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Pressure-Induced Compatibility in PEO/P(EO-*b*-DMS) Polymer Mixtures

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Introduction. There is continuing interest in the effect of pressure on the thermodynamics of polymer blends and block copolymers, and there are general observations about how the critical temperatures of polymer blends vary with pressure.[1−18] For those blends that display UCST behavior (that is, phase separation upon cooling), it is nearly always found that the critical temperature, T_c, increases with pressure; i.e., the effect of increasing pressure is to decrease the range of miscibility. Similarly, in mixtures that display LCST behavior (phase separation upon heating), T_c also increases with pressure; thus, increasing pressure almost always reduces the miscibility range in UCST blends and increases it in LCST blends. To our knowledge, there are only a few examples of the UCST blend. One is the blend of polystyrene and poly(butyl methacrylate) studied by Hammouda and Bauer.[7] However, it should be noted that this blend has a negative interaction parameter that decreases algebraically with pressure (i.e., becomes more negative), indicating some specific interactions are at play. Beiner and co-workers[14] also found the pressure-induced compatibility in a UCST model polymer blend of poly(ethylmethylsiloxane) (PEMS)/poly(dimethylsiloxane) (PDMS). The authors found that the χ value for this blend is small, and $\Delta V_M < 0$ in this case. The abnormal pressure dependence of the phase boundaries in PEE−PDMA and PEP−PDMS binary homopolymer blends and diblock copolymers was also found by Schwahn and co-workers.[17] In our group, a similar enhancement of miscibility in an oligomeric system has been seen when a negative heat of mixing was involved.[1] There are also some theory works in the pressure effects on polymers.[2,3,19−22]

The phase separation of polymer is primarily driven by the reduced entropy of mixing as compared to small molecule analogues. This basic fact is captured by incompressible Flory−Huggins (FH) theory. Note that the FH theory, being incompressible, would suggest that pressure is an irrelevant variable. In contrast to FH theory, as shown above, the experimental results proved that pressure can play an important role in the phase separation of polymer blends.

The starting point of the present work is to test the Sanchez−Lacombe lattice fluid theory under pressure for different polymer systems.

In the present work, the onset of turbidity associated with phase separation was used to investigate the pressure dependence of compatibility in the binary polymer blend using a pressure cell. The pressure dependence of compatibility was found in a UCST polymer blend.

Experimental Section. The experiment was manipulated with a high-pressure overall experimental system which consists of one scattering cell. Other components of the system are the light source (LS), light detector (LD), pressure gauge (PG), pressure generator (PG′), valves, and thermostatic bath. The pressure generator and the parts of the apparatus on one side of the piston in the pressure separator are filled with oil. The other side contains a liquid polymer mixture. The contents of the cylindrical pressure cell are sealed by two quartz windows, which allow the transmittance of the light along the axis of the cylinder. Two especially constructed light guides regulate the light input and output; from the upside which transmits the light from a halogen lamp to the input window of the cell, the

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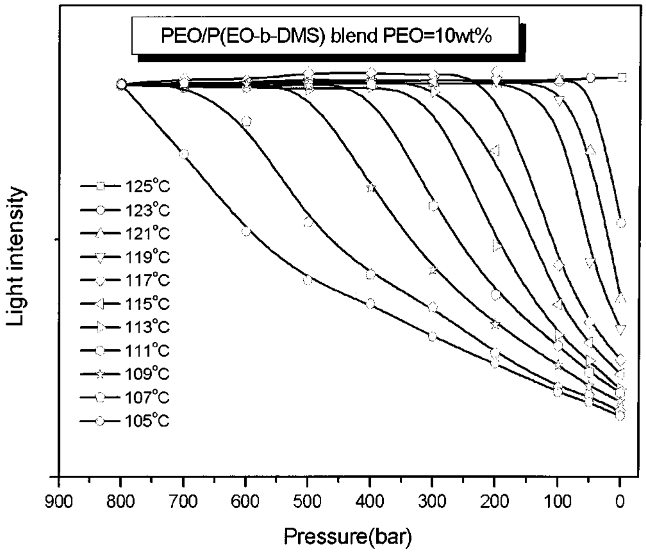

Figure 1. Pressure dependence of the light intensity *I* passing through a mixture of poly(ethylene oxide) (PEO) and poly(ethylene oxide-*b*-dimethylsiloxane) (*P* (EO-*b*-DMS)) for the indicated composition and temperatures in °C. (In SI units: 1 bar = 10^5 N m^{-2}.)

