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Compressibility Effects in a Solvated Polystyrene−Polyisoprene Diblock Copolymer

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Introduction. Strong interest has recently developed in compressibility effects in polymer mixtures as investigated by scattering methods. This was prompted by the construction of two pressure cells for small-angle neutron scattering (SANS) in Julich[1,2] and at NIST[3] and of another one for small-angle X-ray scattering (SAXS) at Princeton.[4] Pressure is an important thermodynamic parameter which enters in most forms of polymer processing and influences many polymer properties such as mixing/demixing aspects, kinetics of phase separation, morphology and texture, etc. Performing small-angle neutron scattering from pressurized polymer mixtures is a convenient way of monitoring miscibility and chain conformations at the same time.

Results of two sets of pressure experiments (using SANS) have been reported so far. Janssen et al.[1,2] have investigated equation of state effects in polystyrene/poly(vinyl methyl ether), in polystyrene/poly(phenylmethylsiloxane), and in isotopic mixtures of polystyrene. Hammouda and Bauer[3] have investigated miscibility effects in polystyrene/poly(vinyl methyl ether) and in polystyrene/poly(butyl methacrylate). Results on polystyrene/poly(vinyl methyl ether) blends from the two groups agreed, and Hammouda and Bauer[3] also investigated composition effects. Janssen et al.[2] combined SANS data and *PVT* data on their polymer systems. They found that for polystyrene/poly(vinyl methyl ether) volume changes due to densification were smaller than decreases in the apparent radius of gyration upon pressurization. This effect was also observed in ref 3 and is believed to be due to pressure-induced changes in monomer−monomer interactions and their effect on chain conformations.

Moreover, experiments on pressurized polystyrene−polyisoprene diblock copolymers (using SAXS) have been performed by Hajduk et al.,[4] who found that the order−disorder transition (ODT) temperature increases at a rate between 10 and 25 °C/kbar; this is lower than the rate of the glass−rubber transition temperature (T_g) which is 74 °C/kbar for the polystyrene block.[5] The SAXS pressure cell uses beryllium windows which introduce a strong incoherent background that interferes with the polymer scattering signal.

Results from SANS experiments on a pressurized PS−PI diblock copolymer dissolved in dioctyl phthalate (DOP) are reported here. The DOP solvent was added in order to lower T_g (way below ambient temperature) so that it does not interfere with observations of the ODT. The amount of added solvent was chosen so as to adjust the ODT to a reasonable temperature (38 °C as measured by optical birefringence). A similar sample had previously been used in another SANS experiment.[6] These constitute the first SANS experiments on pressurized copolymer solutions.

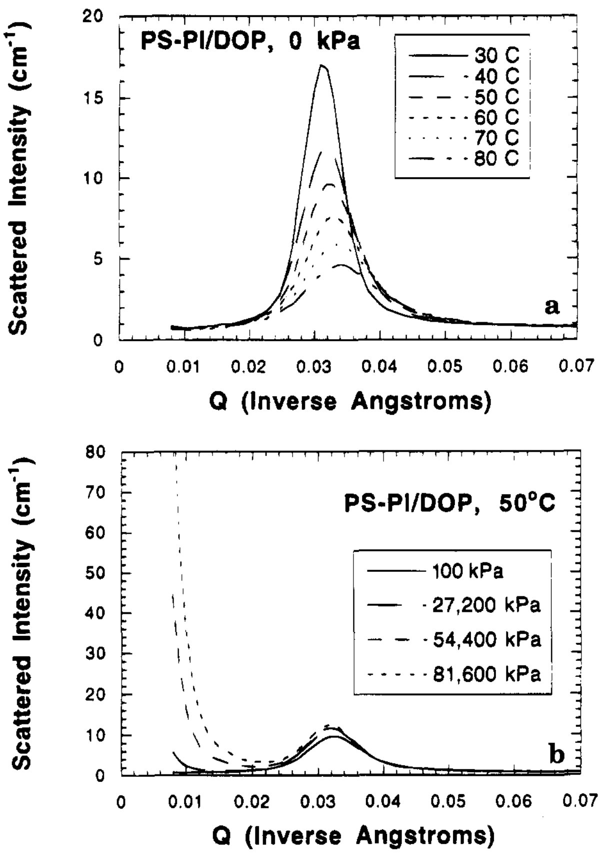

Figure 1. Variation of the scattered intensity with wavenumber for (a) a range of temperatures below and above the ODT (38 °C) at atmospheric pressure (referred to as 100 kPa) and for (b) the four measured pressures at a fixed temperature of 50 °C. Note the development of a peak in the forward scattering direction as pressure is increased.

A number of pressure experiments have been performed on mixtures of (small-molecule) liquids. It was found that cloud-point temperatures could shift upward or downward depending on the sign of the differences in entropy (ΔH) and volume (ΔV) between the two phases. Pressure-induced shifts of the cloud-point temperature obey the Clausius−Clapeyron equation:[7] $\Delta P/\Delta T = \Delta H/T\delta V$, where P is pressure and T is temperature. For example, the isobutyric acid in water mixture is characterized by $\Delta T/\Delta P = -55$ mK/bar, whereas for cyclohexane in methanol, this quantity is equal to +35 mK/bar.

