

SANS From Polymers Under Pressure

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Introduction

Small-Angle Neutron Scattering (SANS) has been an ever-growing characterization method for nanoscale materials over the past 25 years. Improved instrumentation and new and judiciously chosen *in situ* sample environments have fueled this drive. Examples are facilities to control temperature, introduce shear fields and, more recently, to vary pressure. Controlled temperature and temperature jump experiments have been of great value for studies of miscibility and kinetics of phase separation in polymer mixtures. *In situ* shear measurements added another dimension to rheological studies of materials such as copolymers, micelles and colloid systems. There have been many investigations of the effects of a shear field on structures and on thermodynamics. Over the past five years, the introduction of a controlled pressure/temperature facility has led to a good deal of research on SANS from polymers and other soft materials under pressure. Representative efforts using the 30m NG-3 SANS instrument at NIST are summarized briefly in this review.

The NIST hydraulic pressure cell is made of a stainless steel body and uses two sapphire windows to confine the sample. It can be used to pressurize polymer melt mixtures (blends and copolymers) inside a confining oring. Another arrangement is for soft liquid materials (macromolecular solutions, micellar systems) in which a piston inside a tube connected to the cell is used to separate the pressurizing fluid from the liquid sample. This first-generation cell can reach 120 MPa (1.2 kbar) for temperatures up to 200°C. The computer-controlled system can perform pressure scans at fixed temperature and

can automatically adjust pressure when temperature is changed. A number of research groups have made effective use of this system. Highlights of some of their results are included here.

Studies of polymer blends under pressure

A major research thrust has been in investigating the effect of pressure on phase behavior in polymer blends. Some polymer systems go through a mixing transition, i.e. from two phases (demixed) to a single (mixed) phase, upon heating through an upper critical spinodal temperature (UCST). Others make that transition upon cooling through a lower critical spinodal temperature (LCST). Occasionally both types of phenomena are seen in the same system. The Clausius-Clapeyron equation equates the derivative of the temperature with pressure (dT/dP) along the phase separation curve to $\Delta V/\Delta H$, where ΔV and ΔH are the differences in volume and enthalpy between the demixed and mixed phases. In passing from the two-phase to the single-phase region by cooling through a LCST, $\Delta H < 0$. But since the transition is driven by free volume in this case, there is always a volume loss upon mixing, $\Delta V < 0$, so that $dT/dP > 0$. Heating is required to pass from the two-phase region to the single-phase region through a UCST, so $\Delta H > 0$, but ΔV may be either positive or negative, depending on the strength of the interaction between the components and their local packing arrangements.

Pressure was found to favor mixing in the blend mixture deuterated polystyrene/polyvinyl methyl ether (dPS/PVME) that exhibits LCST behavior [1]. A pressure-induced increase of the LCST by about 30° C/kbar was observed in agreement with a previous report [2]. Moreover, both the enthalpic and entropic contributions to the Flory-Huggins interaction parameter χ were found to depend on pressure, as was the radius of gyration, a measure of molecular dimensions. In order to interpret the observed results, a compressible Random Phase

