

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Pressure Effects on Thermodynamics of Polymer Containing Systems

Shichun Jiang¹ and Hongfei Li²

¹*School of Materials Science and Engineering, Tianjin University, Tianjin*

²*State Key Laboratory of Polymer Physics and Chemistry,*

Changchun Institute of Applied Chemistry,

Chinese Academy of Sciences, Changchun,

P. R. China

1. Introduction

The role of pressure on the phase diagram of polymer liquids and also polymer mixtures has been intensely studied in the past decades, and there has been increased interest in the effects of pressure on the miscibility of polymers (An et al. 1997; An & Wolf, 1998; Blaum & Wolf, 1976; Geerissen et al. 1985; Hammouda & Bauer, 1995; Hosokawa et al. 1993; Lefebvre et al. 2000; Maderek et al. 1983; Rabeony et al. 1998; Wolf & Blaum, 1976, 1977; Wolf & Jend, 1977, 1978). One reason is the need for such data to more fully understand polymer miscibility in relation to the various proposed theories and equations of state. Another is the realization that such pressure effects could be important in many situations where such blends are used, e.g., when mixing a blend in an extruder or in forming articles from a blend by injection molding. These needs have led to the development of pressure cells that can be used with both light and neutron scattering such that the phase behavior and interaction strengths of blends can be measured. In past work, a wide range of phase behavior at chosen composition or near critical point of polymer solutions and polymer blends was found (Beiner et al. 1998, 2002; Blaum & Wolf, 1976; Hammouda et al. 1997; Janssen et al. 1993; Lefebvre et al. 1999; Schwahn et al. 2001; Wolf & Blaum, 1977; Wolf & Jend, 1977; Zeman & Patterson, 1972; Zeman et al. 1972). There are also many works on the theories about the pressure effects on the thermodynamics of polymer liquid and blends (An et al. 1997; An & Wolf, 1998; Dudowicz & Freed, 1995, 2006; Kumar, 2000; Patterson & Robard, 1978; Walsh & Rostami, 1985). As several outstanding problems remain unexplained in these blends, we decided to investigate the dependence on pressure, an independent thermodynamic variable.

The phase behavior of polymer liquids is commonly described in the terms of the lattice model of Flory and Huggins (FH), and the thermodynamics of typical polymer containing systems are understood in the framework of the incompressible random phase approximation. According to original FH theory, the rigorous incompressible system should be unaffected by pressure. In contrast to rigid lattice theories, equation-of-state (EOS) theories are capable of predicting the thermodynamics of polymer containing systems.

Alternatively, the influence of pressure also can be deduced by calculating the pressure coefficient dT_{cr}/dP of the critical solution temperature, i.e., the slope of upper critical solution (UCS) in P - T space is described in terms of the excess functions using equations 1 and 2(Imre et al. 2001) :

$$\left(\frac{dT}{dP}\right)_c = \lim_{\substack{T \rightarrow T_c \\ x \rightarrow x_c}} \frac{\partial^2 v_M / \partial x^2}{\partial^2 S_M / \partial x^2} = \lim_{\substack{T \rightarrow T_c \\ x \rightarrow x_c}} T \frac{\partial^2 v_M / \partial x^2}{\partial^2 h_M / \partial x^2} \quad (1)$$

Here x is composition (mole fraction), v_M , S_M and h_M are solution molar volume, entropy and enthalpy, and v^E and h^E (in equation 2) 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.

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

Eq. 2 is valid only at the critical composition. If, as is commonly so, $h^E > 0$, the sign of $(dT/dP)_c$ is governed by the sign of v_c^E , but one must keep in mind that Eq. 2 is only approximate, and it is formulated in detail in reference (Imre et al. 2001).

The Clausius-Clapeyron equation(Ma, 1982) 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 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(Beiner et al. 1998) to date $(dT/dP)_\phi > 0$ implying that $\Delta V_M > 0$.

In this study we carried out cloud-point measurements for binary system trans-decahydronaphthalene(TD)/ polystyrene (PS) in a pressure range up to 800bar to determine coexistence curves and critical lines. The purpose of this paper is to test whether the Sanchez-Lacombe lattice fluid theory (SLLFT) can describe the equilibrium behavior and pressure effects of polymer containing systems. The spinodals, the binodals, the FH interaction parameter, the enthalpy of the mixing, and volume change of the mixing for TD/PS system were calculated as a function of pressure, temperature and composition on the basis of the SLLFT.

2. Theoretical background

In the lattice fluid theory, as formulated by Sanchez and Lacombe(Lacombe & Sanchez, 1976; Sanchez & Lacombe, 1976), the energy of mixing for binary polymer containing systems is related to the Gibbs energy per mer (indicated by the double bar) of the mixture (index M) and that of the pure components (index1or2) by

$$\overline{\Delta G_M} = \Delta G_M / rN = \overline{G_M} - (\phi_1 \overline{G_1} + \phi_2 \overline{G_2}) \quad (3)$$

According to SLLFT(Lacombe & Sanchez, 1976; Sanchez & Lacombe, 1976, 1978), the thermal equation of state and Gibbs energy per mer for the pure components and the binary mixtures are expressed in eqs 2-5, respectively(An et al. 1997; An & wolf, 1998),

$$\tilde{\rho}_i^2 + \tilde{P}_i + \tilde{T}_i \left[\ln(1 - \tilde{\rho}_i) + \left(1 - \frac{1}{r_i^0}\right) \tilde{\rho}_i \right] = 0 \quad (4)$$

$$\bar{G}_i = \frac{G_i}{r_i^0 N_i} = \varepsilon_i^* \left\{ -\tilde{\rho}_i + \tilde{P}_i \tilde{v}_i + \tilde{T}_i \left[(\tilde{v}_i - 1) \ln(1 - \tilde{\rho}_i) + \frac{1}{r_i^0} \ln\left(\frac{\tilde{\rho}_i}{\omega_i^0}\right) \right] \right\} \quad (5)$$

$$\tilde{\rho}_i^2 + \tilde{P}_i + \tilde{T}_i \left[\ln(1 - \tilde{\rho}_i) + \left(1 - \frac{1}{r_i^0}\right) \tilde{\rho}_i \right] = 0 \quad (6)$$

$$\bar{G}_M = \frac{G_M}{rN} = \varepsilon^* \left\{ -\tilde{\rho} + \tilde{P} \tilde{v} + \tilde{T} \left[(\tilde{v} - 1) \ln(1 - \tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} + \frac{\phi_1}{r_1} \ln\left(\frac{\phi_1}{\omega_1}\right) + \frac{\phi_2}{r_2} \ln\left(\frac{\phi_2}{\omega_2}\right) \right] \right\} \quad (7)$$

where r represents the average number of lattice sites occupied by a molecule in the mixtures, rN is the total number of lattice sites occupied in the mixtures, and ϕ_i stands for close-packed volume fractions of component i .

In eqs 4-7, the different symbols have the following meaning: $\tilde{\rho}_i$, \tilde{P}_i , \tilde{v}_i , \tilde{T}_i and $\tilde{\rho}$, \tilde{P} , \tilde{v} , \tilde{T} are the reduced variables of densities, pressures, volumes, and temperatures for the pure components and for the binary mixtures, respectively, which have the following definitions:

$$\tilde{x} = x/x^* \quad x = P, T, P_i, T_i \quad (8)$$

$$\tilde{v}_i = V_i/V_i^* \quad \tilde{v} = V/V^* \quad (9)$$

$$V_i^* = r_i^0 N_i v_i^* \quad V^* = (r_1 N_1 + r_2 N_2) v^* \quad (10)$$

$$\tilde{\rho}_i = 1/\tilde{v}_i \quad \tilde{\rho} = 1/\tilde{v} \quad (11)$$

According to the combining rules (Lacombe & Sanchez, 1976; Rodgers et al. 1991), the close-packed volume of a mer, v^* , and the average number of lattice sites occupied, r , in the mixture are written by:

$$\frac{1}{v^*} = \frac{\phi_1}{v_1^*} + \frac{\phi_2}{v_2^*} \quad (12)$$

$$\frac{1}{r} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2} \quad (13)$$

Therefore, total volume of binary mixtures becomes

$$V = rN v^* \tilde{v} \quad (14)$$

where the symbols ρ_i^* , P_i^* , v_i^* , T_i^* and ρ^* , P^* , v^* , T^* are the close-packed density, scaling pressure, volume per mer and scaling temperature for the pure component and for the binary mixtures, respectively, which can be expressed in terms of the SLLFT (Lacombe & Sanchez, 1976; Sanchez & Lacombe, 1976):

$$P_i^* = \varepsilon_{ii}^* / v_i^* \quad P^* = \varepsilon^* / v^* \quad (15)$$

$$T_i^* = \varepsilon_{ii}^* / k \quad T^* = \varepsilon^* / k \quad (16)$$

k is the Boltzmann constant. The parameters ω_i and ω_i^0 are the number of configurations available to a r_i -mer and r_i^0 -mer in the close-packed state. In this calculation, they are given as their maxima and

$$\omega_i = \delta_{i,\max} r_i / \sigma_i e^{r_i-1} \quad \omega_i^0 = \delta_{i,\max}^0 r_i^0 / \sigma_i^0 e^{r_i^0-1} \quad (17)$$

where $\delta_{i,\max}$ and $\delta_{i,\max}^0$, the maxima of flexibility parameters of an r_i -mer and of an r_i^0 -mer, should be (Sanchez & Lacombe, 1976):

$$\delta_{i,\max} = z(z-1)^{r_i-1} \quad \delta_{i,\max}^0 = z(z-1)^{r_i^0-1} \quad (18)$$

σ_i and σ_i^0 represent the symmetry numbers of the r_i -mer and the r_i^0 -mer and $\sigma_i = \sigma_i^0 = 1$. z is the coordination number of the lattice which equals 12 in the present work.

For the pure component i , the total interaction energy per mer is ε_{ii}^* . In a binary mixture, there are three kinds of interaction energies called ε_{11}^* , ε_{12}^* and ε_{22}^* at normal pressure when there are only non-specific interactions between two components, where ε_{12}^* is defined as the interaction energy of a mer belonging to component 1 when it is surrounded by z mers belonging to component 2. Therefore the total interaction energy per mer in a binary mixture can be written as (Lacombe & Sanchez, 1976)

$$\varepsilon^* = \phi_1^2 \varepsilon_{11}^* + 2\phi_1 \phi_2 \varepsilon_{12}^* + \phi_2^2 \varepsilon_{22}^* \quad (19)$$

If there are specific interactions as described by Sanchez and Balazs (Sanchez & Balazs, 1989), the total interaction energy per mer becomes a function of temperature and is derived as following:

$$\varepsilon_T^* = \phi_1^2 \varepsilon_{11}^* + 2\phi_1 \phi_2 f_{12}^* + \phi_2^2 \varepsilon_{22}^* \quad (20)$$

where f_{12}^* represents the total interaction Helmholtz energy and

$$f_{12}^* = \varepsilon_{12}^* + \delta \varepsilon^* - kT \ln \left[\frac{1+q}{1+q \exp(-2\delta \varepsilon^* / z k T)} \right] \quad (21)$$

$\delta \varepsilon^*$ corresponds to the increment of the total 1-2 interaction energy with specific interactions and q is the ratio of the statistical degeneracies of the nonspecific and specific interaction states.

According to our previous calculations (An et al. 1997; An & wolf, 1998), the total interaction energy per mer should be linearly dependent on pressure besides as a function of temperature, i.e.,

$$\varepsilon_{T,P}^* = \phi_1^2 \varepsilon_{11}^* + 2\phi_1 \phi_2 \varepsilon_{12}^* + \phi_2^2 \varepsilon_{22}^* \quad (22)$$

where g_{12}^* describes the total interaction Gibbs energy between two components and

$$g_{12}^* = f_{12}^* + (P - P_0)v_{12}^* \quad (23)$$

where P_0 is the reference pressure (normally P_0 is chosen as 1 bar or atmosphere) and v_{12}^* represents the change of interaction volume due to increasing of pressure. When the specific interactions are absent at normal pressure, *i.e.*, $\delta\varepsilon^* = 0$, $P = P_0$, then g_{12}^* will be reduced into ε_{12}^* . In this paper, the spinodals and binodals for the systems TD/PS are calculated by means of a new method without the derivatives of Gibbs energy (Horst, 1995; Horst & Wolf, 1992). On the basis of the FH lattice model (Flory, 1953), the FH interaction parameter, γ , can be expressed as

$$\gamma = \frac{\frac{\Delta G_M^{FH}}{kTV} - \left(\frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right)}{\phi_1 \phi_2} \quad (24)$$

where V is the total volume of a binary polymer system; V_i and ϕ_i represent the molecular volume and the volume fraction of component i , respectively; and ΔG_M^{FH} is the Gibbs energy of mixing in the FH theory.

