

Abnormal pressure dependence of the phase boundaries in TL/PEO/P(EO-*b*-DMS) ternary mixtures

Shichun Jiang,^{1,2,*} Wei Jiang,^{1,2} Bernhard A. Wolf,² Lijia An,¹ and Bingzheng Jiang¹

¹State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

²Institute für Physikalische Chemie, Johannes Gutenberg-Universität, Jakob-Welder Weg 13, D-55099 Mainz, Germany

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The cloud-point temperatures (T_c 's) of both binary poly(ethylene oxide) (PEO)–poly(ethylene oxide-*b*-dimethylsiloxane) [P(EO-*b*-DMS)] and ternary[toluene/PEO/P(EO-*b*-DMS)] systems were determined by light scattering measurements at atmospheric pressure. The phase separation behavior upon cooling in the ternary system has been investigated at atmospheric pressure and under high pressure and compared to the phase behavior in the binary system. The phase transition temperatures have been obtained for all of the samples. As a result, the pressure induces compatibility in the binary mixtures, but for the ternary system, pressure not only can induce mixing but also can induce phase separation.

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INTRODUCTION

Phase separation conditions for polymer-containing systems can change markedly as the systems are pressurized. The pressure effect on the phase behavior of mixtures consisting of polymers is of great technical and fundamental interest, and there are general observations on how the critical temperatures of polymer-containing systems vary with pressure.^{1–9} The thermodynamic behavior of polymer blends is well understood in terms of the mean field Flory-Huggins theory and their deviations near the critical point when thermal composition fluctuations become dominant.^{10,11} For those systems that display upper critical solution temperature (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 lower critical solution temperature (LCST) behavior (phase separation upon heating), T_c also increases with pressure; thus, increasing pressure almost always reduces the miscibility range in UCST systems and increases it in LCST systems. Most studies of polymer blends so far show an increase of the phase boundary with pressure, which is quite obvious as the free volume decreases with pressure and thereby diminishes the entropy of mixing.^{1–5}

The phase separation of a polymer-containing system is primarily driven by the reduced entropy of mixing as compared to small molecule analogs. 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-containing systems.^{12–27}

In our group, there has been much research done on pressure effects on the behavior of polymers in both experiment and theory.^{12–14,23–27} In this paper, we examined the behavior of ternary polymer mixtures containing a diblock

copolymer with homopolymer and toluene as a function of mixture composition and temperature to obtain an experimental phase diagram for a solvent/copolymer/homopolymer mixture. In order to avoid the complications associated with the microphase separation of block copolymers, the molar mass of the block copolymer was kept low in our experiment.²⁸

The currently available experimental information concerning pressure effects on a polymer-containing ternary system reveals an abnormal phenomena: under the demixing condition, dT/dP changed from positive to negative with different concentrations of toluene (TL) in the ternary system. The purpose of this study is to determine the coexistence surface of the ternary system consisting of polymers with different pressures. For phase boundaries at normal pressure, chosen temperatures, and chosen compositions, various pressures are measured. Further, the pressure effects on dT/dP of a ternary system are compared with that of a binary system without solvent.

EXPERIMENT

Cloud-point temperatures were obtained visually under normal pressure by means of two closed spaced marks on the back of the test tube, which, as the mixture or solution becomes cloudy, become indistinguishable. The critical composition was determined by the phase volume ratio method for the toluene (TL)–poly(ethylene oxide) (PEO)–poly(ethylene oxide-*b*-dimethylsiloxane) [P(EO-*b*-DMS)] system. The volume ratio measurements were carried out in cylindrical tubes of about 1 cm diameter and 10 cm height. After the mixtures were homogenized at the one-phase range temperature, the mixtures were conveyed to a bath thermostatically controlled to within 0.1 °C. The results remained the same whether or not agitation was applied during equilibration. This was also observed by Rehage *et al.*³⁶ for polystyrene-cyclohexane mixtures. The mixtures were cooled down to a few kelvins below the phase separation temperature, and the volumes of the separated phases were measured. The separation can take from a few days to even

more than one month for these mixtures. The critical concentration is defined by the equal volume of the upper and lower phases.