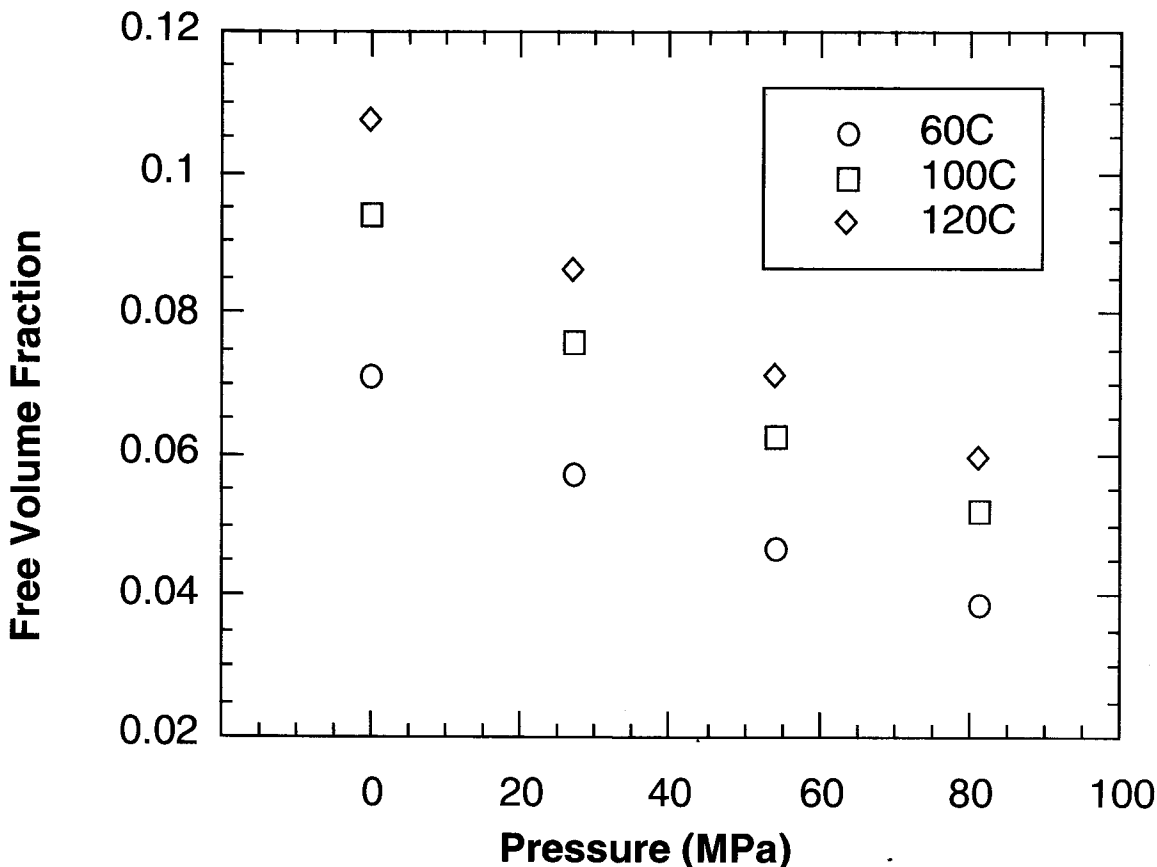


Figure 1. Variation of the free volume component of dPS/PVME (10%/90%) with pressure. The free volume component was obtained by fitting SANS data employing the compressible RPA model and the Lattice Fluid equation of state [3]. Error bars are of the size of symbols.

Approximation (RPA) model was used [3]. Compressibility was introduced through a free-volume component that is governed by an equation-of-state (the Lattice-Fluid model). Solving this set of equations self-consistently gave estimates for the amount of free-volume present in the sample and for the interaction energies that drive phase separation. It was found, for instance, that polymer compressibility alone is not sufficient to explain the previously observed composition dependence of χ . The amount of free-volume was seen to decrease by as much as 5 percent while pressurizing to 100 MPa (1 kbar) or when cooling the sample by 70°C in the one-phase region (Figure 1).

A number of polyolefin blends of polyethylbutylene/deuterated polymethylbutylene (PEB/dPMB) were investigated under pressure [4-7]. These UCST systems always showed a pressure-induced demixing trend with an increase of the phase transition line by as much as 30° C/kbar corresponding to a positive ΔV . Both the binodal and spinodal temperatures were obtained from SANS data and were found to increase with pressure (Figure 2). Moreover, it seems that the nucleation-and-growth region located between these two temperatures, shrinks slightly with pressure (at least for the samples that were measured). For the SANS data from these polyolefin blends, the conventional RPA approach was

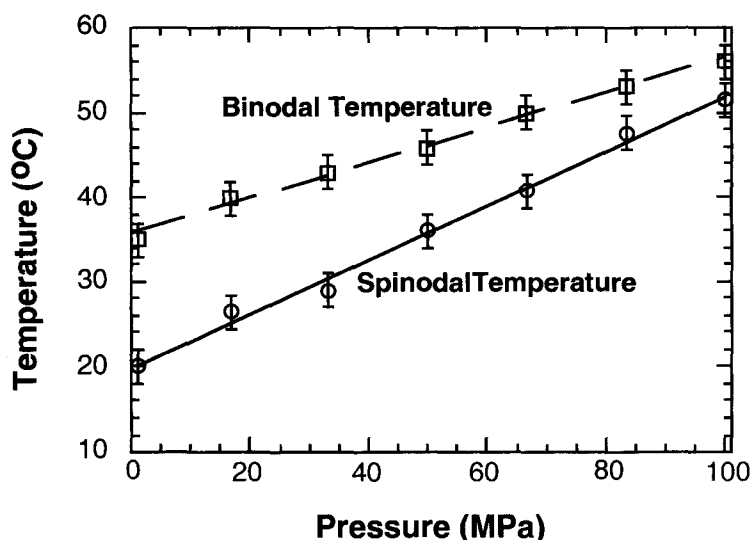


Figure 2. Variations of the spinodal and binodal temperatures with increasing pressure for an off-critical mixture of the PEB/dPMB polyolefin blend. Pressure is seen to disfavor mixing and to narrow the metastable (nucleation-and-growth) region.

used to obtain a pressure-dependent interaction parameter $\chi = D + EP$ where $D(\Delta U)$ and $E(\Delta V)$ are factors dependent on the internal energy change ΔU and volume change ΔV upon mixing [6]. A linear relationship was found between ΔU and ΔV , which means that the increase in volume upon mixing is a linear response to the repulsive interactions between monomers.

