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Small-Angle Neutron Scattering from Pressurized Polyethylbutylene/Polymethylbutylene Blends

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Introduction. The small-angle neutron scattering (SANS) technique is developing into an effective tool to study pressure effects on the miscibility of polymer blends. Pressure is an important thermodynamic parameter which enters in most forms of polymer processing and influences many polymer properties such as mixing/demixing, morphology, and texture, etc. A few pressure experiments have been performed over the past few years. Lower critical spinodal temperature (LCST) blends (polystyrene/polyvinyl methyl ether) were found to undergo a pressure-induced phase mixing,[1−2] this can be understood as a squeezing out of free volume.[3] A few upper critical spinodal temperature (UCST) blends have also been studied under pressure.[1−2] These could either mix or demix when pressurized. SANS preliminary measurements from a polyolefin blend are reported here briefly.

Experiments. Model polyolefins with molecular weights of about 200 000 (g/mol)—polyethylbutylene (hPE), deuterium-labeled polymethylbutylene (dPM), and hPE−hPM diblock copolymer—were synthesized and characterized by methods described in ref 4. The numbers of repeat units per chain in the three components were determined to be $N_{\mathrm{dPM}} = 4260$, $N_{\mathrm{hPE}} = 3350$, and $N_{\mathrm{hPM-hPE}} = 3740$ (based on a 100 A^3 repeat unit); the average number of deuterium atoms per repeat unit in dPM was 3.8 and the relative volume fraction of PE monomers in the hPE−hPM block copolymer was 0.33. A mixture with $\phi_{\mathrm{hPE}}/\phi_{\mathrm{dPM}} = 0.33$ and $\phi_{\mathrm{hPE-hPM}} = 0.45$ was used in this study (ϕ_i is the volume fraction of component *i*). At atmospheric pressure, this sample exhibits a liquid−liquid phase transition at a convenient temperature of 35 °C.

The small-angle neutron scattering (SANS) measurements were performed on the NIST NG3 30 m instrument in two main configurations: one corresponding to "standard" SANS (wavelength of 6 A and sample-to-detector distance of 11 m) and one corresponding to "nonstandard" SANS using a long wavelength (14 A) and the maximum sample-to-detector distance (13 m). In this last configuration, the lower count rates permit the viewing of the direct beam on the area detector (no need for a beam stop). The first configuration was used to characterize phase transition lines and their changes with pressure whereas the second configuration (lowest *Q* possible) permitted the monitoring of phase separation kinetics for long times (many hours). In this last case, multiple scattering was appreciable (as evidenced by low sample transmissions) which smeared the data. We used this technique to follow trends. The scattering profiles reflect the distribution of dPM chains in the mixtures; there is no neutron scattering contrast between hPE and hPE−hPM.

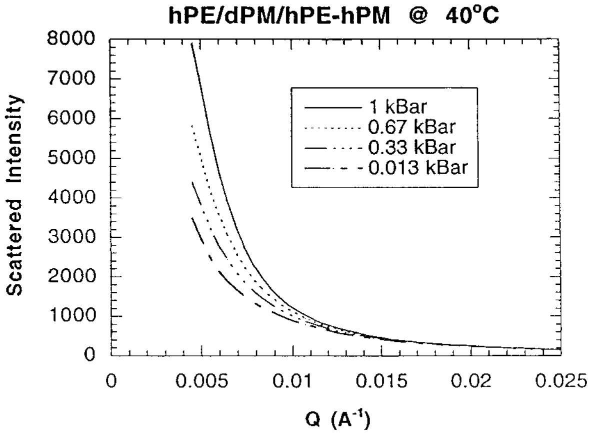

Figure 1. Scattering data at 40 °C for increasing pressures.

In situ pressure was applied to the sample using a hydraulic pressure cell which consists mainly of a stainless steel body where the sample is confined inside an *o*-ring and in between two sapphire windows. The pressurizing fluid (silicone oil) compresses the 1 mm-thick sample through the *o*-ring up to 1 kbar pressures. Temperature was varied up to 160 °C through a band heater. A computer-controlled pump conveniently allows pressure scans at constant temperature.