According to our previous assumptions (An et al. 1997; Sun et al. 1999), eq. 24 can be rewritten by means of the Sanchez-Lacombe (SL) theory,

$$\gamma = \frac{1}{(v^* \tilde{v}) \phi_1 \phi_2} \left\{ \begin{aligned} & \left[\frac{-\tilde{p} + \tilde{P} \tilde{v}}{\tilde{T}} - \left[\phi_1 \frac{-\tilde{p}_1 + \tilde{P}_1 \tilde{v}_1}{\tilde{T}_1} + \phi_2 \frac{-\tilde{p}_2 + \tilde{P}_2 \tilde{v}_2}{\tilde{T}_2} \right] + (\tilde{v} - 1) \ln(1 - \tilde{p}) + \frac{1}{r} \ln \tilde{p} \right. \\ & \left. - \left[\phi_1 \left((\tilde{v}_1 - 1) \ln(1 - \tilde{p}_1) + \frac{1}{r_1^0} \ln \tilde{p}_1 \right) + \phi_2 \left((\tilde{v}_2 - 1) \ln(1 - \tilde{p}_2) + \frac{1}{r_2^0} \ln \tilde{p}_2 \right) \right] \right] \\ & \left. + \phi_1 \left(\frac{1}{r_1^0} \ln \omega_1^0 - \frac{1}{r_1} \ln \omega_1 \right) + \phi_2 \left(\frac{1}{r_2^0} \ln \omega_2^0 - \frac{1}{r_2} \ln \omega_2 \right) \right\} \quad (25) \end{aligned} \right.$$

3. Pressure induced phase separation of TD/PS polymer solutions

The cloud-point temperatures (T_{cl} 's) of trans-decahydronaphthalene (TD)/ polystyrene (PS, $M_w=270\,000$) solutions were determined by light scattering measurements over a range of temperatures (1- 16 °C), pressures (100 to 900 bar), and compositions (4.2-21.6 v% polymer). The system phase separates upon cooling and T_{cl} was found to increase with rising pressure for constant composition. In the absence of special effects this finding indicates positive excess volume for the mixing. Special attention was paid to the demixing temperatures as function of pressure for different polymer solutions and the plots in T - ϕ plane (where ϕ signifies volume fractions). The cloud-point curves of polymer solution under pressures were observed for different compositions, which demonstrates that pressure has more effect on the TD/PS solutions that far from the critical point than that near the critical point. Figure 1 shows isopleths (*i.e.*, lines of constant composition of the solution) cloud-point curves observed for TD/PS polymer solutions 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 $\phi = 4.2, 8.4, 12.8, 17.2$, and 21.6 (v% at $P=1$ bar), respectively.

The clout point curves at each composition behave similarly to one another. The region above the curve is the one-phase homogeneous region, while the region below represents the two-phase region. As shown, the phase separation pressures increase with raising temperature.

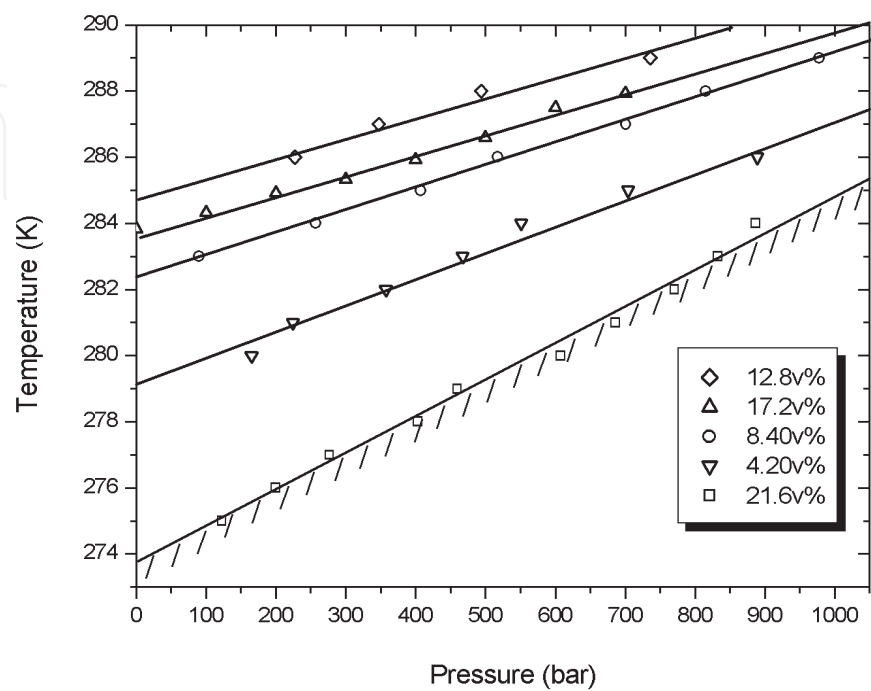


Fig. 1. Pressure dependence of phase transition temperature for TD/PS polymer solution at the indicated compositions (In SI units: 1bar = 10⁵ N m⁻²).

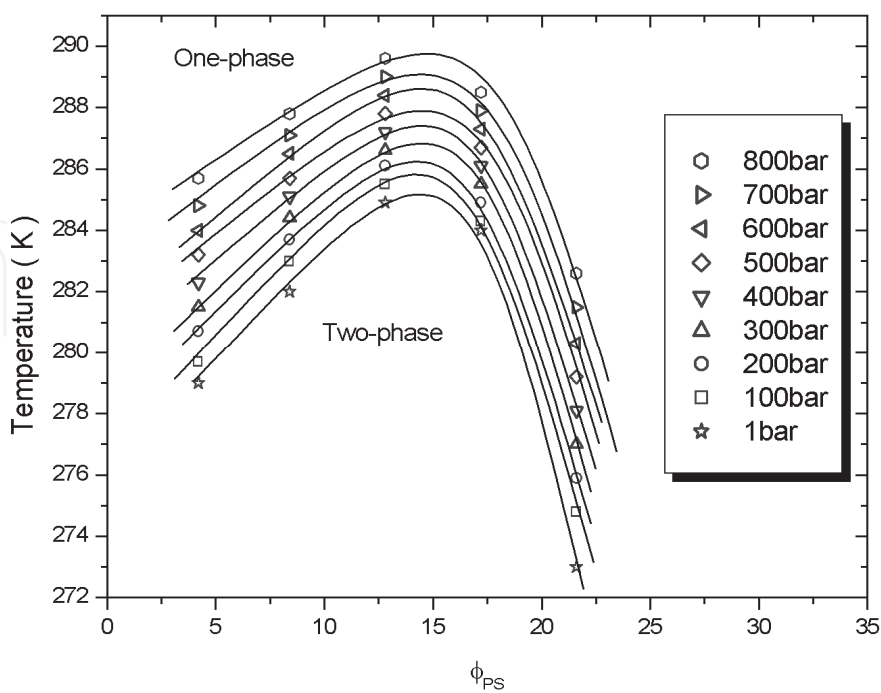


Fig. 2. Coexistence curves of TD/PS system at various pressures on a T - ϕ plane.

With the pre-selected polymer concentrations, isobaric critical lines can be constructed from the isopleths in Figure 1. The thus obtained critical lines from 100 bar to 800 bar, respectively, show in Figure 2 on a $T-\phi$ plane. In Figure 2 the coexistence boundaries are described on a $T-\phi$ plane at the indicated pressures (bar)(the boundary under 1 bar was extrapolated from Figure 1). The shape of the coexistence curve depends only slightly on pressure, which can be recognized by comparing the curve at 100bar with the curve at 800 bar, and this system shows that it is an upper critical solution temperature (UCST) behavior system.

PVT Diagram

The PVT property of PS was determined with a PVT-100 dilatometer. The experimental data was determined as a series of isotherms. Figure 3 presents the selected isobars with the interval of pressure 200bar and shows the specific volume, V_{sp} , of PS as a function of temperature and pressure. The open circles represent the experimental data, the solid lines describe the behavior of the data points in the equilibrium melt state and extrapolated to the glassy state of PS, and the dot lines AB, CD, EF, and GH separate the diagram into five parts; with the increase of temperature, the five parts includes three parts that are glassy (the range between AB and CD), exceptional (the range between CD and EF), and melt states (the range between EF and GH), separately. In the exceptional area, a glass is reformed by pressurization from the melt during isothermal compression (Schmidt & Maurer, 1998; Tait 1888). From Figure 3, it can be seen that the change of the PS specific volume in the glassy state is much smaller than that in the melt state with the changes of temperature and pressure. The PS specific volume decreases rapidly with the increase of pressure in the melt state. From the experimental results of the phase behavior of TD/PS polymer solution under pressure we knew that during the experiment for the measurements of TD/PS polymer solution phase behavior under pressure, PS is in the equilibrium state and at relative low temperature that is the glassy temperature for bulk PS. We deduced that the scaling parameters of PS fitted from low temperature and high temperature must be different. In order to get the data in equilibrium state at low temperature, we extrapolated the lines from the melt state to the glassy state. Both of the data from the equilibrium melt state and the extrapolated were used to obtain two series scaling parameters of PS by fitting the PVT data to the SL equations of state as described above and to estimate which series scaling parameters could be used to describe the thermodynamics of TD/PS polymer solution under pressure better.

Scaling Parameters

Fitting the PVT data that in the range between AB and CD (extrapolated to the glassy state temperature in Figure 3) and in the range between EF and GH (equilibrium melt state in Figure 3) to the SL equations of state, *i.e.*, eqs 4 and 6, we obtained two series scaling parameters, each includes three scaling parameters P^* , ρ^* , and T^* (or ε^* , v^* , and r) of PS. The scaling parameters of PS and TD are listed in Table 1. In order to evaluate the scaling parameters that obtained from different state of the sample, we used them for the calculations in SLLFT based on the data in Figure 2 in atmospheric pressure. The calculated spinodals are shown in Figure 4. From Figure 4, it can be seen that the critical temperature (T_c) calculated with the scaling parameters obtained from the extrapolated data of PS is close to the experimental results (Figure 4b). We can know that the scaling parameters

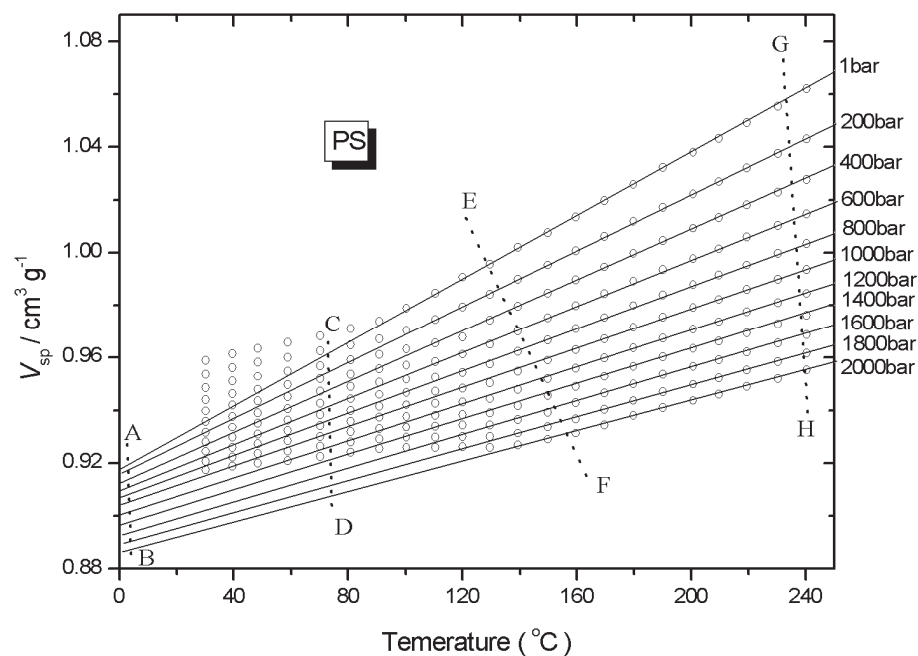


Fig. 3. Specific volume, V_{sp} , of PS as a function of temperature and pressure. The open circles represent the experimental data, respectively, and the solid lines AB, CD, EF and GH separate the diagram into five parts, which including glassy, exceptional and melt states.