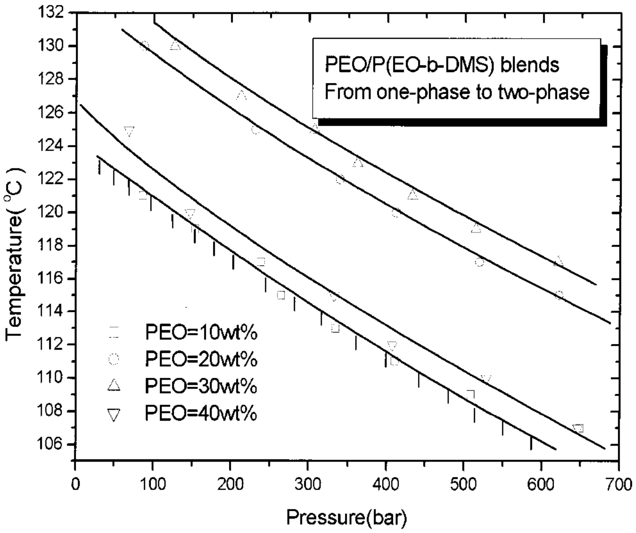

Figure 2. Pressure dependence of *T* for the PEO/P(EO-*b*-DMS) system.

signal of the light passing through the cell is electronically converted to a digital signal, and possible changes in the intensity of the light are collected with a recorder. During the experiment process, the pressure cell is put in a temperature equilibrium thermostatic bath (temperature constancy better than ±0.1 °C), and the applied pressure can be read on a Heise manometer.

The polymer mixtures were prepared at 140 °C in argon atmosphere with 3 h stirring. After loading the system with the polymer mixture at a target concentration, fully homogeneous conditions are achieved by manipulation of the pressure and temperature. Then at a given temperature, moving the piston at controlled rates brings about pressure changes. The pressure dependence of demixing for four near-critical binary systems containing poly(ethylene oxide) (PEO) (Fluka, M_w = 35 kg/mol, used as received) and poly(ethylene oxide-*b*-dimethylsiloxane) (P(EO-*b*-DMS)) (ABCR, M_m = 1.8 kg/mol, EO_{27}-DMS_8, used as received) was determined with the high-pressure apparatus. These materials will be referred to as PEO and P(EO-*b*-DMS), respectively. Additionally, PEO is referred to as "component 1"and P(EO-*b*-DMS) as "component 2". Polymer mixtures were measured in the composition range 10–40 wt % PEO homopolymer up to 800 bar at several preselected temperatures. The pressure dependence of isothermal demixing was measured in the optical pressure cells. The stainless steel cell was fitted with quartz windows. Silicon oil was used as hydraulic pressurizing fluids; dilution of the mixtures in the optical path was avoided by separating the cell and pressure generator with a long metal capillary tube containing the hydraulic fluid/polymer mixture interface near the midpoint. In one part the apparatus was filled with the polymer mixture, and in the other part the apparatus was filled with the hydraulic fluid. The cutoff in transmitted light intensity as the system goes through the liquid–liquid phase transition was used to define the cloud point. In the typical run, *T* was held constant and *P* changed step-by-step. The demixing plots on the *P*–*T* plane are shown in Figure 2. (The isothermal scans and isobar scans were compared for mixtures of polystyrene in *trans*-decalin, a UCST system that T_c increases with pressure, and PEO/P(EO-*b*-DMS) mixtures. The results showed that there is little difference with isothermal and isobar scans for the two systems. For the convenience of experimental manipulation, we measured the samples with isothermal scans.)

Results and Discussion. Figure 1 shows the plots of the transmitted light intensity of the pressure windows vs the system pressure at different fixed temperatures. At pressures above 800 bar and temperatures above 105 °C the difference in turbidity of the polymer mixtures becomes negligible, indicating the high thermodynamic quality of the mixture under these conditions. Our main interest in the present investigation is the pressure at which *I* becomes zero for a given composition at the particular temperature *T* chosen. According to theory,[23] the pressure thus obtained constitutes the spinodal pressure for given composition and *T*; i.e., the variables of state characterize the conditions at which the particular polymer mixture becomes unstable.

The typical dependence of *I* on pressure *P* falls into two parts, as can be seen from Figure 1. The solids serve as a guide for the eye. At high pressures *I* runs asymptotically into the limiting value for the homogeneous polymer mixture I_0, where a linear decrease is observed when the pressure approaches the spinodal pressure. The spinodal pressures are identified from these plots as the pressure corresponding to the points where the transmitted light intensity starts to display a marked decrease. From this figure, the P(EO)/P(EO-*b*-DMS) mixture shows compatibility under pressure.