Observations. The effect of pressure was seen to shift the phase boundary lines upward in temperature (by as much as 30 °C/kbar), i.e., pressure favors demixing in this UCST system. This was evidenced by the enhancement of the scattered intensity upon pressurization (see Figure 1). Careful monitoring of the SANS intensity (when the sample is in the one-phase region) is a good indicator of the proximity of phase transition lines. A conventional method (extrapolation of $1/I_0$ vs $1/T$ where T is the absolute sample temperature and I_0 is the extrapolated SANS intensity in the forward direction) was used to determine the spinodal temperature (T_s). Moreover, $1/I_0$ (intercept of the Zimm plot) becomes negative when the sample phase separates, i.e., when it crosses the onset-of-phase-separation line. In the terminology of polymer thermodynamics, this is called the binodal line; in light scattering, it is called the cloud point; in the case of neutron scattering, it could be referred to as "neutron cloud point" or "neutron binodal"—here we will loosely refer to it as the binodal line. The binodal temperature was also located by plotting $1/I_0$ vs $1/T$ and identifying the temperature at which deviations from linearity were observed. These results are shown in Figure 2. It is interesting to see that, in our sample, the region between the binodal and spinodal lines (which we loosely refer to as the nucleation-and-growth region) narrows down under pressure. This suggests that the upward shift of phase transition lines is not a simple vertical translation; it may correspond to a lateral shift as well. This cannot be confirmed until the full-phase diagram is determined using samples of many different compositions.

Pressure jumps (at fixed temperature) from the one-phase region to the two-phase region have been performed. Kinetics of phase separation have been followed for many hours whereby a spinodal peak appeared and then built up while moving to lower *Q* values. Figure 3a shows a jump from 0.013 kbar (almost ambient)

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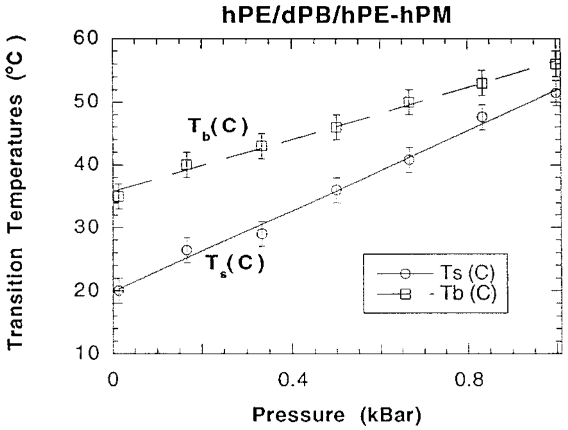

Figure 2. Estimated variations of the spinodal temperature (T_s) and binodal temperature (T_b) with pressure.

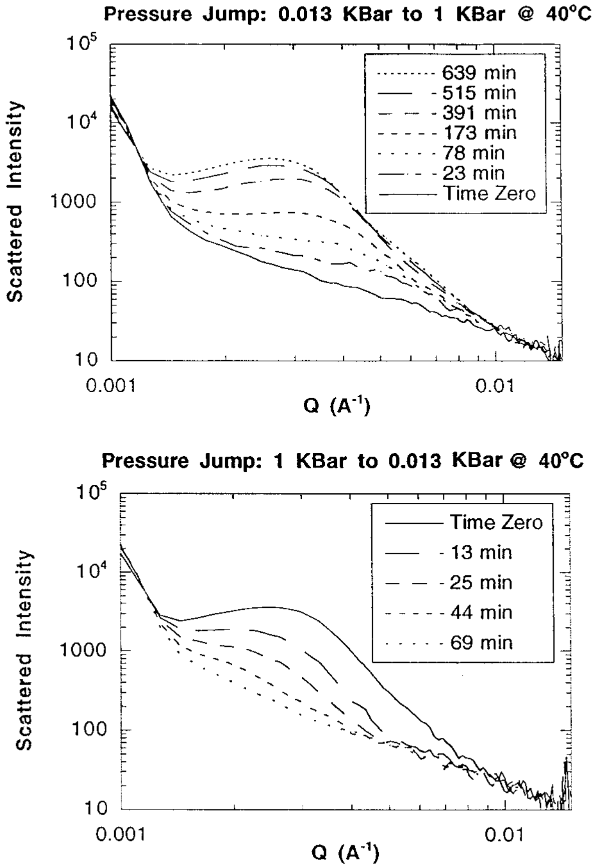

Figure 3. (a) Pressure jump from ambient pressure to 1 kbar at fixed temperature (40 °C) corresponding to a jump from the one-phase region to deeply into the spinodal region. (b) Reverse pressure jump from 1 kbar to ambient pressure at fixed temperature (40 °C) corresponding to a jump from the spinodal to the one-phase region.