After carefully mapping out the phase separation lines for the PEB/dPMB polyolefin blend, pressure jump experiments were performed from the one-phase region to the spinodal two-phase region and vice versa in order to investigate phase separation mechanisms and the time scales involved. Pressure jumps are much faster than temperature jumps and are therefore preferred in order to avoid undesired transient phase-separation kinetics. Following a demixing jump, a spinodal ring developed in the 2-D SANS data, evolved towards low- Q ,

then merged with the transmitted direct neutron beam. Both demixing jumps and reverse (mixing) quenches (Figure 3) were performed. Power laws for the spinodal peak position (Q_{\max}) and intensity (I_{\max}) with time were investigated and compared to predicted values. In the slow-kinetics demixing process, early stages of spinodal decomposition were observed whereas advanced stages were observed in the fast mixing process [4].

Pressure jumps leading into the nucleation-and-growth region instead were performed on binary polyolefin (PEB/dPMB) blends away from the critical composition [7]. These studies demonstrated that these blends could be undercooled (or superpressurized) deep into the metastable region without detectable signs of phase separa-

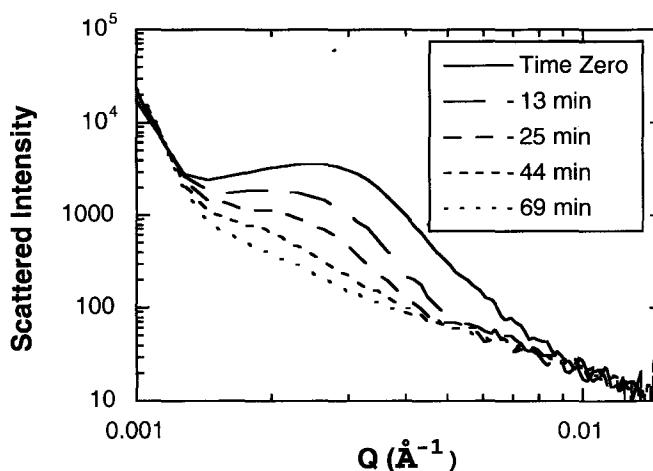


Figure 3. SANS intensity versus Q in PEB/dPMB. After a reverse pressure jump from 100 MPa (1 kbar) to ambient pressure at 40°C, the peak corresponding to the two phases existing in the spinodal region decreases as the system makes a transition to the mixed single-phase state. Each of these kinetics SANS data curves corresponds to 1 min. counting time.

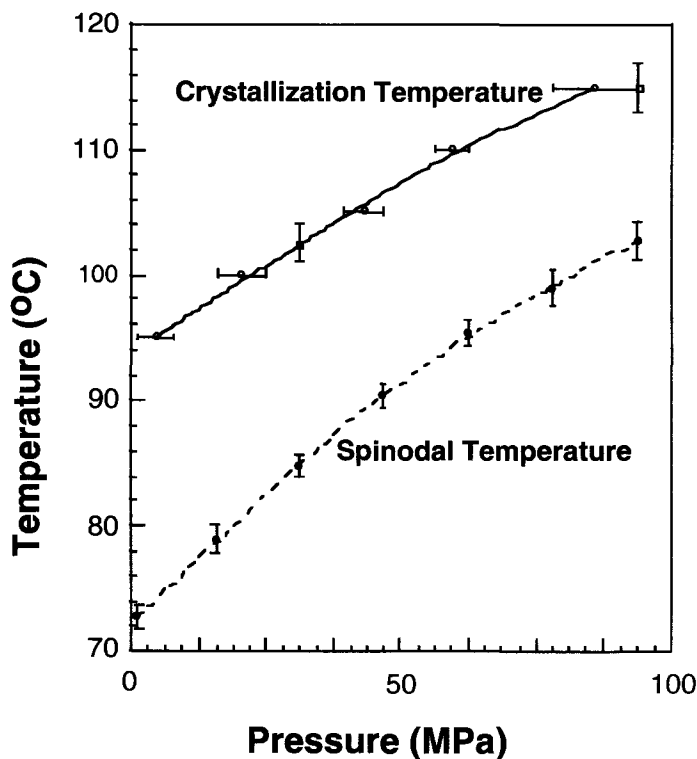


Figure 4. Variation of the spinodal and crystallization temperatures with pressure for the semicrystalline blend of polyolefins poly(ethylene-*r*-butene). The spinodal temperature was obtained from the low Q and the crystallization temperature from the high Q SANS data.