The phase separation characteristics as obtained from diagrams of the type shown in Figure 1 are given in Figure 2, in which the spinodal pressures are plotted as a function of temperature for the indicated compositions. Figure 2 shows isopleths (i.e., lines of constant composition of the mixture) cloud-point curves observed for polymer mixtures on a temperature–pressure plane. The open circles indicate experimental points, and the solid curves describe the behavior of the data points. Curves were measured at composition = 10, 20, 30, and 40 wt % of PEO. The cloud-point curves at each composition behave similarly to one another. By similar determinations conducted at different temperatures, the

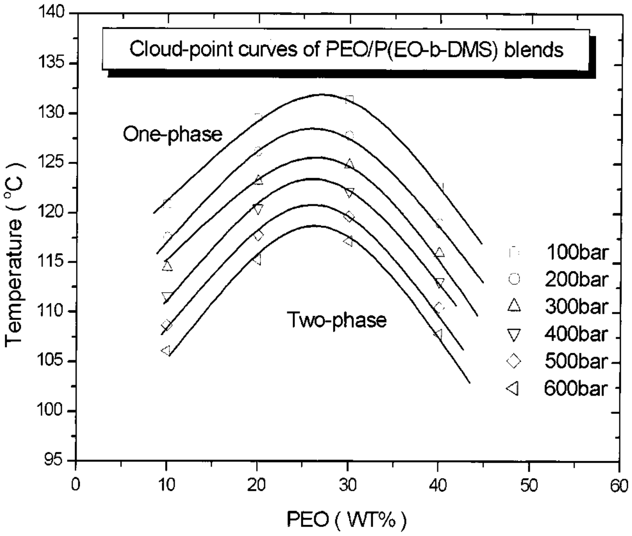

Figure 3. Coexistence curves of PEO/P(EO-*b*-DMS) system at various pressures on the *T*−composition plane.

phase boundary show in Figure 2 was determined. The region above the curve is the one-phase homogeneous region, while the region below represents the two-phase region. As shown, the demixing pressures decrease with increasing temperature. This figure shows that d*T*/d*P* of this system is negative, and this means that the pressure decreases the phase separation temperature of PEO/P(EO-*b*-DMS) blends.

This binary system has been studied at four contents: 10, 20, 30, and 40 wt % of PS. With the reservations concerning polymer concentrations, isobaric critical lines can be constructed from the isopleths of Figure 2. The thus obtained critical lines from 100 to 600 bar are shown in Figure 3 on a *T*−composition plane. In Figure 3 the coexistence boundaries are described on a *T*−composition plane at the indicated pressures (bar). The shape of the coexistence curve depends only slightly on pressure, which can be recognized by comparing the curve at 100 bar with the curve at 600 bar, and this system shows that it is a UCST system. Pressure extends the one-phase region of this system within the observed composition.

Figure 4 shows isotherms (i.e., lines of constant temperature of the solution) for the coexistence condition, i.e., the composition dependence of the phase separation pressure for PEO/P(EO-*b*-DMS) mixtures of the indicated temperature. We depict the isotherm coexistence curves on a *P*− composition plane from Figure 2. From Figure 4, we can observe that PEO/P(EO-*b*-DMS) mixtures show it is a UCSP system at different temperatures.

The pressure effects on the demixing temperatures of PEO/P(EO-*b*-DMS) mixtures are shown in Table 1. From the date in Table 1, we not only can recognize the degree of the pressure effect on the phase separation temperature of PEO/P(EO-*b*-DMS) mixtures, but also can find that the pressure affected phase separation temperature of this system is almost independent of the composition. The slope of UCS in ($P < T$) space is described in terms of the excess functions using eqs 1 and 2:[24]

$$\left(\frac{\mathrm{d}T}{\mathrm{d}P}\right)_{\mathrm{c}} = \lim_{\substack{T\to T_{\mathrm{c}}\\ x\to x_{\mathrm{c}}}} \frac{\partial^2 v_{\mathrm{M}}/\partial x^2}{\partial^2 S_{\mathrm{M}}/\partial x^2} = \lim_{\substack{T\to T_{\mathrm{c}}\\ x\to x_{\mathrm{c}}}} T\,\frac{\partial^2 v_{\mathrm{M}}/\partial x^2}{\partial^2 h_{\mathrm{M}}/\partial x^2} \qquad (1)$$