pressure to 1 kbar (deeply into the spinodal region) at a temperature of 40 °C. The SANS direct beam is also shown at low Q values. Reverse pressure jumps (two-phase region to one-phase region) have also been performed and kinetics of dissolution of the formed structure have been investigated. In this dissolution (or structure melting) process, the peak intensity decreases while the peak position moves (also) to lower Q values. The dissolution process is a much faster process (see figure 3b for example). In order to isolate the kinetics of spinodal decomposition, the initial (time independent) polymer structure (bottom scattering curve in Figures 3a,b) was subtracted from the scattering

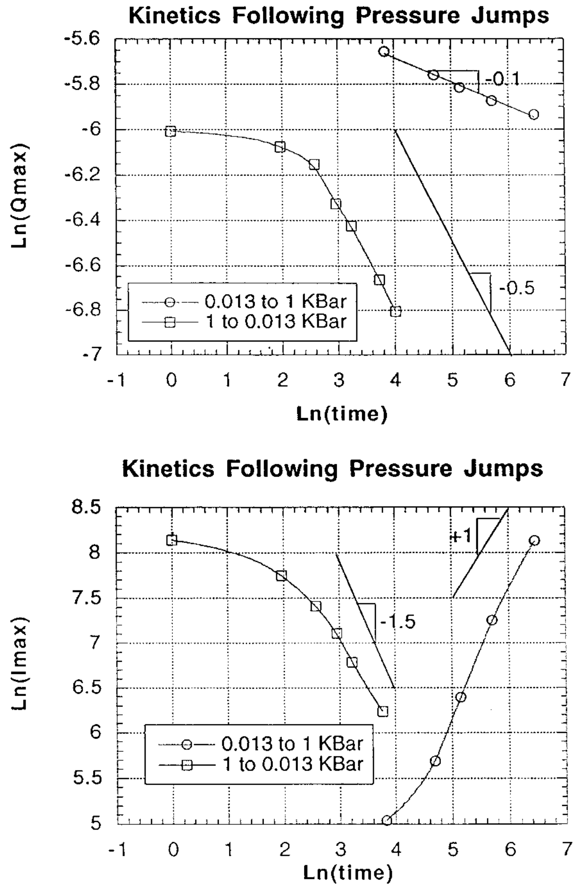

Figure 4. (a) Variation of the spinodal peak position Q_{max} with time for the direct pressure jump (ambient pressure to 1 kbar) and reverse jump (1 kbar to ambient pressure) shown in Figures 3a,b. Ln represents the natural log, the time is in minutes, and Q_{max} is in A^{-1}. Note that time zero is always defined as the jump (or reverse jump) time. These two cases are included on the same figure. (b) Variation of the spinodal peak intensity I_{max} with time for the direct pressure jump (ambient pressure to 1 kbar) and reverse jump (1 kbar to ambient pressure) shown in Figures 3a,b. I_{max} is in arbitrary units.

curves. The difference scattering curves showed the spinodal peaks more clearly. We mapped out the time variations of the peak position (Q_{max}) and maximum intensity (I_{max}) that are shown in Figures 4a,b. The initial pressure jump (one-phase to two-phase) showed a low log(Q_{max}) vs log(t) exponent (−0.1) indicative (maybe) of the fact that this measured time region corresponds still to the early stage of spinodal decomposition. The intermediate stage is expected to show a scaling exponent of −1/3. The observed spinodal ring merges with the direct beam before the intermediate region is reached. The second pressure (reverse) jump on the other hand (two-phase to one-phase region) corresponds to advanced stages of dissolution and is characterized by reasonable scaling exponents for log(Q_{max}) vs log(t) (−0.5) and log(I_{max}) vs log(t) (−1.5). These observations agree with predictions and previous experiments for reverse temperature jumps (two-phase to one-phase).[5,6] Pressure jumps from the one-phase region to other parts of the phase diagram have also been undertaken. For instance, jumps that end up in the nucleation/growth region do not show the formation of a scattering ring.