Many "free volume" models[8−10] describe pressure effects in polymer mixtures. These either incorporate free volume as part of the monomer volume (Flory) or assume it to be a separate component (Simha and Sanchez−Lacombe) that does not interact. A compressible random-phase approximation approach[11,12] has been introduced for polymer blend mixtures.

Experiments. Our sample consisted of a PS−PI diblock copolymer (molecular weights of the PS and PI blocks were 1.1×10^4 and 1.7×10^4, respectively, and polydispersity was less than 1.07) dissolved in DOP with a 65% polymer weight fraction (which corresponds to the lamellar morphology at ambient temperature). DOP is a nonvolatile good solvent for both PS and PI especially within the temperature range of our measurements. The ambient-pressure ODT has a strong dependence on the polymer weight fraction; it is be-

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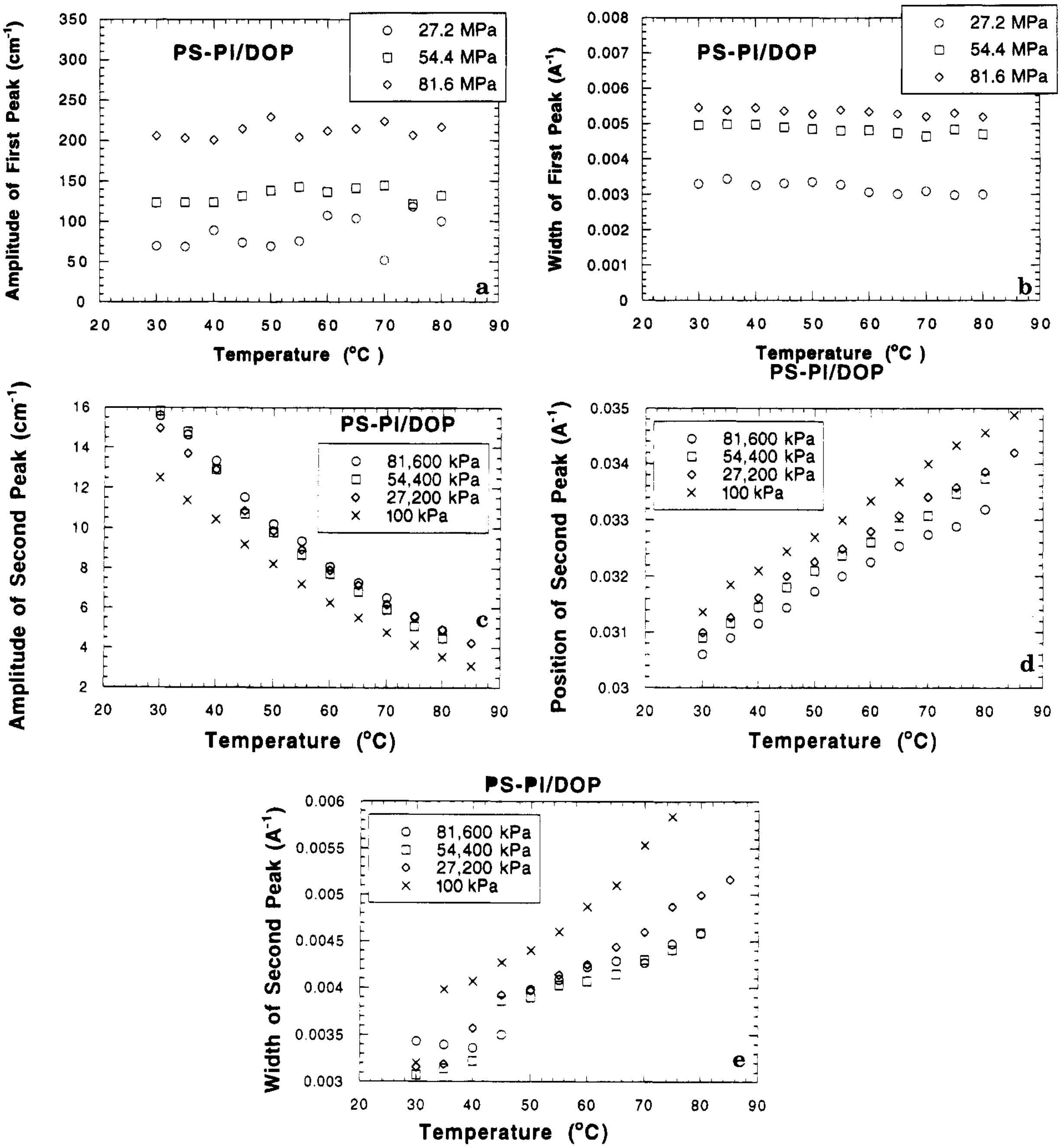