At elevated pressures, an apparatus system, consisting of one scattering cell, was used. 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 specially constructed light guides regulate the light input and output. From the upper side, which transmits light from a halogen lamp to the input window of the cell, the signal of the light passing through the cell is electronically converted to a digital signal. Possible changes in the intensity of the light are collected with a recorder. During the experiment, the pressure cell is put into a temperature equilibrium thermostatic bath (temperature constancy better than $\pm 0.1^\circ\text{C}$), and the applied pressure can be read on a Heise manometer.

The processing of binary polymer mixtures under high pressure was reported.²¹ Ternary polymer-containing systems were prepared at about 10°C higher than the phase separation temperatures according to the ternary system phase diagram. The phase separation temperatures under high pressure for the ternary system were measured with a method similar to that for the binary system. The pressure dependence of the phase separation for four near-critical binary systems containing poly(ethylene oxide) (PEO) (Fluka, $M_m=35$ kg/mol, used as received) and poly(ethylene oxide-*b*-dimethylsiloxane) [P(EO-*b*-DMS)] (ABCR, $M_m=1.8$ kg/mol, EO₂₇-DMS₈, used as received) and four chosen compositions [two of them at critical points, and two of them chosen at the highest composition of toluene (TL) in the ternary system phase diagram] were determined with the high pressure-apparatus. These materials will be referred to as PEO, P(EO-*b*-DMS), and TL, respectively. Additionally, PEO is referred to as component 1, P(EO-*b*-DMS) as component 2, and TL as component 3.

Polymer binary mixtures and ternary solutions were measured 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 was used as the hydraulic pressurizing fluid. Dilution of the mixtures or solutions in the optical path was avoided by separating the cell and pressure generator with a long metal capillary tube containing the hydraulic fluid/polymer-containing fluid interface near the midpoint. In one part the apparatus was filled with the polymer-containing fluid, 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 was changed step by step. The demixing plots on the P - T plane are shown in Fig. 3.