The last idea that we experimented with was based upon setting up a sequence of regular pressure jumps in order to observe the response and time scale of the

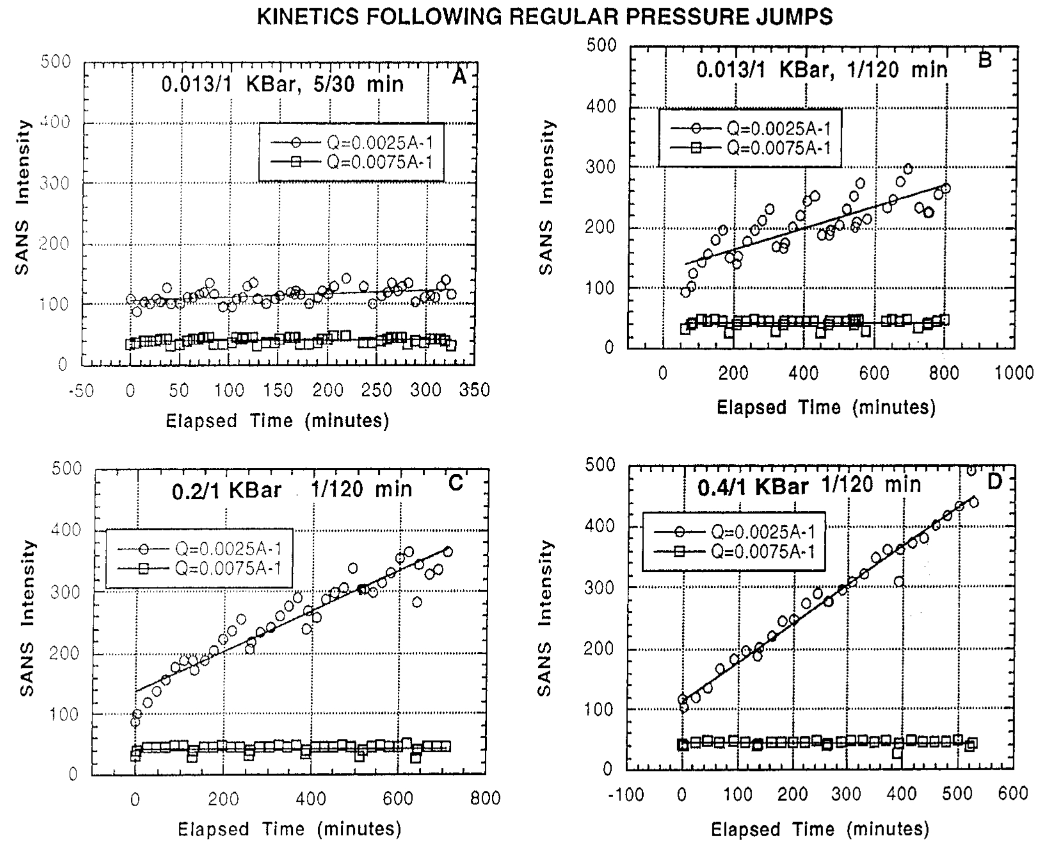

Figure 5. Kinetics of phase separation following four regular periodic pressure jump sequences; these correspond to: (A) jumps from 0.013 kbar (5 min in the one-phase) to 1 kbar (30 min in the two-phase) regions; (B) jumps from the same pressures (0.013 to 1 kbar) with faster dissolution sequence (1 min in one-phase and 120 min in two-phase); (C) jumps from the binodal line (1 min) to deeply into the two-phase region (120 min); (D) jumps from the nucleation/growth region (1 min) to deeply into the two-phase region (120 min).

phase mixing/demixing kinetics. In this last series of experiments, we studied the response of the dPM/hPE/hPM–hPE blend to pressure oscillations.[7] In Figures 5A,B we plotted the time dependence of the scattered intensity at low Q ($Q = 0.025$ A^{-1}) and higher Q ($Q = 0.075$ A^{-1}) values respectively. In Figure 5A the two-phase structure that formed when the sample was quenched into the spinodal region (1 kbar for 30 min) dissolved completely when the pressure was reduced back to ambient pressure (0.013 kbar for 5 min). On the other hand, when the timing of the pressure oscillation is changed (staying 1 min in the one-phase region and 2 h in the two-phase region), we find that the scattering at low Q grows with time whereas the scattering at high Q does not as shown in Figure 5B. This indicates the selective growth of large-scale structures.

These preliminary measurements are full of interesting observations that still remain to be quantitatively analyzed. Pressure jumps are easier to realize experimentally than temperature jumps and may prove to be helpful in the processing of polymer mixtures. One could imagine growing structures (using ingenious pressure/temperature jump sequences) in polymer mixtures to desired sizes. Systematic studies as well as extensive data analyses are planned.

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(7) The blend used in these oscillatory pressure experiments was not identical to that used in the first series of experiments (Figures 1–4). One of the components (dPM) was synthesized in a separate batch. We mapped out the phase diagram before doing these experiments and found that the phase transition temperatures were lower by about 4 °C. We therefore made the oscillatory pressure measurements on this sample at 36 °C instead for consistency.

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