Figure 2. Temperature variation of (a) the amplitude of the forward scattering (first) peak, (b) the width of the first peak, (c) the amplitude of the second (correlation) peak, (d) the position of the second peak, and (e) the width of the second peak for fixed pressures. The first peak position is in the forward direction.

lieved, however, that solvent acts mainly as a "plasticizer" and is uniformly distributed throughout the sample.[13] Because of the natural contrast between PS and PI, no deuterium labeling was necessary. The ODT temperature (38 °C) was measured by birefringence and verified by SANS.[6]

Small-angle neutron scattering measurements were performed on the NG3 30m instrument[14] at the National Institute of Standards and Technology, Cold Neutron Research Facility. A wavelength of 5 Å and a wavelength spread of 15% were used along with a sample-to-detector distance of 3 m and tight collimation (source-to-sample distance of 11.67 m) in order to minimize resolution effects. In-situ pressure measurements were performed using a hydraulic pressure cell comprising a stainless steel body in which the sample is confined within an O-ring and in-between two sapphire windows. The pressurizing (brake) fluid compresses the 1.2-mm-thick sample through the O-ring up to high pressures (about 100 MPa). Even though the neutron beam diameter was 9.5 mm, the O-ring size (diameter) used was 17 mm in order to make sure that no brake fluid would ever be in the neutron beam. Temperature was computer-controlled through band heaters and temperature feedback sensing. Temperature scans (from 30 to 85 °C in 5 °C steps) were performed at fixed pressure. SANS measurements were performed at four pressures (up to 81.6 MPa which corresponds to 12 000 psi). Because pressure was set manually, it drifted slightly with temperature (at 81.6 MPa, pressure increases of order 5% were observed for temperature increases of 50 °C). Note that, for notation convenience, we are referring to the atmospheric pressure condition (14.7 psi) as 100 kPa. In order to ensure reproducibility, the 30 °C scan was repeated after cooling of the sample. SANS data from the PS–PI sample were corrected for empty pressure cell scattering and beam blocked background and were scaled to an absolute cross section (units of cm^{-1}) using a silica sample as a secondary standard.

Discussion and Conclusions. The ambient-pressure SANS data show the usual variation of the correlation hole peak with temperature (Figure 1a). This peak shifts to higher wavenumbers, decreases in amplitude, and broadens as the temperature is increased; it is much sharper below the ODT (38 °C) where the lamellar structure is reminiscent of regular "crystalline" structures. As temperature is increased above the ODT, correlations decrease substantially in the homogeneous phase region. The Leibler mean-field description[15] of the ODT transition for diblock copolymer melts predicts a critical point for a segregation parameter of $(\chi N)_s = 10.5$ (where χ is the Flory–Huggins interaction parameter between copolymer segments and N is the degree of polymerization for symmetric diblocks). The effect of critical fluctuations[16] is to raise this prediction to higher values of $(\chi N)_s$ (i.e., fluctuations lower the ODT temperature prediction). Imposing pressure can be expected to dampen critical fluctuations, therefore lowering the predicted $(\chi N)_s$ closer to the mean-field value. This simple argument predicts a pressure-induced upward shift of the ODT temperature.

When pressure is increased, the correlation hole peak shows little change, whereas another peak shows up in the forward scattering direction as shown in Figure 1b. This new peak was not expected and could have two possible origins: it could be due to "solution effects" (appearance of a pressure-induced spinodal line) or due to a pressure-induced selectivity of the solvent (under pressure, solvent–monomer interactions change such that interactions with one of the blocks are favored); both possibilities are due to the presence of solvent. These conclusions are still pure conjectures; the purpose of this short paper is to report the observed experimental trends qualitatively.

The two SANS peaks were fitted to the sum of two Gaussian functions whereby amplitudes and widths were allowed to float; moreover, the peak position of the second (correlation hole) peak was also allowed to float. Results are shown in Figure 2. Looking at these figures, a general observation is that the first peak is strongly pressure dependent and weakly temperature dependent, while the second peak shows the opposite trend. Pressure-induced variations of the second peak characteristics are equivalent to a shift of the ODT upward with increasing pressure, i.e., to the favoring of demixing as expected. Inspection of the data points to a shift of the ODT upward by 18 °C for an increase of 800 bars of pressure. What is interesting is that even the 30 °C data (below the ODT) show pressure variation. At 70 °C, the position of the second peak varies with pressure by 3–4%; i.e., more than what is expected from densification (less than 1% based on the isothermal compressibility of the two polymer blocks).

In these experiments, solvent was added to the diblock copolymer in order to avoid "T_g effects" and their interference with observations of the ODT. This addition seems to have, however, brought about another ("polymer solution") effect which is hopefully decoupled from the ODT effect (two separate peaks with little interference). The next step (future investigation) will be to find out whether mixing polystyrene and/or polyisoprene homopolymers in DOP solutions would show the same behavior (appearance of a pressure-induced peak in the forward direction), therefore helping sort out whether the first peak is a "polymer solution effect" or a "selective solvent effect".

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