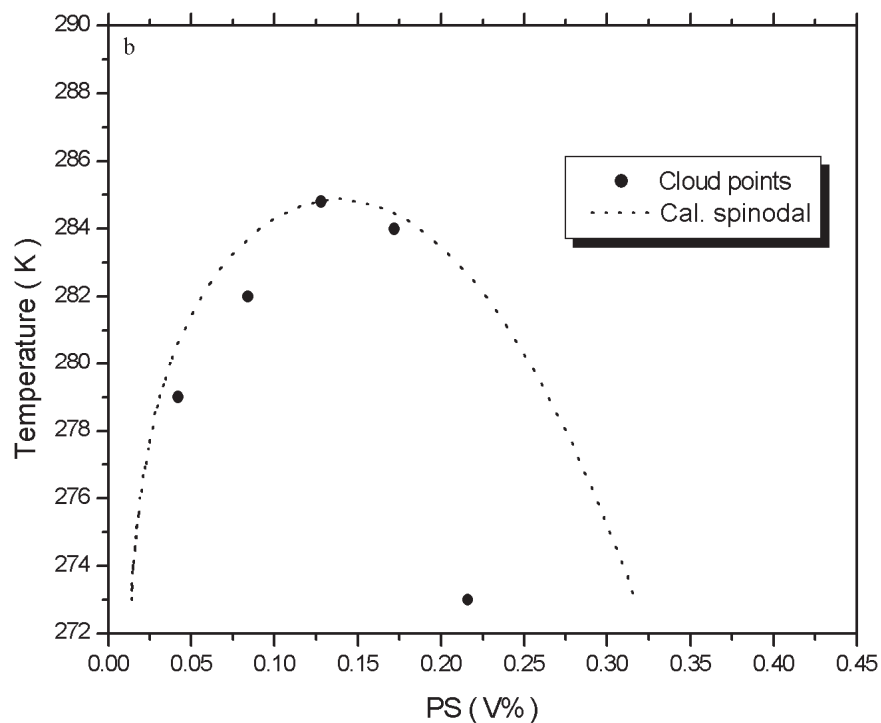


Fig. 4. The calculated spinodals of TD/PS polymer solutions by SL theory with two series of PS scaling parameters and compared with the experimental result at atmosphere (a: the calculation according to the scaling parameter of PS* in Table 1; b: the calculation according to the scaling parameters of PS in Table 1).

obtained from the glassy state temperature (the temperature range for the measurements of TD/PS phase behavior under pressure) of PS fit the experimental results better than that obtained from the equilibrium melt state (Figure 4a). The reason is that the phase separation behavior of the polymer solutions was measured in the temperature range that bulk PS is at glassy state temperature but in equilibrium state. The further calculations were based on the series scaling parameters obtained from the data of PS that extrapolated to the glassy temperature in Figure 3.

Pressure dependence of phase separation behaviors

From eqs 20, 21 and 23, the interaction Gibbs energy without specific interactions can be re-expressed into(An & Wolf, 1998)

$$g_{12}^* = \varepsilon_{12}^*(P = P_0) - (P - P_0)v_{12}^*$$

(26)

where $\varepsilon_{12}^*(P = P_0)$ for infinite molecular weight results to be -12.7K and for the present system the corresponding evaluation yields $v_{12}^*N_A = 0.033 \text{ cm}^3/\text{mol}$, where N_A is the Avogadro number.

	T_i^*/K	P_i^*/bar	$\rho_i^*/\text{g cm}^{-3}$
TD	621	3110	0.935
PS	714	4432	1.068
PS*	725	4041	1.025

Table 1. Scaling parameters of TD and PS.The scaling parameters for TD were taken from the literature (Inre et al. 2001); those of PS stem from the evaluation of PVT data in the melt state and PS* stem from the evaluation of PVT data extrapolated from the measurements at higher temperature into the *T*-region of experiment for TD/PS polymer solution.

Spinodals and binodals under pressure

Like the spinodals and binodals of ternary and quaternary polymer blends were calculated with the method(Horst 1995; Horst & Wolf, 1992) (the knowledge of the first and second derivatives of ΔG with respect to the composition variables is not required), the spinodals and the binodals of the TD/PS system were calculated with the SL theory under different pressures.

Figure 5 shows the calculated results of the spinodals and the binodals compared with the experimental data as showed in Figure 2. The dashed and the solid lines represent the spinodals and the binodals calculated with the SL theory under indicated pressures, respectively; the solid circles represent the experimental data, respectively, which were obtained from Figure 2. In Figure 5 the qualitative agreement between the spinodals and the binodals calculated and the experimental cloud points is acceptable at different pressure. From Figure 5, it can be seen that the critical temperatures (T_c) calculated by means of FL theory under different pressure increase with pressure.

Interaction energy parameters under pressure

In previous paper (An et al, 1997; An & Wolf, 1998), the only one adjustable interaction energy parameter, g_{12}^*/k , in the SLLFT was evaluated by comparing the theoretical and the experimental phase diagrams at atmospheric pressure. For the high pressure, g_{12}^*/k was

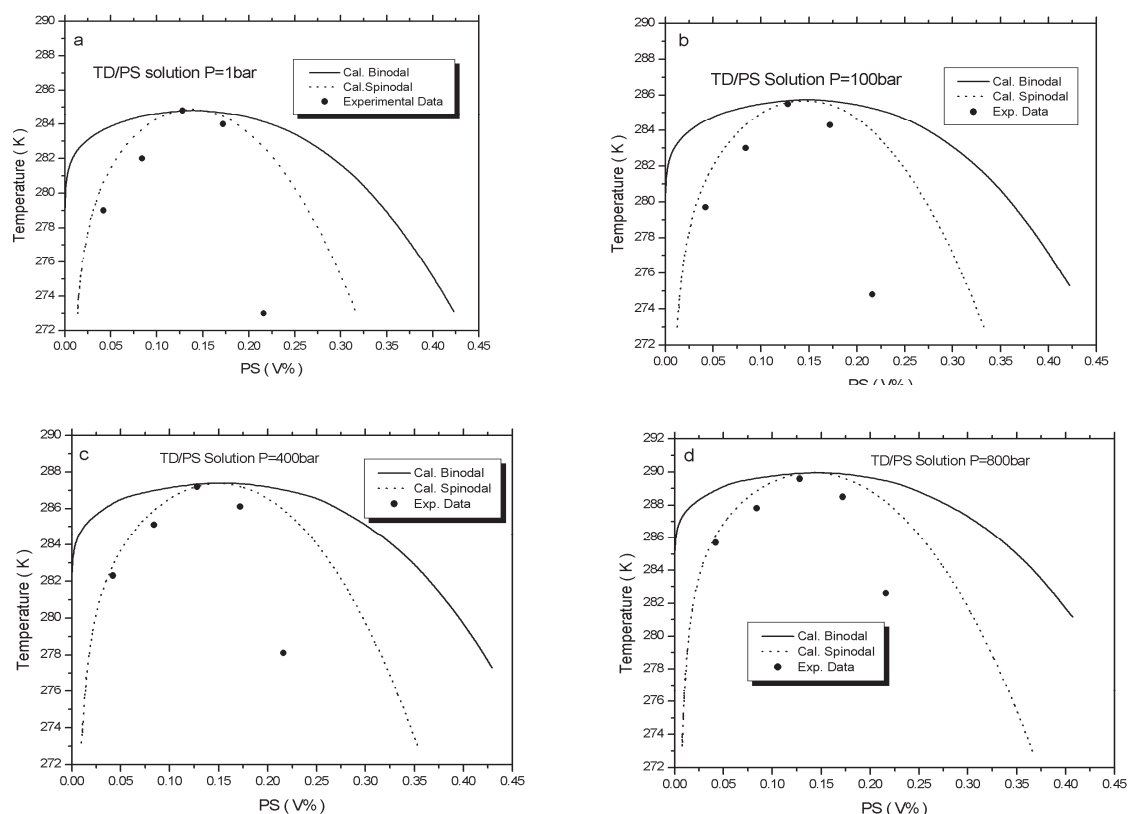


Fig. 5. Spinodals and binodals of TD/PS polymer solutions calculated with SL theory under the indicated pressures (the experiment data obtained from Figure 3).

calculated by eq. 25, and then used for the phase diagram calculation under pressure. In this work, however, g_{12}^*/k can be fitted from experimental cloud points, and the fitted g_{12}^*/k with pressure was shown in Figure 6. The solid circles are the fitted results from experimental cloud points and the dot curve represents the values of fitted data. From Figure 6 we can see that the interaction energy parameter deduces with pressure, which is different from the result that calculated from eq. 26. In that equation, the interaction energy parameter will be linearly reduced with pressure, but for the result from Figure 6 is not the case.

FH interaction parameter

In the Flory-Huggins theory model (Koningsveld & Staverman, 1968), the interaction parameter (γ) was considered as a function of composition and temperature. The Flory-Huggins interaction parameter was dependent on the concentration of the components, temperature and pressure in the mean-field lattice-gas (MFLG) model and semi-phenomenological treatment (van Opstal & Koningsveld, 1992). According to the results of our calculation, the Flory-Huggins interaction parameter should be as a function of P , T , and ϕ for the system of TD/PS.

The FH interaction parameter, γ , was calculated with eq. 24 under different pressures. Figure 7 shows the temperature and blend composition dependences of γ for the TD/PS polymer solutions under the indicated pressures.

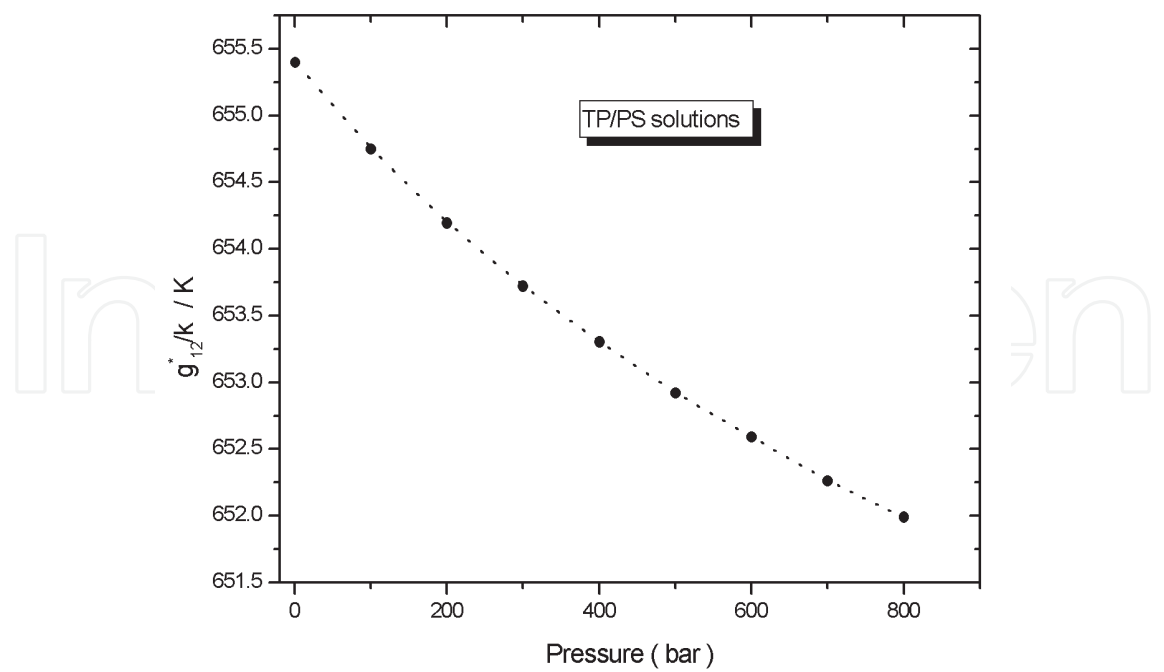


Fig. 6. Fitted interaction energy parameter under pressure with experimental results by the means of SL theory.

