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Small angle neutron scattering data for a mixture of deuterated polystyrene (dPS) and 4-cyano-4′-*n*-octylbiphenyl (8CB) are reported. The molecular weight of dPS is 49500 g/mol and the composition of the investigated system is 75weight% (wt%) 8CB and 25wt% dPS. Scattering data are taken in the range of temperature from 25°C to 75°C in which pure 8CB exhibits a smectic-A order (21.5°C-33.5°C), a nematic order (33.5°C-40.5°C) and is isotropic above 40.5°C. Variations of the scattered intensity as a function of temperature and wave vector are discussed.

Keywords: Polymer; liquid crystal; neutron scattering; phase behavior; forward intensity; chain swelling

INTRODUCTION

Recently, we reported a study of thermo-physical properties of linear polystyrene (PS) and 4-cyano-4'-*n*-octyl-biphenyl (8CB) mixtures[1]. Phase diagrams of three systems with different molecular weights of PS

were established by different techniques and analyzed using a combination of the Flory-Huggins[2] theory of isotropic mixing and the Maier-Saupe-McMillan[3-5] theory of nematic and smectic-A order. Here, we report on small angle neutron scattering (SANS) measurements on a similar system using the liquid crystal (LC) 8CB and a deuterated PS (dPS) with a molecular weight M_w=49500g/mol. A fixed composition was chosen (i.e. 75weight(wt)% 8CB and 25wt% dPS) and the scattered intensity was analyzed as a function of wave vector q and temperature T. To the best of our knowledge, SANS studies reported so far in the literature focus more on polymers with side chain liquid crystal groups[6-8] and only few systems similar to dPS/8CB were considered before[9,10].

EXPERIMENTAL PART

Materials and sample preparation

Deuterated PS (dPS) was prepared using a standard procedure. The molecular weight and the molecular weight distribution were obtained as M_w=49500g/mol and M_w/M_n=1.07 (GPC measurements in tetrahydrofuran at room temperature, calibrated with PS samples). The LC 4-cyano-4'-*n*-octyl-biphenyl or 8CB was obtained from Frinton Laboratories (New Jersey, USA) exhibiting crystalline, smectic-A, nematic, and isotropic phases (T_{KS}=21.5°C, T_{SN}=33.5°C, T_{NI}=40.5°C).

Small angle neutron scattering

The small angle neutron scattering experiments were performed at the 2-dimensional PAXY instrument of the Laboratoire Léon Brillouin of the CEA-CNRS at Saclay. The scattered beam was collected on a plane of the two-dimensional detector using a wavelength λ=8Å and a

multidetector–sample distance of 6m in order to cover the small angle range. The data were normalized and the backgrounds removed. The samples were aligned in situ with a magnetic field of 1T oriented in the horizontal direction and perpendicular to the incident beam.

In a SANS experiment, the intensity $I(q)$ is proportional to the number of neutrons impinging on the detector surface A per unit time at a distance R from the sample. If ϕ is the incident neutron flux of wavelength λ (flux expressed in $cm^{-2}s^{-1}$), letting $\Delta\Omega$ the solid angle and $d\sigma/d\Omega$ the differential scattering cross section, one has[7,8,11,12]

$$I(q)=\phi\frac{d\sigma}{d\Omega}\Delta\Omega \tag{5}$$

where $\Delta\Omega=A/R^2$. The differential scattering cross section $d\sigma/d\Omega$ has a unit of a surface and is proportional to the scattering structure factor $S(q)$. After having subtracted the incoherent background, the coherent differential scattering cross section $d\sigma/d\Omega$ is proportional to $S(q)$ within a contrast factor

$$\frac{d\sigma}{d\Omega}\propto\left(a-b\frac{v_A}{v_0}\right)^2 S(q) \tag{6}$$

where a is the coherent scattering length of 8CB, b is the coherent scattering length of dPS, v_A is the partial molar volume of 8CB and v_0 a reference volume.

RESULTS AND DISCUSSION

Before performing the SANS measurements, the phase behavior of the present system was explored to check if the deuteration of PS introduces any change in its miscibility with 8CB as compared to the analogous PS/8CB considered before[1]. The phase behavior of the