tion. The conventional RPA approach was found to apply equally well to that metastable region, which means that concentration fluctuations in that region are still of a mean-field character. In conditions where liquid-liquid phase separation occurred in the metastable region, the general features of nucleation were independent of quench depth and the nature of the quench (pressure quench or temperature quench). The early stages of nucleation were characterized by a slow amplification of concentration fluctuations (formation of critical nuclei), followed by a regime of rapid growth of the nuclei. A time-pressure superposition principle was observed between phase separation time (after quench) and quench-depth pressure. In analogy to the time-temperature shift factor for viscoelastic behavior of polymers, a

nucleation time-pressure shift factor describing the slowing down of nucleation kinetics with decreasing quench depth was introduced [7].

Another set of experiments on pressurized polymer blends focused on mixing crystalline and amorphous components [8]. Blends of poly(ethylene-*r*-butene) gave a controlled way to vary crystallinity in each of the components of the blend. SANS data from these UCST blends yielded a complete picture of the phase separation thermodynamics (low Q) and crystallization (high Q) of the sample in response to pressure and temperature treatments. A jump in the level of incoherent scattering was observed at the crystallization point. The result for one of the measured samples (26 percent butene content blended with 8 percent deuterated butene content) gave an increase of the spinodal temperature of 30° C/kbar and an increase of the crystallization temperature of 23° C/kbar upon pressurization (Figure 4). Cases where phase separation precedes crystallization were characterized by substantial temperature hysteresis (irreversible behavior when heating or cooling).

The last polymer blend system that will be described here is characterized by a miscibility gap, the first polymer blend found to behave this way [1]. The dPS/polybutylmethacrylate (PBMA) blend system phase separates both upon heating

and upon cooling (i.e., it has both an LCST and a UCST). Applying pressure was seen to widen the miscibility gap by raising the LCST and lowering the UCST. As described above, the LCST is expected to increase with pressure. The lowering of the UCST corresponds to a negative volume change upon mixing.

Studies of block copolymers under pressure

The diblock copolymer version of the previously described polymer blend (dPS-PBMA) also shows a miscibility gap when the block length (N) is five times that of the equivalent homopolymer blend (phase separation occurs for $\chi N = 2$ in blends, whereas it occurs for $\chi N = 10$ in copolymers). Because of the high molecular weight of the diblock, the dPS glass-rubber transition tempera-

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ture overwhelms the UCOT branch of the phase diagram; the LCOT branch however was observed to increase by as much as 150° C/kbar [9]. Note the slightly different terminology for copolymers (UCOrderingT) and polymer blends (UCSpinodalT).

Microphase separation in a family of similar diblock copolymers of polystyrene (PS) with a homologous series of *n*-alkyl methacrylates (*n* = 1 to 12) was investigated [10-11] in order to quantify the effect of local molecular architecture on phase behavior. Out of this series of diblock copolymers, some were found to exhibit LCOT behavior (*n* = 2, 3, and 4) while others exhibited UCOT behavior (*n* = 1, 6, 8, and 12). Here also, the Clausius-Clapeyron equation gives the sign of the volume change upon mixing ΔV for the UCOT behavior ($\Delta V < 0$ for *n* = 1, 6, and 8 and $\Delta V > 0$ for *n* = 12). The specific volume decreases upon mixing because of the bulky side-groups. When the side-chain becomes too long, this trend is reversed. Group theory calculations were used to predict solubility parameters and the lattice fluid equation-of-state model was used to obtain specific volumes. This approach formed a reliable basis to understand the observed trends. The above-mentioned simple model was used to predict phase diagrams using only the pure-component properties of mass density, solubility parameter and thermal expansion coefficient. This model yielded reasonable explanations of the pressure effects, including the observed baroplastic effect (pressure induced flow by disordering the copolymer).

Future outlook

The brief research summaries presented here are only representative and do not include all of the pressure work conducted on the NG3 SANS instrument. *In situ* pressure measurements have brought about a better understanding of the interactions driving phase transitions in polymers and have also stimulated the need for better thermodynamic models to describe compressible polymer mixtures. The hope is that these efforts will help develop "smarter" strategies in polymer processing. Pressure work is also valuable in other areas such as biology, and microemulsions. Future growth of such

research is expected, motivated mostly by the coming online of a second-generation pressure system that can achieve up to 300 MPa (3 kbar) with a temperature window from -10° C to 200° C. We can look forward to a long and prosperous era to come.

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