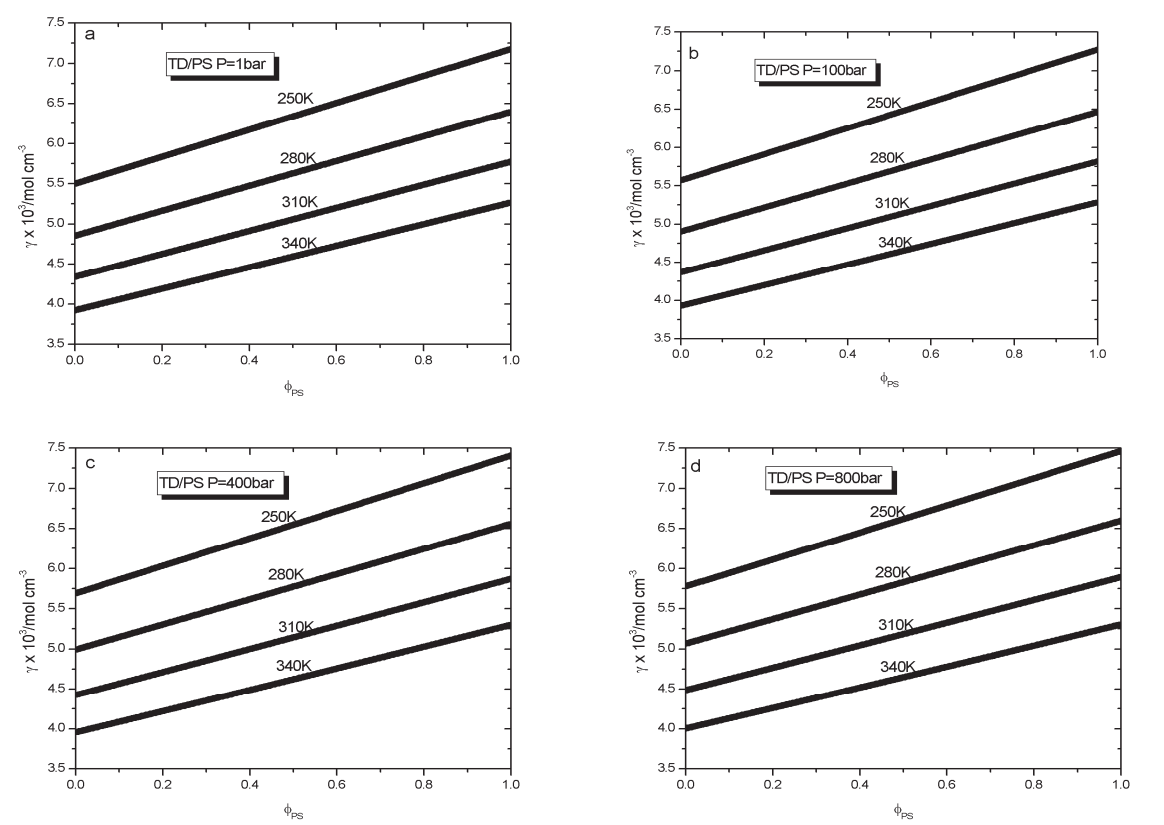


Fig. 7. Temperature and polymer solution composition dependences of the FH interaction parameter, γ , for the TD/PS polymer solutions under the indicated pressures.

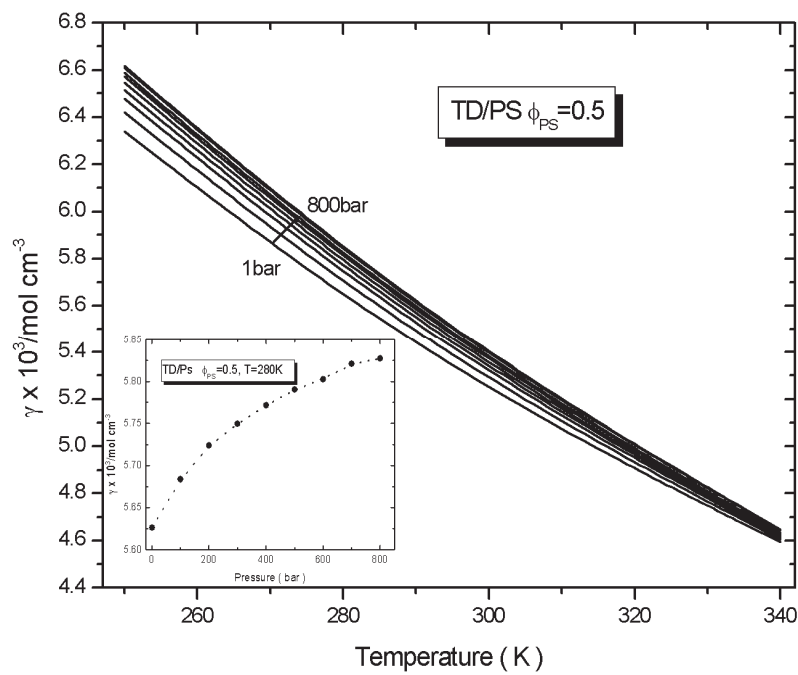


Fig. 8. Temperature dependences of the FH interaction parameter, γ , for the TD/PS polymer solutions at the indicated composition (the curves are the isobaric curves under 1, 100, 200, 300, 400, 500, 600, 700 and 800bar. The inserted figure shows pressure dependences of the FH interaction parameter, γ , for the TD/PS polymer solutions with fixed composition and temperature).

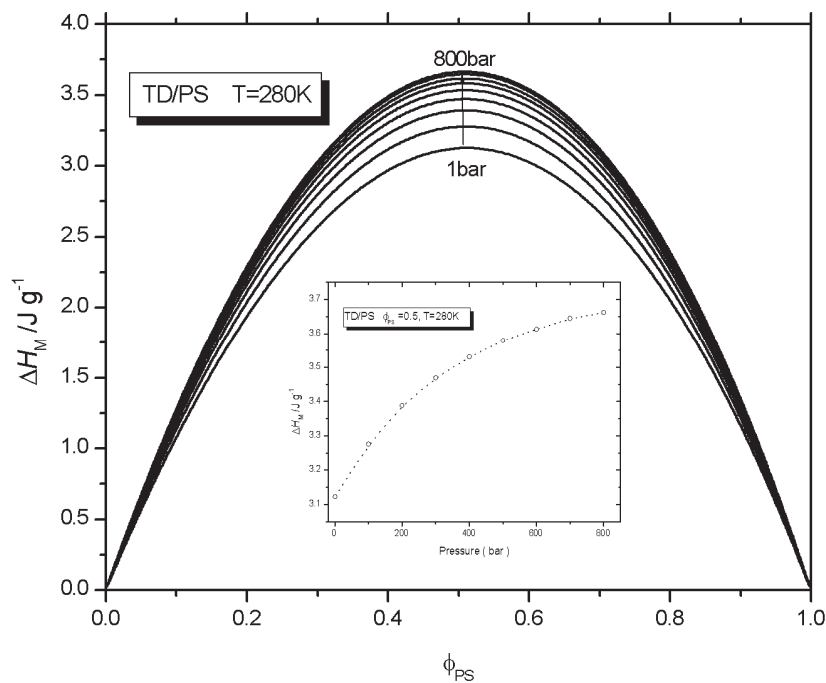


Fig. 9. Pressure and polymer solution composition dependences of the enthalpy of the mixing, ΔH_M , for the TD/PS polymer solutions at the indicated temperature (the inserted figure shows pressure dependences of the enthalpy of the mixing, ΔH_M , for the TD/PS polymer solutions with fixed composition and temperature).

Figure 7 shows the dependence of Flory-Huggins interaction parameter on pressure and temperature against concentration. We can see that the Flory-Huggins interaction parameter is linear increasing with the composition of PS increases. It also can be observed that the FH interaction parameter reduces with the increasing of temperature at the fixed composition and pressure, which agrees with the experiment result that this system exhibits UCST behavior. The effects of pressure and temperature on γ are identical with that derived by de Loos *et al.* for the systems polyethylene/ethylene (de Loos *et al.* 1983).

Figure 8 shows the plots of the Flory-Huggins interaction parameters against temperature at fixed PS concentration ($\phi_{ps} = 0.5$) under different pressures. It is shown that γ is almost linear with the temperature and decreases with the increasing of temperature, and the inserted figure shows that γ increases with pressure at fixed temperature and composition, which is consistent with the experimental measured results that TD/PS system shows low critical solution pressure (LCSP) behavior.

From these results calculated, the relations of temperature, pressure, and concentration of TD/PS polymer solutions are presented. The influence of pressure on calculated Flory-Huggins interaction parameter of TD/PS polymer solution shows that Flory-Huggins interaction parameter increases on raising the pressure, i.e., miscibility is reduced.

Enthalpy of mixing

It is known that the Gibbs energy can be split into its enthalpic and entropic parts in the SL theory (Lacombe & Sanchez, 1976; Sanchez & Lacombe, 1978). The enthalpy of mixing per mer, $\Delta \bar{H}_M$, is given by

$$\Delta \bar{H}_M = \frac{\Delta H_M}{rN} = \bar{H}_M - \phi_1 \bar{H}_1 - \phi_2 \bar{H}_2 = \varepsilon^* (-\tilde{\rho} + \tilde{P}\tilde{v}) - \phi_1 \varepsilon_{11}^* (-\tilde{\rho}_1 + \tilde{P}_1 \tilde{v}_1) - \phi_2 \varepsilon_{22}^* (-\tilde{\rho}_2 + \tilde{P}_2 \tilde{v}_2) \quad (27)$$

where \bar{H}_M and \bar{H}_i are the enthalpies per mer of the blend and component i , respectively. In order to investigate the pressure effects on $\Delta \bar{H}_M$ of TD/PS polymer solution, we calculated $\Delta \bar{H}_M$ under different pressures with eq. 27 at fixed temperature, and the results are shown in Figure 9. The insert Figure shows the pressure effects on $\Delta \bar{H}_M$ in TD/PS polymer solution, when the composition $\phi_{ps} = 0.5$ and the temperature is 280K. From Figure 9, we can see that the calculated $\Delta \bar{H}_M$ increases with pressure, which means that increasing pressure on TD/PS polymer solution is not favorable for TD/PS system to be homogeneous polymer solution.

Volume change of mixing

As the Clausius-Clapeyron indicates that the phase behavior of a mixture under pressure is governed by the sign of the excess volume of mixing; for polymer solution is the same. Therefore we will analyse the reduced excess volume or the volume change of mixing. In the SL theory (Lacombe & Sanchez, 1976; Sanchez & Lacombe, 1978), volume changes upon mixing are calculable. The volume change of mixing, ΔV_M , is respectively given by

$$\Delta V_M = V - V_1 - V_2 = V^* \tilde{v} - V_1^* \tilde{v}_1 - V_2^* \tilde{v}_2 \quad (28)$$

where V_i and V are the volumes of pure component i and the solution, respectively.