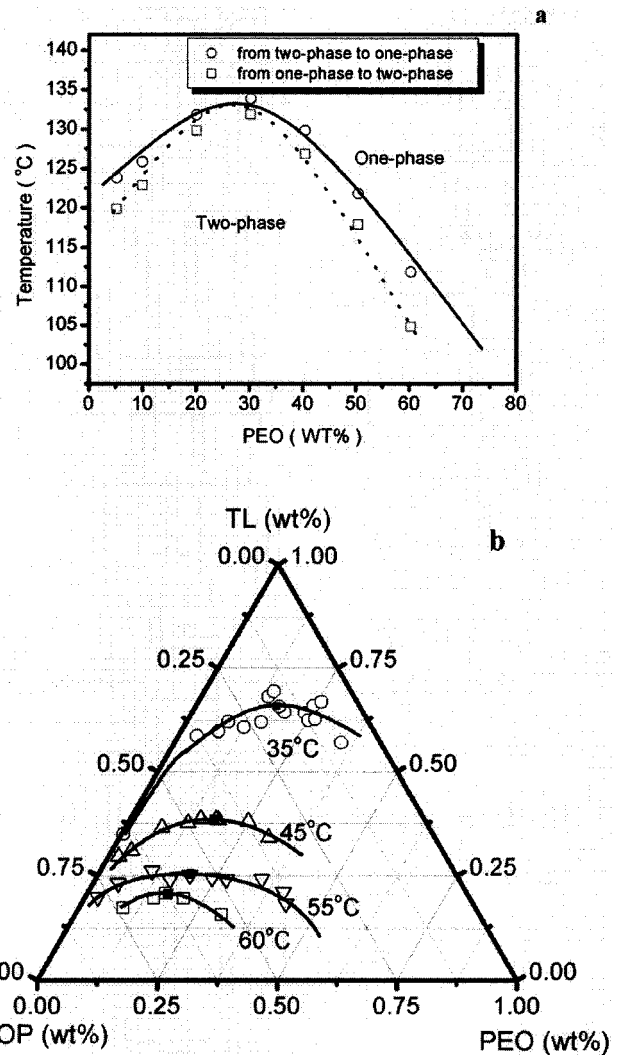


FIG. 1. Phase diagrams under normal pressure. (a): Phase diagram of PEO/P(EO-*b*-DMS) binary mixtures under normal pressure; (b): phase diagrams of TL/PEO/P(EO-*b*-DMS) ternary solutions under normal pressure at indicated temperatures.

RESULTS AND DISCUSSION

The measured cloud-point curves of polymer-containing binary mixtures and ternary systems at normal pressure are shown in Fig. 1. Figure 1(a) shows the measured transition temperatures of PEO/P(EO-*b*-DMS). The open circles indicate experimental points obtained from the measurements of the transition temperature when the system changed from one phase to two phases, i.e., the heating process and the solid curve describe the behavior of the data points. The open squares indicate experimental points for measurements of the transition temperature when the system changed from one phase to two phases, i.e., the cooling process and the dotted curve describe the behavior of the data points. The lines are polynomial fits and serve as a guide for the eye (for other figures as well). Figure 1(b) shows the cloud points of the TL/PEO/P(EO-*b*-DMS) ternary system at 35, 45, 55, and 60°C under atmospheric pressure. The solid squares on the curves at 35 and 45°C represent the ternary system compo-

sition that was chosen for the pressure investigation, and the solid squares on the curves at 55 and 60 °C are the measured critical points at those temperatures and they were also investigated under pressure. It was found that toluene has a great effect on the phase transition temperature of this ternary system. However, the shape of the coexistence curve depends only slightly on the ratio of PEO:P(EO-*b*-DMS) in the ternary system, which can be recognized by comparing the curve at 35 °C with the curve at 60 °C, so the position of cloud-point curves depend on the concentration of TL in the ternary system.

The determination of the exact position of the critical point on the cloud-point curve is a problem not only with multicomponent systems. In the case of binary mixtures the coexistence curves are often very flat in the neighborhood of the critical concentration, which is difficult to determine. It is established practice then to use the rectilinear diameter and assume that upon linear extrapolation the locus of the mean of the tie lines passes through the critical point. This implies that if the volume fraction is used as the concentration variable, the volume ratio of the vanishing phases at the critical point should equal unity.²⁹

This does not mean that the diameter passing through the critical point is linear. For single-component systems Bruhat has shown that the gas-liquid diameter may be curved close to the critical point.³⁰

This argument can be extended to cover systems consisting of more than two components. Therefore, a necessary and sufficient criterion for determining whether a composition is the critical concentration appears to be the equality of the phase volumes as measured at a temperature very close to the cloud point of that concentration. As shown in Fig. 2, we obtained only the critical point for the mixtures at 55 °C and 60 °C, which are represented in Fig. 1(b). However, at lower temperatures, it is very difficult for us to observe the macrophase separation in this system even though the experiment lasted for more than one month.

Figure 3 shows isopleths (i.e., lines of constant composition of the solution), cloud-point curves, observed for ternary polymer-containing solutions on a temperature-pressure plane, and the pressure effect on the binary polymer mixtures has been reported elsewhere.²³ The open circles indicate experimental points and the solid curves describe the behavior of the data points. The region above the curve is the one-phase homogeneous region, while the region below represents the two-phase region. As shown in Ref. 23, the demixing pressures decrease with increasing temperature for the binary polymer mixtures, and dT/dP of the binary system is negative. This means that increasing pressure decreases the phase separation temperature of PEO/P(EO-*b*-DMS) blends. Figure 3 shows the experimental measured phase transition temperatures versus pressure for the compositions shown in Fig. 1(b) as solid squares. As shown in Fig. 3, abnormal pressure effects on the ternary system were found, i.e., at low TL concentrations of this system, pressure induces compatibility, but for high TL concentration pressure decreases compatibility of this system.