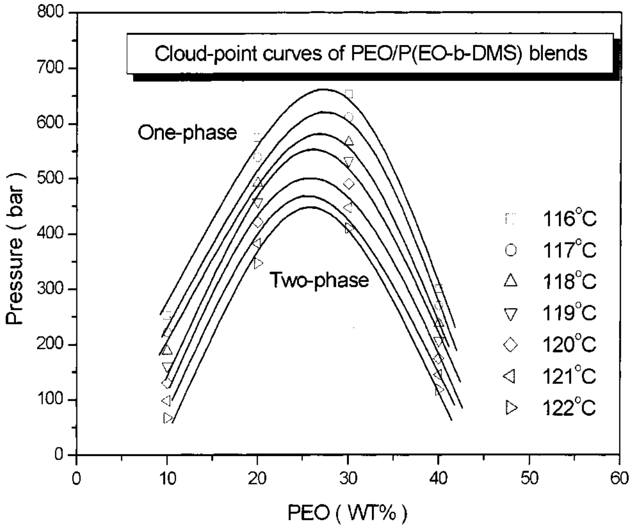

Figure 4. Coexistence curves of the PEO/P(EO-*b*-DMS) system at various temperatures on the *P*−composition plane.

Table 1. Pressure Effects on the Phase Separation Temperatures of PEO Composition in PEO/P(EO-*b*-DMS) Mixtures

PEO composition (wt %)	10	20	30	40
dT/dP (K/kbar)	28.7	28.1	27.5	29.8

Here x is the composition (mole fraction), v_{M}, S_{M}, and h_{M} are solution molar volume, entropy, and enthalpy, and (below) v^{E} and h^{E} are the excess volume and enthalpy, respectively. Subscript c denote the critical quantities. The strict equalities in eq 1 simplify should v^{E} and h^{E} have identical functional forms describing their T and x dependences.

$$\left(\frac{\mathrm{d}T}{\mathrm{d}P}\right)_{\mathrm{c}} \approx \frac{T_{\mathrm{c}} v_{\mathrm{c}}^{\mathrm{E}}}{h_{\mathrm{c}}^{\mathrm{E}}} \qquad (2)$$

Equation 2 is valid only at the critical composition. If, as is commonly so, $h^{\mathrm{E}} > 0$, the sign of $(\mathrm{d}P/\mathrm{d}T)_{\mathrm{c}}$ is governed by the sign of $v_{\mathrm{c}}^{\mathrm{E}}$, but one must keep in mind that eq 2 is only approximate, and it is formulated in detail in ref 24.

The Clausius−Clapeyron equation[25] describes the coexistence line of two phases in a $T-P$ plane according to $(\mathrm{d}T/\mathrm{d}P)_{\phi} = T\Delta V_{\mathrm{M}}/\Delta H_{\mathrm{M}}$, which is similar to eq 2. Since ΔH_{M}, the enthalpy change on mixing, is positive at the critical point, the sign of this derivative is controlled by ΔV_{M}, the volume change on mixing. In most polymer blends investigated[14] to date $(\mathrm{d}T/\mathrm{d}P)_{\phi} > 0$, implying that $\Delta V_{\mathrm{M}} > 0$. Table 1 shows that $(\mathrm{d}T/\mathrm{d}P)_{\phi} < 0$ in present system that indicates $\Delta V_{\mathrm{M}} < 0$, and it is independent of the composition, which is different from TD/PS system. (We found that $(\mathrm{d}T/\mathrm{d}P)_{\phi} > 0$, and it is dependent on the composition for TD/PS polymer solutions.) The quantitative evaluation of observed dependences for the thermodynamic characterization of the demixing behavior will be discussed in more detail elsewhere.

Conclusion. Pressure-induced demixing has been observed in four PEO/P(EO-*b*-DMS) mixtures with pressure up to 800 bar. We found an enhanced compatibility with pressure in the PEO/P(EO-*b*-DMS) system, which is unusual as pressure normally leads to a decreased compatibility. The phase diagrams of the PEO/P(EO-*b*-DMS) system under pressure play UCST and UCSP behavior, and the pressure dependence of the critical temperature $(dT/dP)_\phi$ is negative and composition independent, which means that $\Delta V_M < 0$ in this system within the measured T, P, and composition range exhibits UCST and UCSP behavior.

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