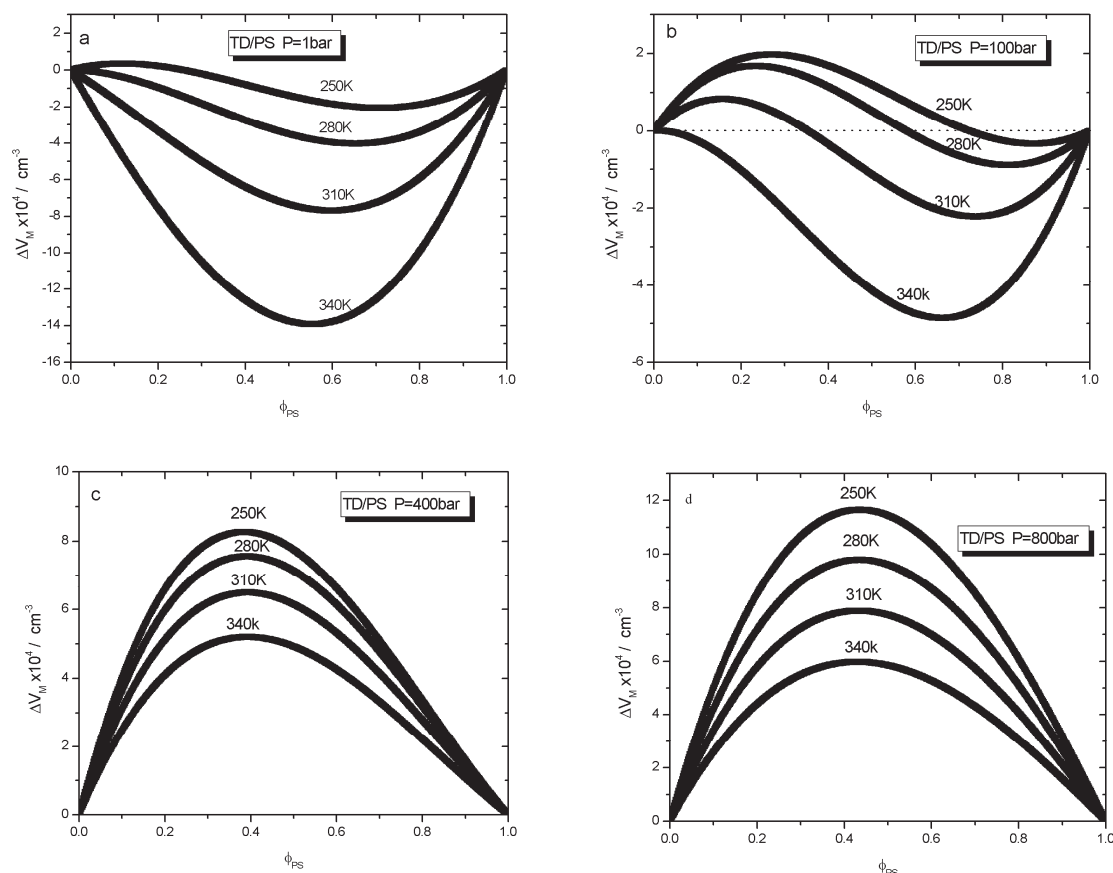


Fig. 10. Temperature and polymer solution composition dependences of the volume change of the mixing, ΔV_M , for the TD/PS polymer solutions under the indicated pressures.

Figure 10 shows the temperature and polymer solution composition dependences of ΔV_M calculated with eq. 28 for the TD/PS solutions under the indicated pressures. For fixed pressure and composition, the volume change of mixing reduces with temperature increasing. Within the calculated range, for low pressure and high temperature it is negative but becomes positive on raising the pressure or reducing the temperature.

In order to observe the pressure effects on the volume change of mixing for TD/PS polymer solution, we calculated the excess volume of TD/PS polymer solutions at 280K for various pressures. Figure 11 shows the volume change of TD/PS polymer solutions vs composition calculated with eq. 28 at 280K for the indicated pressures. We can know more clearly from Figure 11 that for low pressure the volume change is negative but becomes positive on raising the pressure. The change of sign occurs at about 100bar. At this pressure ΔV_M is still positive for low concentrations of PS, while for high PS concentrations it is already negative. This means that in this pressure range the miscibility on the PS-rich side is improved by raising pressure and is lowered on the TD-rich side, i.e., the phase diagram becomes distorted. Therefore, the shift of the temperatures of mixing and demixing on varying the pressure is small, so that the shape of the phase diagram hardly changes.

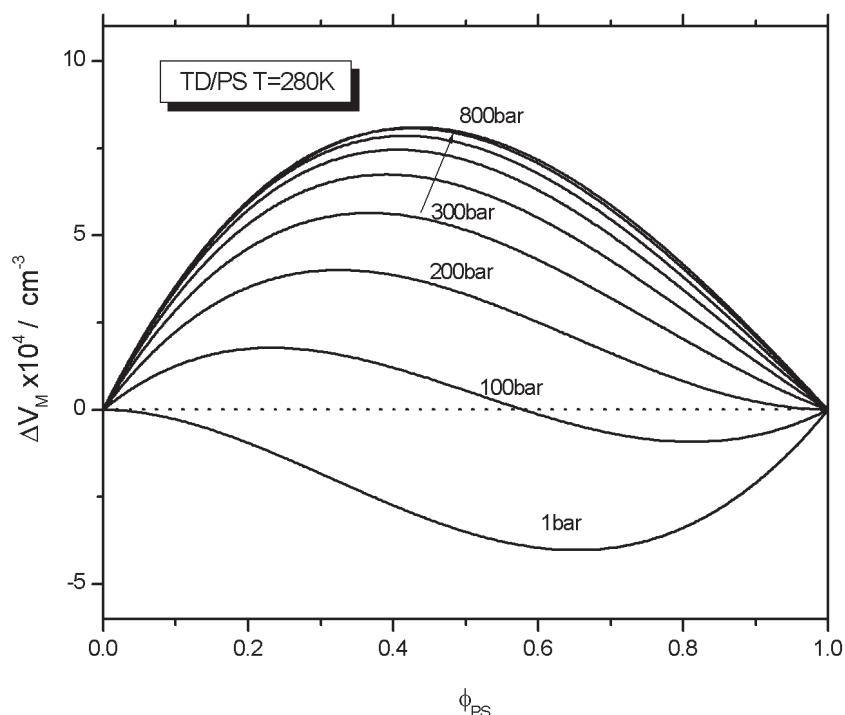


Fig. 11. Pressure and polymer solution composition dependences of the volume change of the mixing, ΔV_M , for the TD/PS polymer solutions at the indicated temperature.

4. Pressure induced miscibility in PEO/(P (EO-b-DMS) mixtures

The cloud-point temperatures (T_{cl} 's) of poly (ethylene oxide) (PEO) and poly (ethylene oxide-b-dimethylsiloxane) (P (EO-b-DMS)) homopolymer and block-oligomer mixtures were determined by turbidity measurements over a range of temperatures (105 to 130 °C), pressures (1 to 800 bar), and compositions (10-40 wt% PEO). The system phase separates upon cooling and T_{cl} was found to decrease with rising pressure for constant composition. In the absence of special effects this finding indicates negative excess volumes. Special attention was paid to the demixing temperatures as function of pressure for different polymer mixtures and the plots in T - Φ plane (where Φ signifies volume fractions). The cloud-point curves of polymer mixture under pressures were observed for different compositions. Figure 12 shows isopleths (i.e., curves of constant composition of the mixtures) cloud-point curves observed for polymer mixtures on a temperature-pressure plane. The open circles indicate experimental points and the solid curves are just a guide for the eye. The curves were measured at $\Phi = 9.7, 19.4, 29.2$, and 39.1 (PEO v% at $P=1$ bar), respectively. The region above the curves is the one-phase homogeneous region, while the region below represents the two-phase region. As shown, the demixing pressures increase with increasing temperature.

This binary system has been studied at four compositions under pressure. With the reservations concerning polymer concentrations, isobaric critical lines can be constructed from the isopleths of Figure 12. The thus obtained critical lines from 1 bar to 600 bar, respectively, show in Figure 13 on a T - ϕ plane (the cloud points at $P=1$ bar were measured with laser apparatus at atmosphere). In Figure 13 the coexistence boundaries are described on a T - ϕ plane at the indicated pressures (bar). The shape of the coexistence curve depends

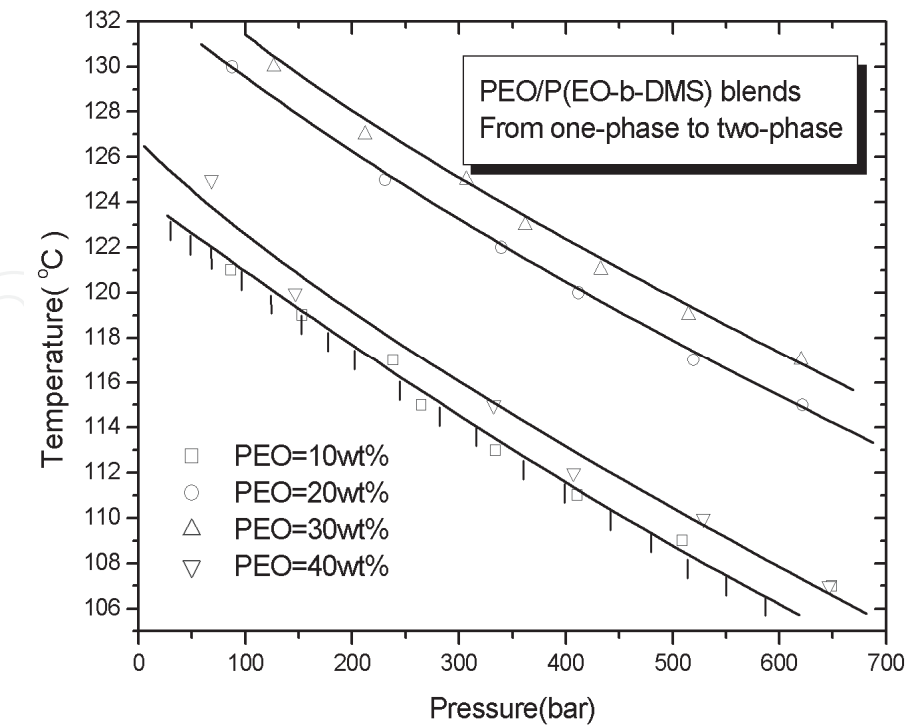


Fig. 12. Pressure dependence of T_{cp} for the system PEO/P(EO-b-DMS) (In SI units: 1bar = 10^5 N m^{-2}).

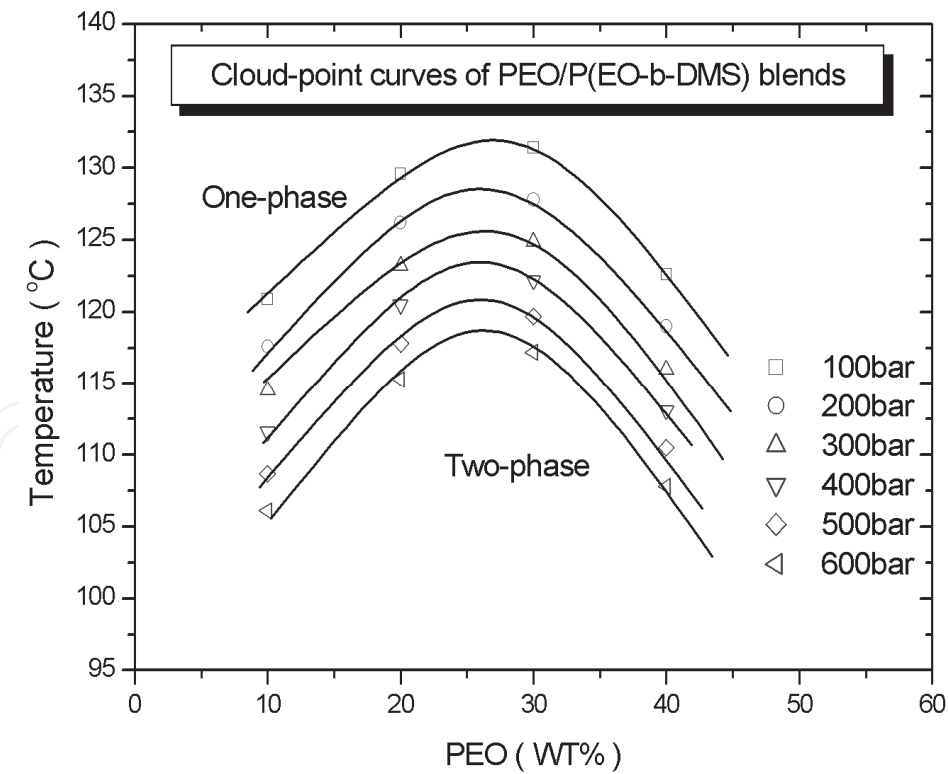


Fig. 13. Coexistence curves of PEO/P(EO-b-DMS) system at various pressures on a $T-\phi$ plane. only slightly on pressure, which can be recognized by comparing the curve at 1bar with the curve at 600 bar, and this system shows that it is a UCST behavior system.

Scaling Parameters.