With reservations concerning the critical polymer concentration, indicated in the Fig. 1(a), Fig. 4 was constructed

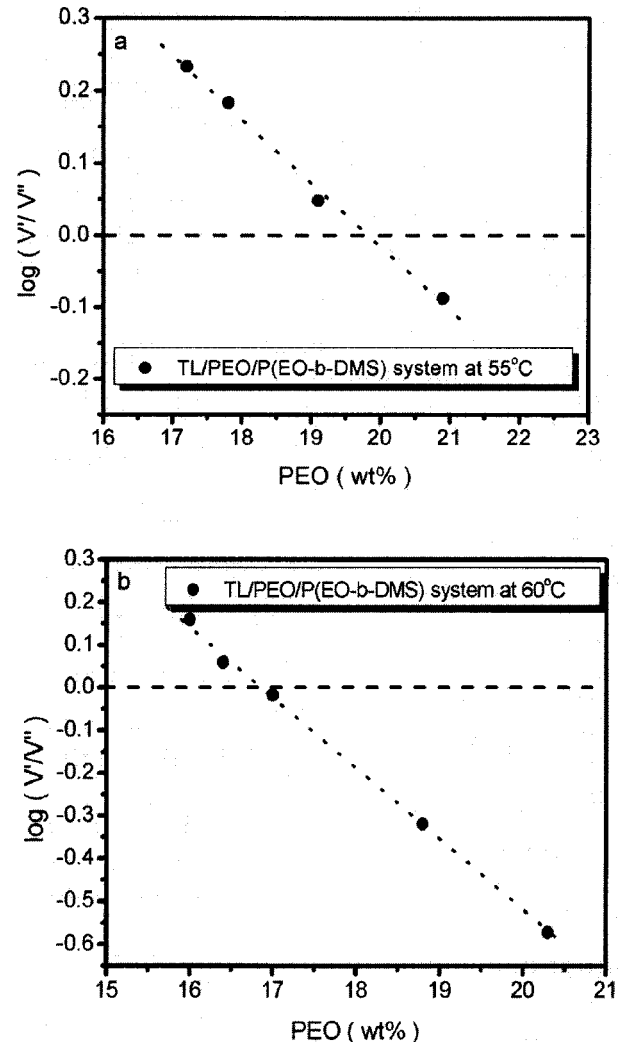


FIG. 2. Phase-volume ratio measurement for TL/PEO/P(EO-*b*-DMS) mixtures (a) at 55 °C and (b) at 60 °C.

from the phase diagram of PEO/P(EO-*b*-DMS) binary mixtures as shown in Fig. 1(a) by plotting $T_H - T_c$ versus PEO wt % (T_H corresponding to the temperature of heating process, i.e., the spinodal temperature; T_c corresponding to the temperature of cooling process, i.e., the binodal temperature). The transition value of $T_H - T_c$ was considered as the critical composition of this binary system.

The pressure effects on the demixing temperatures of the polymer-containing binary system and ternary system are shown in Fig. 5. Figure 5(a) shows the slopes of isopleths (dT/dP) in Ref. 23 versus PEO composition for PEO/P(EO-*b*-DMS) binary mixtures. From this figure, we not only can recognize the degree of the pressure effect on the phase separation temperature of PEO/P(EO-*b*-DMS) mixtures, i.e., $dT/dP \cong 28$ °C/kbar, but also can find that the pressure-affected phase separation temperature of this binary system is nearly independent of the composition. Figure 5(b) shows the slopes of isopleths (dT/dP) in Fig. 3 versus TL concentration for TL/PEO/P(EO-*b*-DMS) ternary solutions. The pressure effect on the ternary system where the TL concentration is can be seen in Fig. 4. Figure 5(a), shows the pres-

