g/mol$ is used with LC concentrations 60 and 75 wt%. The scattering intensity is measured as a function of the amplitude of the wave vector q in a wide range of temperature T.

EXPERIMENTAL PART

Materials and Sample Preparation

Deuterated PS (dPS) has been prepared using a standard procedure. The molar mass and its distribution were obtained as $M_w = 49500\,g/mol$ and $M_w/M_n = 1.07$ (GPC measurements in tetrahydrofuran at room temperature, calibrated with standard PS samples). The LC 4-cyano-4′-*n*-octyl-biphenyl or 8CB has been obtained from Frinton Laboratories (New Jersey, USA). It shows crystalline (K), smectic-A (S), nematic (N), and isotropic (I) phases with transition temperatures given in the same order by $T_{KS} = 21.5°C$, $T_{SN} = 33.5°C$, and $T_{NI} = 40.5°C$.

Mixtures of PS and 8CB with 60 and 75 wt% LC were heated slowly from room temperature to roughly 15 degrees above the transition temperature leading to the isotropic phase. The homogeneous samples were left approximately 5 min in the isotropic state and then transferred to sample holders specially constructed for SANS experiments while the temperature was kept constant. Afterwards, samples were cooled down allowing phase separation to take place.

Small Angle Neutron Scattering

The SANS data were taken using PAXY instrument of the Laboratoire Léon Brillouin (CEA-CNRS) in Saclay. The scattered beam was collected on a plane of the two-dimensional detector using the wavelength $\lambda = 8\,Å$ and the detector–sample distance R was set at 6 m to reach the small angle range. Data were normalized and the incoherent background substracted.

The scattered intensity $I(q)$ is proportional to the number of neutrons reaching the detector surface A per unit time at a distance R from the sample. Letting $\Delta\Omega$ the solid angle, $\mathrm{d}\sigma/\mathrm{d}\Omega$ the differential scattering cross section and ϕ the incident neutron flux (expressed in $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$) of wavelength λ yields [1,2,18]

$$I(q) = \phi \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} \Delta\Omega \tag{3}$$

where $\Delta\Omega = \sigma/R^2$. The $\mathrm{d}\sigma/\mathrm{d}\Omega$ has a unit of a surface and is proportional to the structure factor $S(q)$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \left(a - b\frac{v_A}{v_0}\right)^2 S(q) \tag{4}$$

where a is the coherent scattering length of 8CB, b is the coherent scattering length of dPS, and v_0 is a reference volume.The partial molar volume of the LC v_A can be related to its volume fraction ϕ_A and its molar concentration c_A via $\phi_A = c_A\, v_A$.

RESULTS AND DISCUSSION

In order to see whether deuteration of polymer influences its miscibility with 8CB, we established its phase diagram and indeed found similar results with a small shift upward of the transition temperature not exceeding a couple of degrees. The measurements were made for systems with 60 and 75 wt.-% LC in a temperature range covering regions where the LC exhibits the orderings indicated earlier. Typical results are shown in Figure 1 where the scattered intensity is represented in terms of the wave vector $q = (4\pi/\lambda)\ \sin(\theta/2)$, θ being the scattering angle and λ the wavelength of the neutron incident beam. In this figure, we collected the results for the 2 systems with LC concentration 60 wt.-% (empty symbols) and 75 wt.-% (filled symbols) to allow a direct comparison. For the sake of clarity, we give the curves corresponding to 4 temperatures only spanning the range between 30 and 70°C. It is worthwhile to recall that the phase diagram established independently reveal that between 30 and 33.5°C, a swollen isotropic polymer phase coexists with a pure LC phase in the smectic-A order while in the range between 33.5 and 40.5, the LC in droplets exhibits a nematic order. As the system is heated up to 50°C, one observes 2 coexisting isotropic phases with different compositions and degrees of swelling by the low molecular weight LC acting as a solvent. Above 50°C, the system shows a single homogeneous isotropic phase [6].

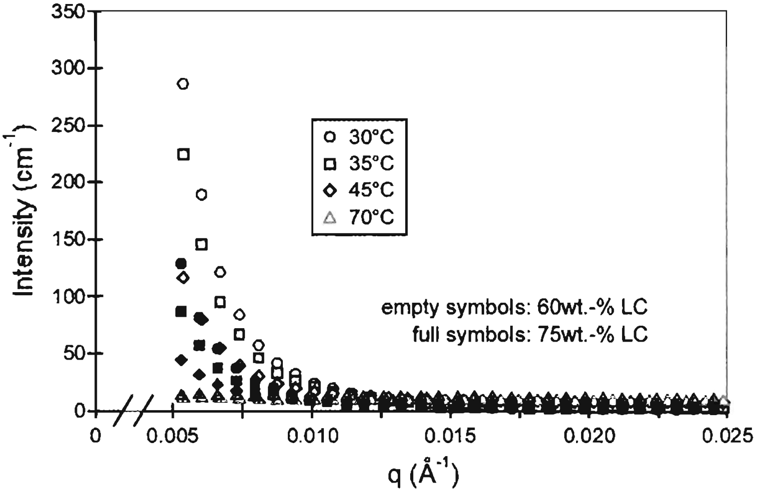

FIGURE 1 The SANS data representing $I(q)$ versus q for the two systems corresponding to 60 wt.-% (empty symbols) and 75 wt.-% 8CB (filled symbols). The temperatures are indicated on the figure.