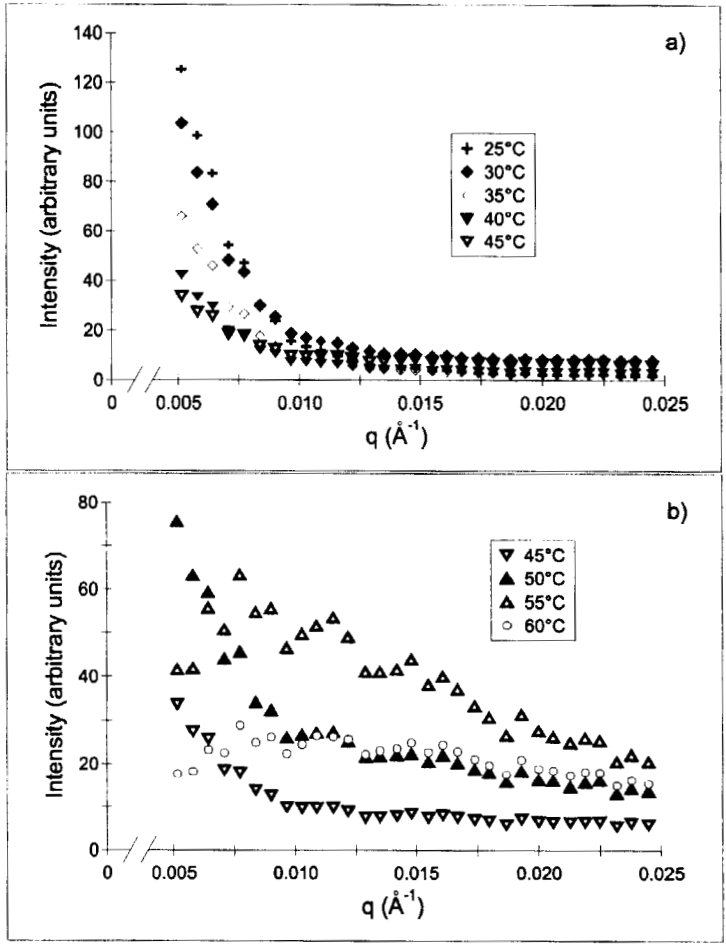

FIGURE 1 The SANS data representing $I(q)$ versus q of 25 wt%dPS (M_w=49500g/mol)/75wt%8CB system. a) The symbols correspond to data taken at different temperatures in the range from 25°C to 45°C; b) The same as above in the range of temperatures from 45°C to 60°C.

PS/8CB mixture with a PS molecular weight M_w=44000g/mol is practically the same as the system studied in the present work. Only a

small shift upward of the transition temperature not exceeding few degrees was observed. Briefly, the phase behavior of the present system can be summarized as follows. Between 25°C and 33.5°C, it exhibits an

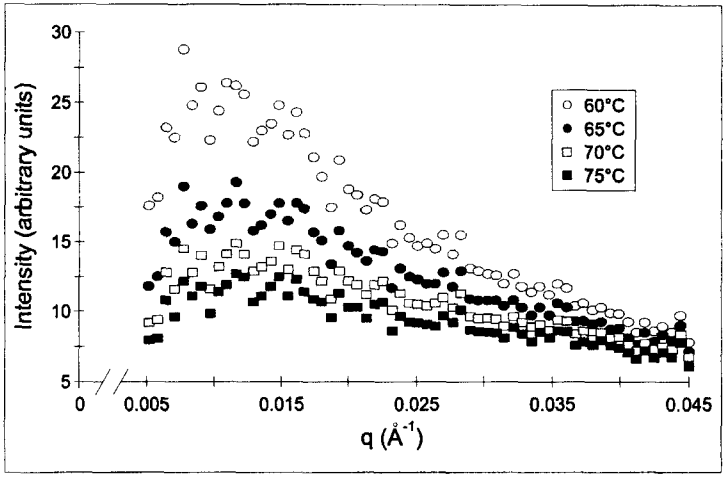

FIGURE 1 c) The same representation as above in the range of temperatures from 60°C to 75°C.

isotropic phase with a collapsed polymer coexisting with a smectic-A pure 8CB phase. Between 33.5°C and 40.5°C, a swollen isotropic polymer rich phase coexists with a pure nematic 8CB phase. As the temperature is raised from 40°C to slightly above 50°C, the system exhibits two coexisting isotropic phases where the polymer rich phase is swollen by an isotropic LC. Above 50°C, the system presents a single isotropic phase. The SANS data lead to different structural properties in these ranges of temperature. Both the amplitude of the scattered intensity near q=0 and the slope of I^{-1} versus q^2 were examined as a function of T. Figure 1a shows the scattering curves $I(q)$ versus q in the range of temperature (25 - 45°C) showing a shift downward of the