Within the framework of the Sanchez-Lacombe theory, we set up the following combining rules for the molecular weight and the scaling parameters for P(EO-b-DMS) block copolymer:

$$M_{COP}^{SL} = M_{P(EO-b-DMS)} + M_f \quad (29)$$

$$P_{COP}^{*SL} = \phi_{PEO} P_{PEO}^* + \phi_{PDMS} P_{PDMS}^* + \phi_{PEO} \phi_{PDMS} P_f^* \quad (30)$$

$$T_{COP}^{*SL} = \phi_{PEO} T_{PEO}^* + \phi_{PDMS} T_{PDMS}^* + \phi_{PEO} \phi_{PDMS} T_f^* \quad (31)$$

$$\rho_{COP}^{*SL} = \phi_{PEO} \rho_{PEO}^* + \phi_{PDMS} \rho_{PDMS}^* + \phi_{PEO} \phi_{PDMS} \rho_f^* \quad (32)$$

where M_{COP}^{SL} , P_{COP}^{*SL} , T_{COP}^{*SL} and ρ_{COP}^{*SL} are the modified molecular weight and reduced pressure, temperature, density of the block copolymer according to the new combining rules for Sanchez-Lacombe theory; $M_{P(EO-b-DMS)}$, P_{PEO}^* , P_{PDMS}^* , T_{PEO}^* , T_{PDMS}^* , ρ_{PEO}^* , and ρ_{PDMS}^* are the real molecular weight for the block copolymer, the reduced pressure, temperature and density of PEO and PDMS; M_f , P_f^* , T_f^* , and ρ_f^* are the adjusting parameters for the molecular, reduced pressure, temperature, and the density of the block copolymer; ϕ_{PEO} and ϕ_{PDMS} are the volume fraction of PEO and PDMS in the block copolymer. According to the new combining rules, we can get the characteristics of the homopolymer and the block copolymer, and they are collected in Table 2.

The scaling parameters for PEO were taken from the literature (Konowalow, 1903), those of P(EO-b-DMS) were calculated with the chemical structure of P(EO-b-DMS) and P(EO-b-DMS)* were calculated with the new combine rules for the diblock copolymer parameters. In this paper, the parameters of P(EO-b-DMS)* were used for the calculation as the parameters of block copolymer component.

In order to evaluate the new combining rules and the scaling parameters that obtained in Table 2, we used them for the calculations in SLLFT based on the experimental data in Figure 14 which obtained at atmospheric pressure. The calculated spinodals with the different scaling parameters and the measured data are shown in Figure 14. From Figure 14, it can be seen that the critical temperature (T_c) calculated with the scaling parameters obtained from the new combining rules for P(EO-b-DMS) is close to the experimental results (Figure 14b). We can know that the scaling parameters obtained from the new combining rules for the block copolymer fit the experimental results better than that obtained from the molecular structure (Figure 14a). The reason is that PEO/P(EO-b-DMS) polymer mixture is a special polymer blend system, the structures of the two components i.e., PEO and P(EO-b-DMS) are special, and the molecular weight of PEO is much larger than that of the block copolymer; at the same time, maybe the two components constitute the cluster in the mixtures, and the structures of the components are not the original structures of PEO and P(EO-b-DMS). So the molecular weight and the scaling parameters obtained with the new combining rules for the block copolymer fit the experimental data better. The further calculations were based on the series scaling parameters obtained from the new combining rules for the block copolymer.

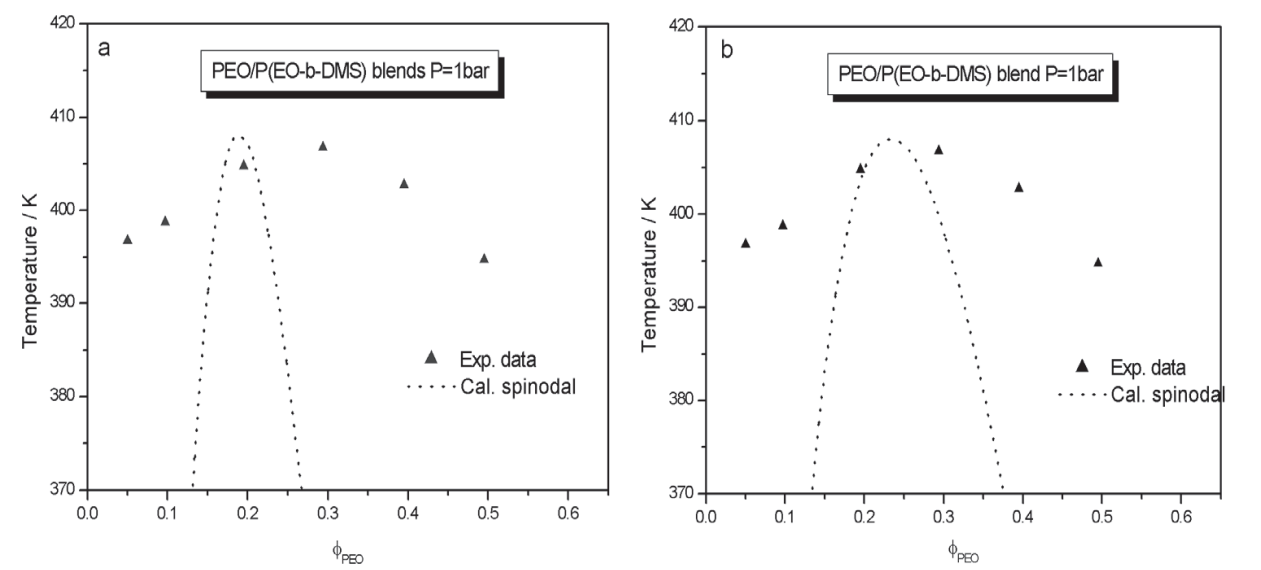


Fig. 14. The calculated spinodals of PEO/P(EO-b-DMS) polymer mixtures by SL theory compared with the experimental result (a: the calculation according to the scaling parameter of P(EO-b-DMS) in Table 1; b: the calculation according to the scaling parameters of P(EO-b-DMS)* in Table1).

Polymer	$M_w/\text{kg mol}^{-1}$	T_i^*/K	P_i^*/bar	$\rho_i^*/\text{g cm}^{-3}$
PEO	35.0	656	4922	1.178
P(EO-b-DMS)	1.8	609	4413	1.160
P(EO-b-DMS)*	3.0	622	4555	1.165

Table 2. Sample characteristics of PEO and P(EO-b-DMS).

Spinodals and binodals under pressure

Like the spinodals and binodals of ternary and quaternary polymer blends were calculated with the method(Horst 1995; Horst & Wolf, 1992) (the knowledge of the first and second derivatives of ΔG with respect to the composition variables is not required), the spinodals and the binodals of the PEO/P(EO-b-DMS) system were calculated with the SL theory under different pressures. Figure 15 shows the calculated results of the spinodals and the binodals compared with the experimental data as showed in Figure 14. The dashed and the solid lines represent the spinodals and the binodals calculated with the SL theory under indicated pressures, respectively; the open circles represent the experimental data, respectively, which were obtained from Figure 14. In Figure 4 the qualitative agreement between the spinodals and the binodals calculated and the experimental cloud points is acceptable at different pressure. From Figure 15, it can be seen that the critical temperatures (T_c) calculated by means of FL theory under different pressure increase with pressure.

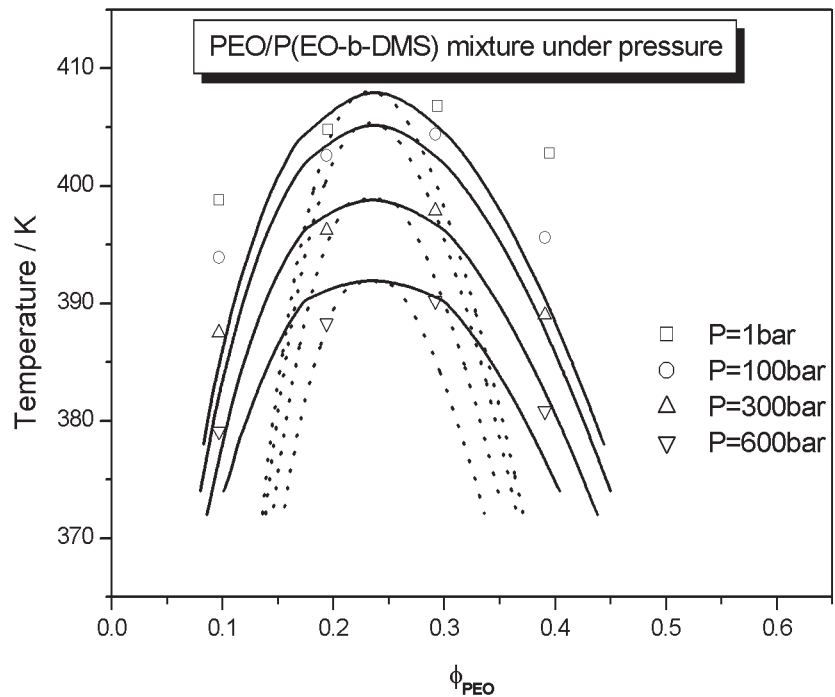


Fig. 15. Spinodals and binodals of P(EO-b-DMS) polymer mixtures calculated with SL theory (the experiment data obtained from Figure 13).

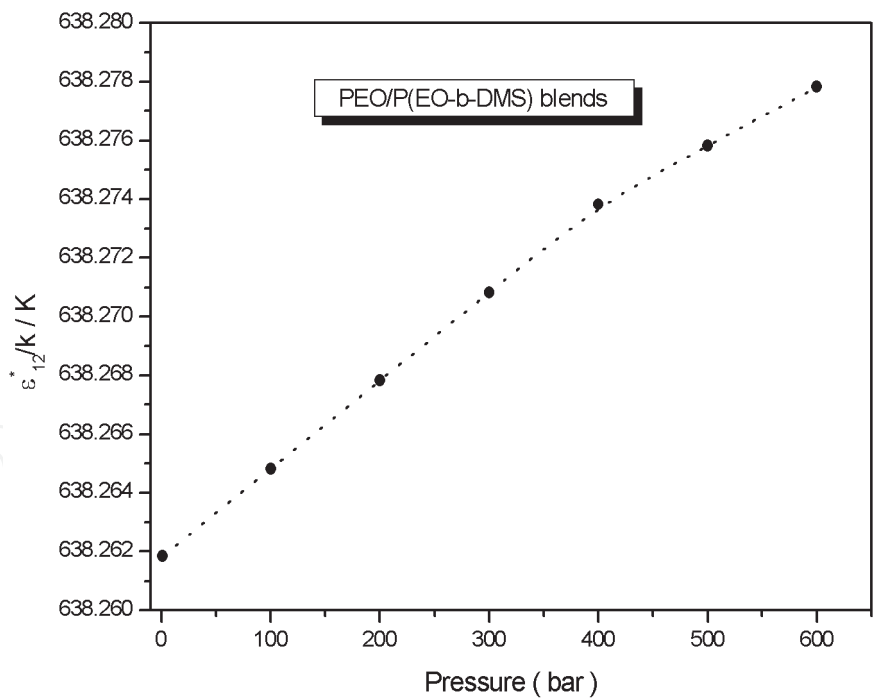


Fig. 16. Fitted interaction energy parameter under pressure with experimental results by the means of SL theory.

Interaction energy parameters under pressure

In the reports(An et al. 1997; An & Wolf, 1998), the only one adjustable interaction energy parameter, g_{12}^* / k , in the SLLFT was evaluated by comparing the theoretical and the

experimental phase diagrams at atmospheric pressure. For the high pressure, g_{12}^*/k was calculated by eq. 26, and then used for the phase diagram calculation under pressure. In this work, however, g_{12}^*/k can be fitted from experimental cloud points, and the fitted g_{12}^*/k with pressure was shown in Figure 16. The solid circles are the fitted results from experimental cloud points and the dot curve represents the values of fitted data. From Figure 16 we can see that the interaction energy parameter increases with pressure, which is different from the result that calculated from eq. 26. In that equation, the interaction energy parameter will be linear coherent with pressure, but for the result from Figure 16 is not the case.

FH interaction parameter

In the Flory-Huggins theory modified (Koningsveld & Staverman, 1968), the interaction parameter (γ) was considered as a function of composition and temperature. The Flory-Huggins interaction parameter was dependent on the concentration of the components, temperature and pressure in the MFLG model and semi-phenomenological treatment (van Opstal & Koningsveld, 1992). According to the results of our calculation, the Flory-Huggins interaction parameter should be as a function of P , T , and ϕ for the system of PEO/P(EO-b-DMS).