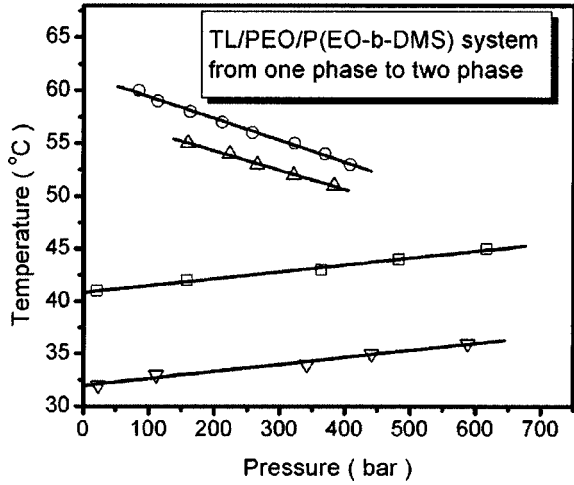


FIG. 3. Pressure dependence of T on the T - P plane [the transition temperatures for TL/PEO/P(EO-*b*-DMS) ternary solutions at indicated temperatures (60 °C (○), 55 °C (△), 45 °C (□), and 35 °C (▽)] and the compositions corresponding to Fig. 1(b) indicated.

sure effect on the critical composition of PEO/P(EO-*b*-DMS) binary mixtures. Figure 5(b) shows the transition for dT/dP with different concentration of TL within the measured composition in the ternary system. The slope of UCS in $P < T$ space is described in terms of the excess functions using Eqs. (1) and (2).³¹

$$\left(\frac{dT}{dP}\right)_c = \lim_{x \rightarrow x_c} \frac{\partial^2 v_m / \partial x^2}{\partial^2 S_m / \partial x^2} = \lim_{x \rightarrow x_c} T \frac{\partial^2 v_m / \partial x^2}{\partial^2 h_m / \partial x^2}. \quad (1)$$

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. The subscript c denotes the critical quantities.

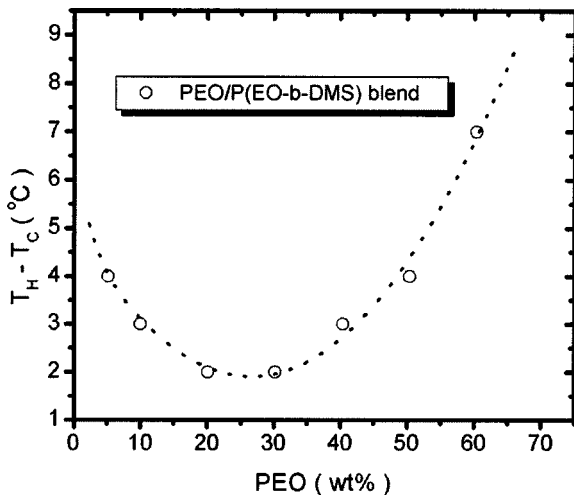


FIG. 4. $T_H - T_C$ vs PEO wt% in the binary system (T_H and T_C are the phase transition temperatures of heating and cooling process).

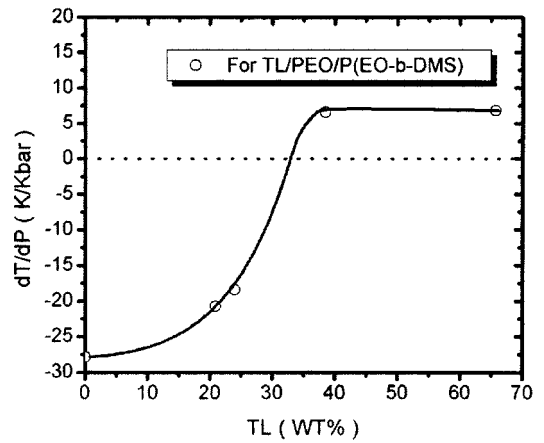
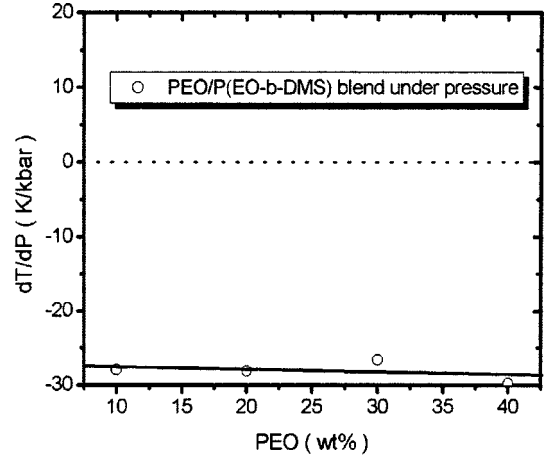