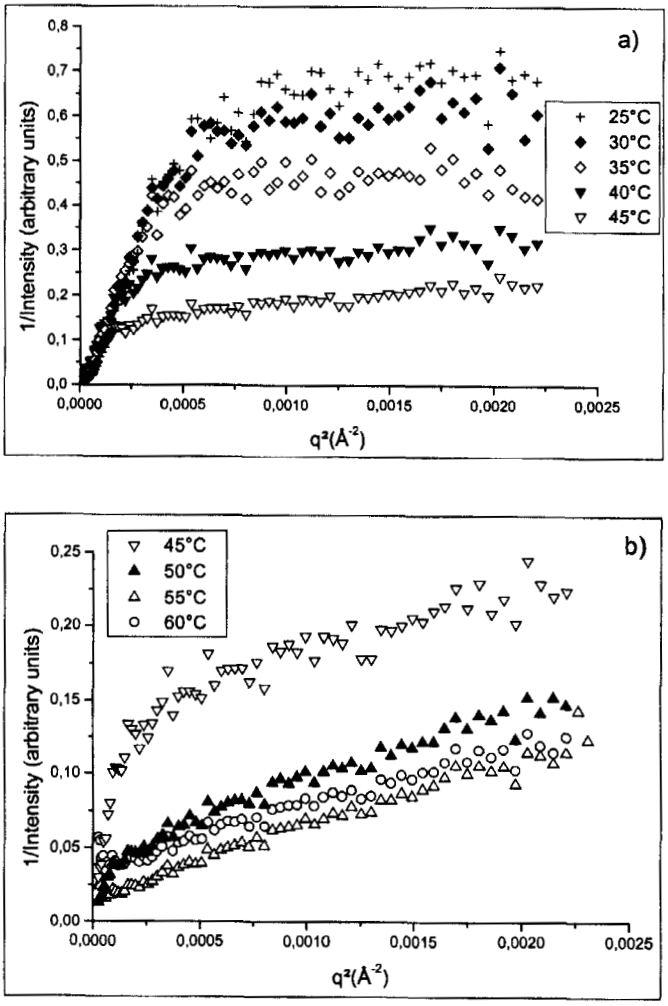

FIGURE 2 a) The SANS data of Figure 1a represented in the form of $I^{-1}(q)$ versus q^2. b) The same as Figure 1b in the form of $I^{-1}(q)$ versus q^2

the scattering curves with temperature. This may be explained by noting

that the Flory-Huggins interaction parameter decreases with increasing temperature. Figure 1b shows a reversed tendency of the scattering

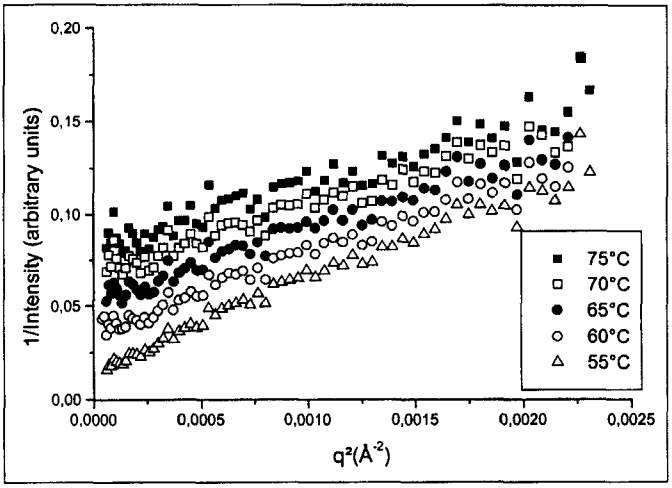

FIGURE 2 c) The same as Figure 1c in the form of $I^{-1}(q)$ versus q^2.

curves upon further heating from 45°C to 75°C. The shift upward of the curves may be a signal for overwhelming fluctuations that increase as the critical point is approached. Above 55°C, the system exhibits the homogeneous single phase with weak fluctuations and the scattering intensity decreases only slightly with the temperature (see Figure 1c).

The slope of I^{-1}(q) versus q^2 also changes with temperature as one can see in Figure 2a. Although the data are somewhat scattered from 25 to 45°C, one can distinguish a slight increase of the slope that could be compared with the chain swelling and decrease of the Flory-Huggins interaction parameter suggested by Figure 1a. Above 45°C, Figures 2b and 2c indicate that the slope remains essentially constant. To confirm these results, it is necessary to perform additional SANS experiments

and explore other compositions in the (T, φ_1) diagram of the dPS/8CB system.

CONCLUSIONS

SANS data of dPS/8CB of 75wt% 8CB are reported in the range of temperature 25-75°C. The forward scattered intensity I(q=0) and the slope of $I^{-1}(q)$ versus q^2 yield consistent results and show chain swelling from 25 to 45°C. Above 45°C the slope of $I^{-1}(q)$ versus q^2 remains constant. The preliminary results reported here show interesting tendencies and give a clear demonstration that SANS is an excellent technique to probe the interactions of polymer chains in anisotropic solvents. They suggest to pursue this effort and cover a wider range of the (T, φ_1) phase diagram of dPS/8CB.

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