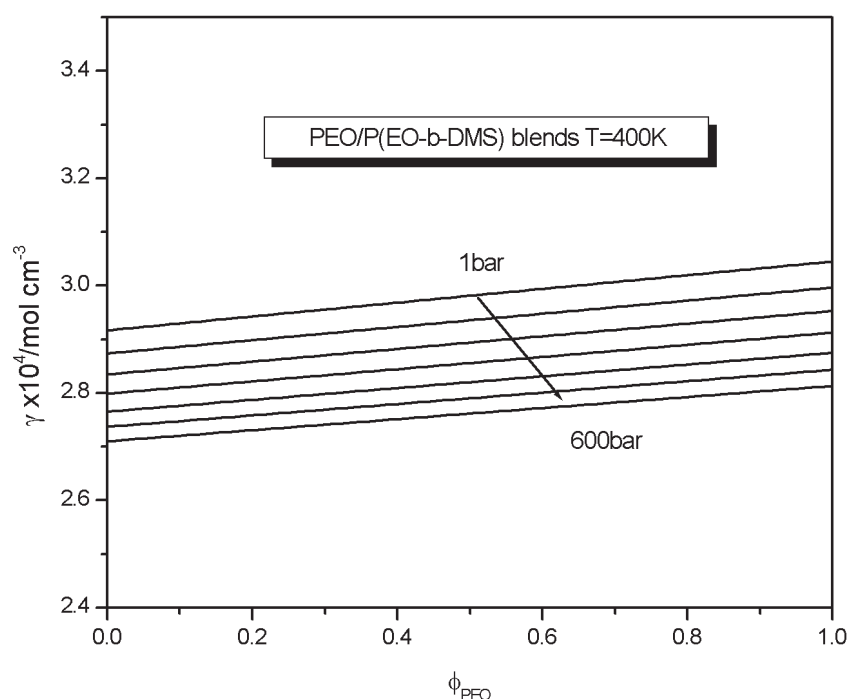


Fig. 17. Pressure and polymer mixture composition dependences of the FH interaction parameter, γ , for the P(EO-b-DMS) polymer mixtures under the indicated temperature.

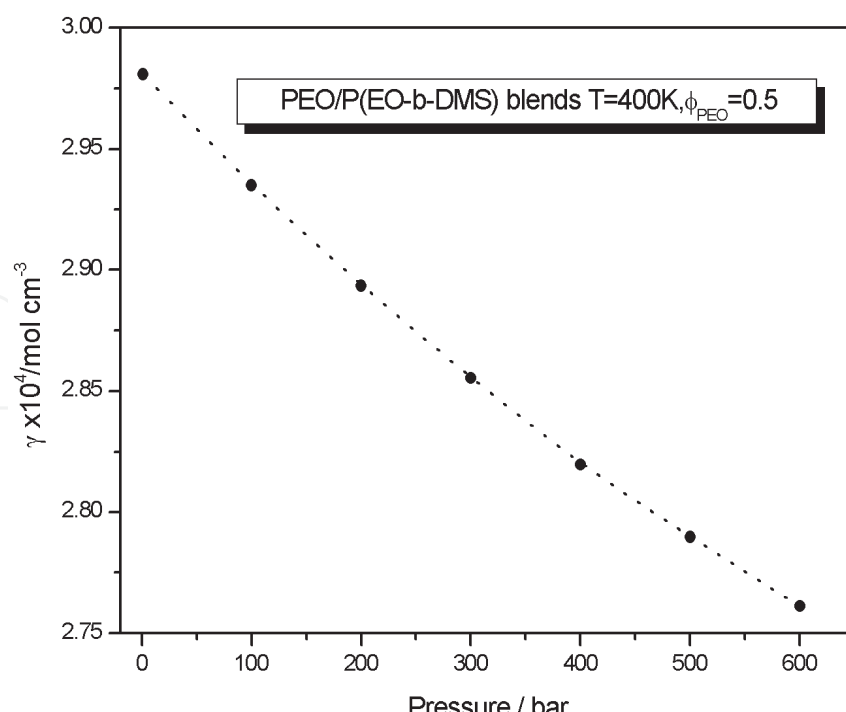


Fig. 18. Pressure dependences of the FH interaction parameter, γ , for the P(EO-b-DMS) polymer mixtures at the indicated composition and temperature.

The FH interaction parameter, γ , was calculated with eq. 25 under different pressures. Figure 17 shows the temperature and blend composition dependences of γ for the PEO/P(EO-b-DMS) mixtures under the indicated pressures.

Figures 17 shows the dependence of Flory-Huggins interaction parameter on pressure and temperature against concentration. We can see that the Flory-Huggins interaction parameter is almost linear increasing the composition of PEO increases at fixed temperature and pressure. It also can be observed that the FH interaction parameter reduces with the increasing of temperature at the fixed composition and pressure, which agrees with the experiment result that this system exhibits UCST behavior. The effects of pressure and temperature on γ are identical with that derived by de Loos *et al.* for the systems polyethylene/ethylene(de Loos *et al.* 1983).

Figure 18 shows the plots of the Flory-Huggins interaction parameters against PEO concentration at fixed temperature ($T=400\text{K}$) under different pressures. It is shown that γ reduces with pressure at the fixed PEO concentration in the mixture, which is consistent with the experimental measured result that PEO/P(EO-b-DMS) system shows pressure-induced miscibility behavior.

From these results calculated, the relations of temperature, pressure, and concentration of PEO/P(EO-b-DMS) mixtures are presented. The influence of pressure on calculated Flory-Huggins interaction parameter of PEO/P(EO-b-DMS) mixtures shows that Flory-Huggins interaction parameter deduces on raising the pressure, i.e., miscibility is enhanced.

Enthalpy of mixing

In order to investigate the pressure effects on ΔH_M of PEO/P(EO-b-DMS) mixture, we calculated ΔH_M under different pressures with eq. 30 at 400K, and the results are shown in Figure 19. Figure 20 shows the pressure dependences of calculated ΔH_M on the fixed

temperature and composition. From Figure 19 and 20, we can see that the calculated ΔH_M is not affected so much by the pressure and temperature. But in all calculated case, $\Delta H_M > 0$, which means that increasing pressure on PEO/P(EO-b-DMS) mixture is favorable for PEO/P(EO-b-DMS) system to be homogeneous polymer blend.

Volume Change of Mixing.

The volume change of mixing, ΔV_M , and the fractional volume change of mixing, $\Delta V_M / V$, is respectively given by eq. 28 and

$$\frac{\Delta V_M}{V} = 1 - \frac{1}{\tilde{v}}(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2) \quad (33)$$

Figure 21 shows the temperature and polymer mixture composition dependences of $\Delta V_M / V$ calculated with eq. 33 for the PEO/P(EO-b-DMS) mixtures under the indicated pressures. For fixed pressure and composition, the volume change of mixing increases with temperature increasing. Within the calculated range $\Delta V_M / V$ is negative, which means this system exhibits abnormal phase behavior under pressure.

In order to observe the pressure effects on the volume change of mixing for PEO/P(EO-b-DMS) mixture, we calculated the excess volume of PEO/P(EO-b-DMS) mixtures at 400K for various pressures. Figure 22 shows $\Delta V_M / V$ of PEO/P(EO-b-DMS) mixtures vs composition calculated with eq. 33 at 400K for the indicated pressures. We can know more clearly from Figure 22 that for low pressure the volume change is more negative and $\Delta V_M / V$ decreases on raising the pressure.

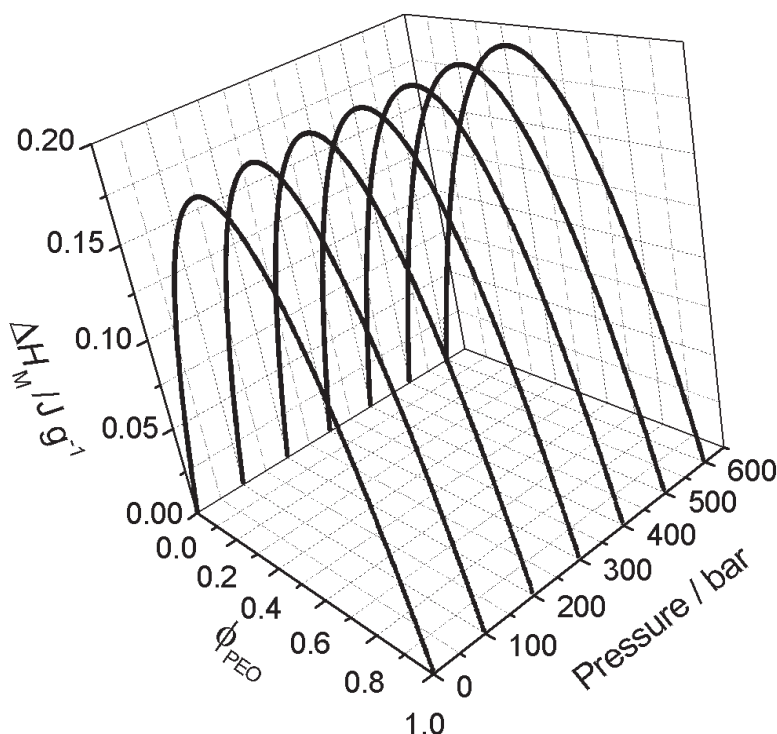


Fig. 19. Pressure and composition dependences of the calculated enthalpy of the mixing, ΔH_M , for the P(EO-b-DMS) polymer mixtures at the indicated temperature ($T=400K$).

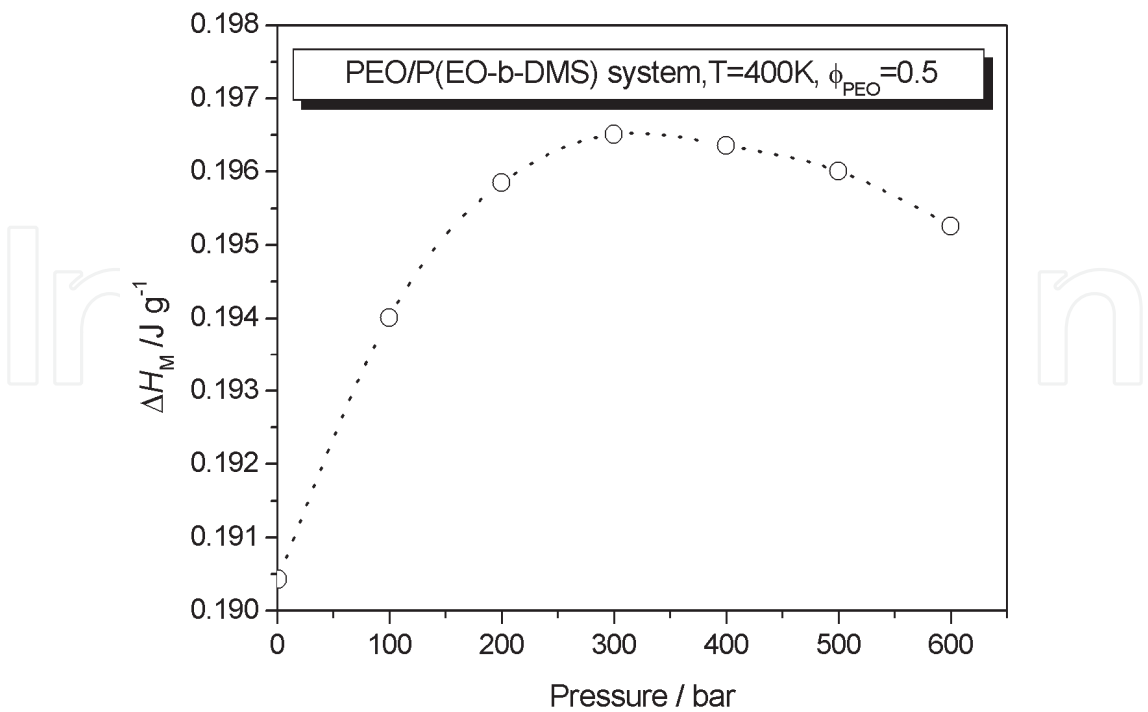


Fig. 20. Pressure dependences of the enthalpy of the mixing, ΔH_M , for the P(EO-b-DMS) polymer mixtures with fixed composition and temperature).