Figure 1 illustrates how the scattering intensity changes with composition and temperature. Both the value of the scattering intensity near $q = 0$ and the shape of the curve $I(q)$ versus q are modified. Since the contrast is due to the difference in the coherent scattering lengths of dPS and 8CB, the neutron beam effectively probes the polymer/LC interface. One sees that the scattering curves shift downward with increasing LC concentration and temperature. These results are consistent with the prediction of Eq. (2). First one expects that the Flory-Huggins interaction parameter increases with decreasing temperature which is what we observe. On the other hand, as the system is diluted with a higher amount of low molecular weight LC, the range of composition fluctuations described by the correlation length ξ increases meaning that $I(q)$ drops down at a given q. Typically ξ has values near few nm or higher depending on the temperature.

Another representation of these results is displayed in Figures 2a and 2b where the inverse intensity $I^{-1}(q)$ is plotted versus q^2 for 60 and 75 wt.-% 8CB, respectively. Here, we limited ourselves to a temperature domain where the LC is isotropic acting as a solvent with varying degree of compatibility towards the high molecular weight polymer. In both figures, the slope of I^{-1} vs q^2 increases slightly with decreasing temperature. This results from a drop in the solvent quality as the temperature decreases. Furthermore, the intercept with the y-axis decreases significantly following

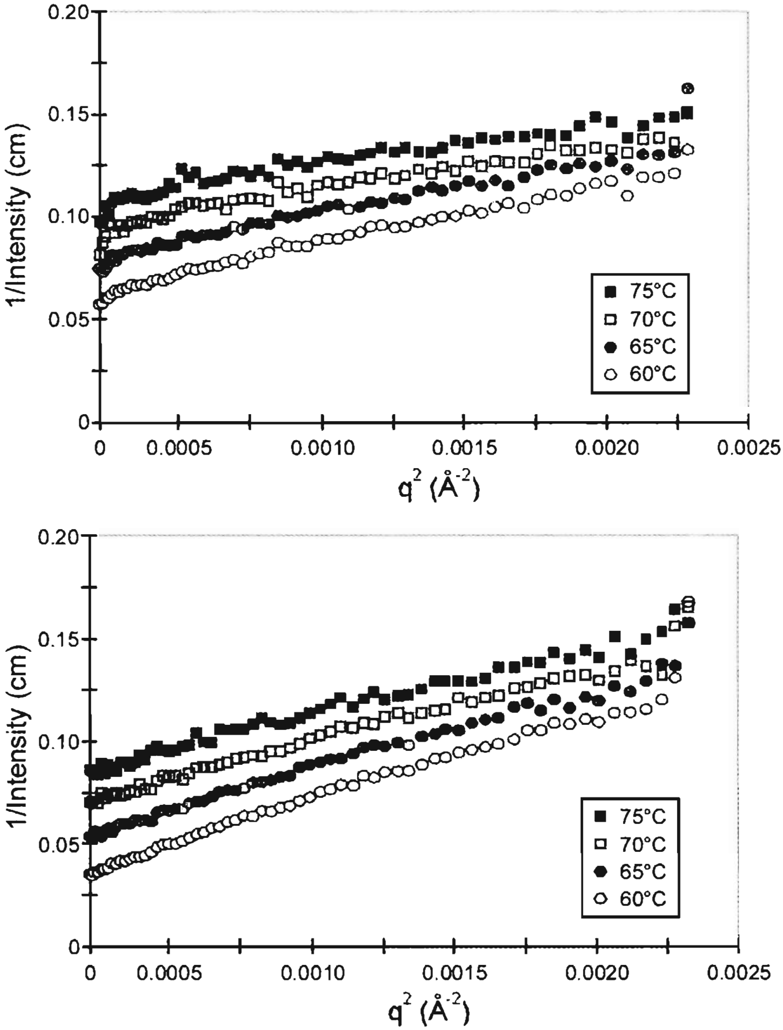

FIGURE 2 $I^{-1}(q)$ versus q^2 for the system with a) 60 wt.-% 8CB (above) and b) 75 wt.-% 8CB (below) for several temperatures as indicated on the figure.

a cooling down of the system since χ_{AB} increases. This behavior is predicted by Eq. (2). Comparing Figures 2a and 2b confirms the observation made above concerning the effects of LC concentration. A close analysis of data in a wider range of temperature and in the immediate vicinity of $q = 0$ reveals other aspects such as polymer chain swelling upon heating the system. At small q's, the inverse intensity I^{-1} versus q^2 shows a curvature following a substantial increase of intensity near zero angle that could be due to the incoming beam but quickly (above 10^{-2} Å^{-1}) the curves level off showing the trends of Figures 2a and b. Some data scattering is observed up to 40°C but the trends of linear increase I^{-1} versus q^2 is clear. Additional SANS experiments are under way to explore other compositions in the temperature, composition frame of the phase diagram of the dPS/8CB system. The results will be reported in the near future.

CONCLUSIONS

Structural properties of dPS/8CB mixtures are explored in a wide range of temperature for two LC concentrations. Data are consistent with simple predictions of the RPA model for polymer blends. The scattered intensity decreases with temperature and dilution with the low molecular weight LC. Upon heating the system, the Flory-Huggins interaction parameter χ_{AB} drops and the scattered intensity $I(q)$ decreases especially in the vicinity of $q = 0$. The correlation length of composition fluctuations is inferred from the slope of $I^{-1}(q)$ versus q^2 curves. This slope decreases slightly upon heating consistent with an expected miscibility enhancement and a decrease in the interaction parameter. More importantly, the intercept of the curves representing I^{-1}(q) vs q^2 with the y-axis decreases upon cooling as a result of an increase in χ_{AB}.

This investigation shows that the SANS technique provides a unique tool to get access to precise structural properties of systems such as the PDLC compound investigated here. It could be very useful to pursue this effort and cover a wider range in the temperature versus composition frame of the phase diagram of the PS/8CB system.

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