FIG. 5. Pressure dependence of the transition temperatures (dT/dP) vs referred composition (a): for binary mixtures; (b): for ternary solutions.

The strict equalities in Eq. (1) simplify if v^E and h^E have identical functional forms describing their T and x dependences:

$$\left(\frac{dT}{dP}\right)_c \approx \frac{T_c v_c^E}{h_c^E}. \quad (2)$$

Equation (2) is valid only at the critical composition. If, as is commonly so, $h_c^E > 0$, the sign of dP/dT_c is governed by the sign of v_c^E , but one must keep in mind that Eq. (8) is only approximate, and it is formulated in detail in Ref. 31.

The influence of pressure can be deduced by calculating the pressure coefficient (dT_c/dP) of the critical solution temperature, which given by¹²

$$dT_c/dP \approx T \Delta V_m / \Delta H_m, \quad (3)$$

where ΔV_m and ΔH_m are the excess volume and the enthalpy of mixing. Since ΔH_m is positive at the critical point, the sign of this derivative is controlled by ΔV_m . The Clausius-Clapeyron equation³² describes the coexistence line of two phases in a T - P plane according to $(dT/dP)_\phi = T \Delta V_m / \Delta H_m$, which is similar to Eqs. (2) and (3). 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 to date $(dT/dP) > 0$, implying that $\Delta V_m > 0$. A simple equation of state, such as the lattice fluid model (which extends the FH theory through the addition of free volume), shows that to leading order for binary mixtures³³

$$\Delta V_m = \phi(1 - \phi)\{4\chi - [(\varepsilon_{11} - \varepsilon_{22})/RT]^2\}, \quad (4)$$

where ϕ is the volume fraction of component 1, χ is the interaction parameter, and R is the gas constant. For many common blends, such as those studied in past work, the χ parameter is larger, and therefore the lattice model predicts $\Delta V_m > 0$. In contrast, for a carefully selected system with chemically similar monomers, where χ is positive but small, there exists a possibility for $\Delta V_m < 0$. These predictions are consistent with the work of Freed and co-workers using the lattice cluster model.^{34,35} According to Fig. 5(b) and Eq. (4), we can qualitatively predict the pressure effect on this ternary system, i.e., the pressure effects on ΔV_m in this system. At the same time, we also get information on pressure effects on the χ parameter for this system, i.e., with increasing TL concentration in this system, the χ parameter increases from small to large.

CONCLUSIONS

We find that the binodal and spinodal could be measured for PEO/P(EO-*b*-DMS) binary mixtures and the shape of cloud-point curves for TL/PEO/P(EO-*b*-DMS) ternary solutions depends on the ratio of PEO:P(EO-*b*-DMS) in the solutions. Also, the concentration of TL in the solutions affects the position of the curves directly. Under pressure, dT/dP for PEO/P(EO-*b*-DMS) binary mixtures is always negative, but for the TL/PEO/P(EO-*b*-DMS) ternary system, when the TL concentration is low, dT/dP is negative; when the TL concentration is high, dT/dP is positive. The causes of this abnormal complexity require further investigation.

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*corresponding author. Email address: scjiang@ciac.jl.cn

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