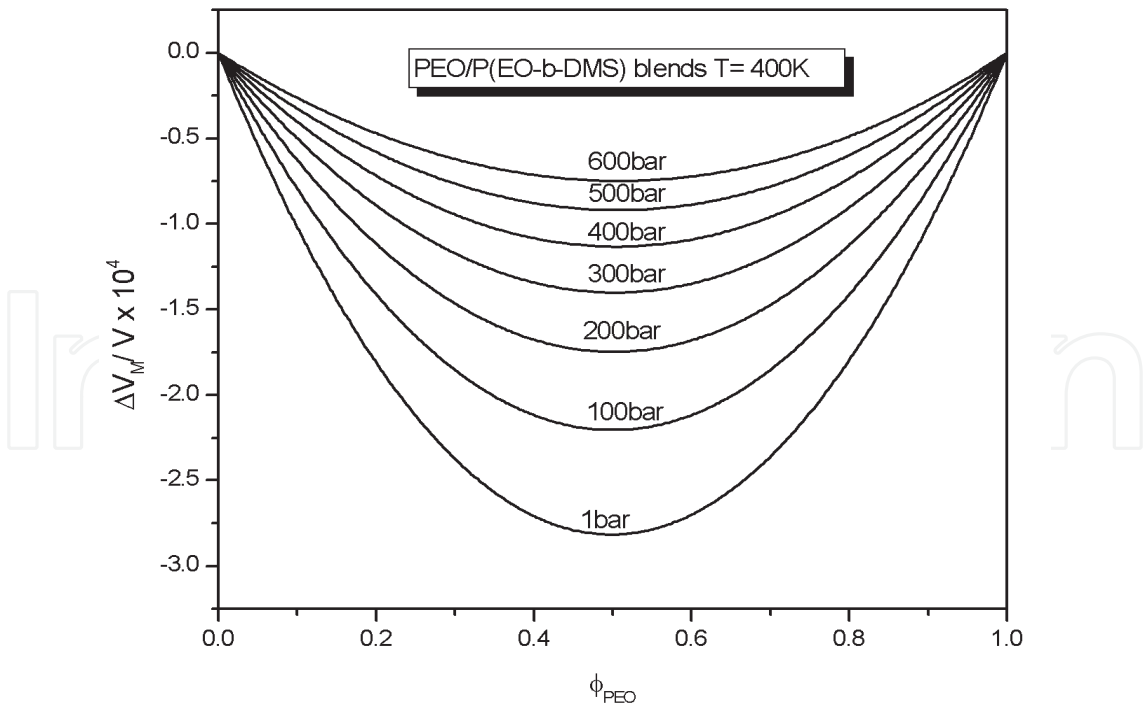


Fig. 21. Pressure and polymer mixture composition dependences of the volume change of the mixing, $\Delta V_M / V$, for the P(EO-b-DMS) polymer mixtures under the indicated temperature.

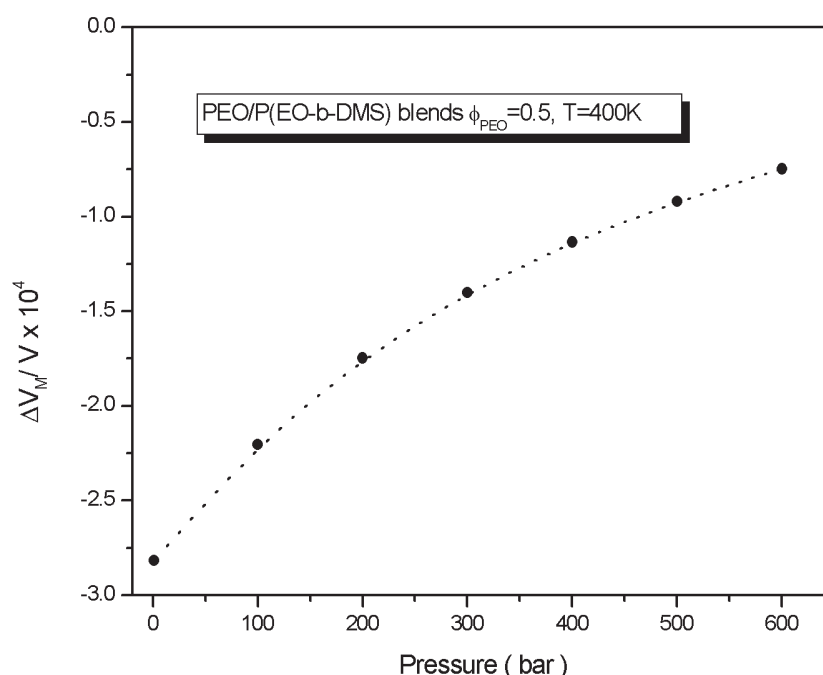


Fig. 22. Pressure dependences of the volume change of the mixing, $\Delta V_M / V$, for the P(EO-b-DMS) polymer mixtures at the indicated temperature and composition.

After calculating the ΔH_M and ΔV_M for PEO/P(EO-b-DMS) system, we know that just as the Clausius-Clapeyron equation (Ma, 1982) predicted the coexistence line of two phases in a T-P plane of PEO/P(EO-b-DMS) system according to $(dT/dP)_\phi = T\Delta V_M / \Delta H_M$. Since ΔH_M , as calculated according to the Sanches-Lacombe theory 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 the calculated temperature and pressure range, ΔV_M is negative in this system, which indicates that $(dT/dP)_\phi < 0$ for PEO/P(EO-b-DMS) mixtures. In most polymer blends investigated (Geerissen et al, 1985) to date $(dT/dP)_\phi > 0$ implying that $\Delta V_M > 0$, which means that PEO/P(EO-b-DMS) mixture display the abnormal pressure effects on the phase separation and the root is $\Delta V_M < 0$.

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

The phase separation conditions for polymer-containing systems can change markedly as the systems pressured and 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. 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 (An & Wolf, 1998; Hammouda & Bauer, 1995). For those systems 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 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 diminish the entropy of mixing (Janssen et al. 1995; Rudolf & Cantow, 1995; Schwahn et al. 1995).

The phase separation of 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 showed above, the experimental results proved that pressure can play an important role in the phase separation of polymer containing systems (Hajduk et al., 1995, 1996; Jiang et al. 2002).

The behavior of ternary polymer mixtures containing a diblock copolymer with homopolymer and toluene as a function of mixture composition and temperature were investigated to obtain experimental phase diagram for solvent/copolymer/ homopolymer mixture. In order to avoid the complications associated with the microphase separation of block copolymers, the molar mass of block copolymer was kept low in our experiment (Madbouly & Wolf, 2002).

The presently available experimental information concerning pressure effects on polymer containing ternary system reveals an abnormal phenomena: under demixing condition, (dT/dP) changed from positive to negative with different concentration 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. The phase boundaries at normal pressure, chosen temperatures and the chosen compositions, various pressures are measured. Further, the pressure effects on (dT/dP) of ternary are compared with that of binary system without solvent.

The measured cloud point curves of polymer containing binary mixtures and ternary systems at normal pressure are shown in figure 23. Figure 23a shows the measured transition temperatures of PEO/P(EO-b-DMS). The open circles indicate experimental points that got from the measurements of the transition temperature during the system changed from one-phase to two-phase, i.e. the heating process and the solid curve describes the behavior of the data points; the open squares indicate experimental points that got from the measurements of the transition temperature during the system changed from one-phase to two-phase, i.e. the cooling process and the dot curve describes the behavior of the data points. The lines are polynomial fits and serve as a guide for the eye (for other figures are the same). Figure 23b shows the cloud points of TL/PEO/P(EO-b-DMS) ternary system at 35, 45, 55, and 60 °C under atmosphere pressure. The solid squares on the curves at 35 and 45 °C represent the ternary system composition that were 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 much effect on the phase transition temperature of this ternary system, on the contrary, 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 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 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 (Konowalow, 1903).

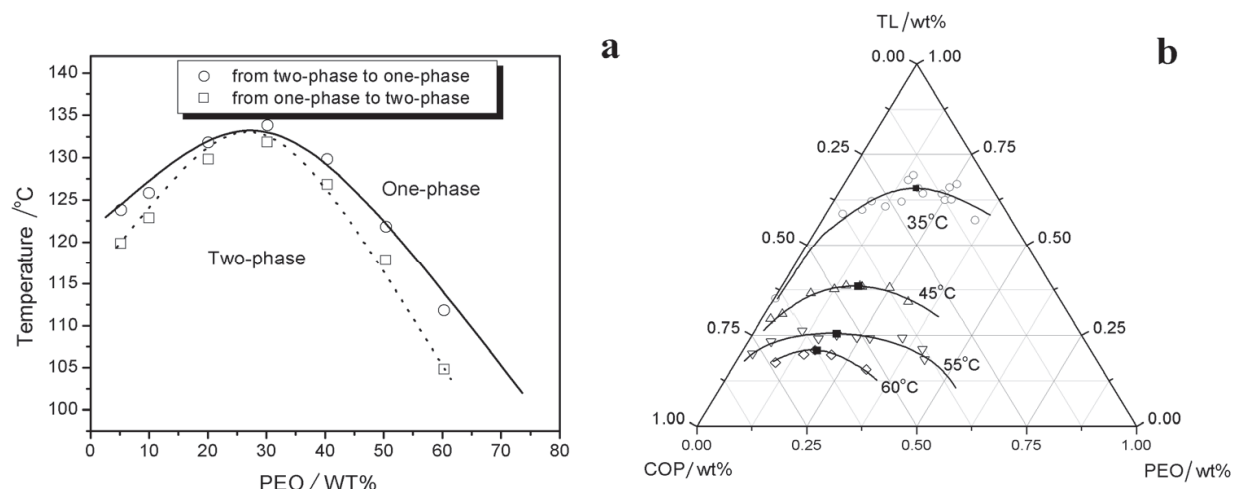


Fig. 23. Phase diagrams under normal pressure (a: phase diagram of PEO/P(EO-b-DMS) binary mixtures under normal pressure; b: phase diagrams of TL/PEO/P(EO-b-DMS) ternary solutions under normal pressure at indicated temperatures).

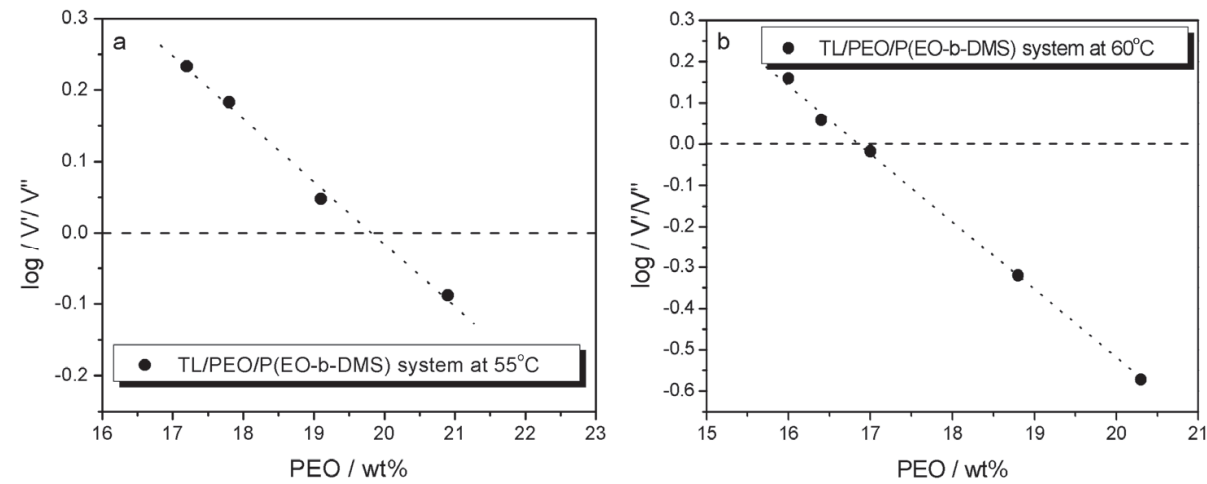


Fig. 24. Phase-volume ratio measurement for TL/PEO/P(EO-b-DMS) mixtures (a) at 50 °C and (b) at 60 °C.

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 (Bruhat, 1930). 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 figure 24, we just obtained the critical point for the mixtures at 55 °C and 60 °C which represented in

figure 23b, however, at the lower temperatures, it is very difficult for us to observe the macrophase separation in this system even the experiment lasted for more than one month. Figure 25 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 mentioned in section 4. 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 reference (Jiang et al, 2002), the demixing pressures decrease with increasing temperature for the binary polymer mixtures, and (dT/dP) of the binary system is negative, and this means that the pressure decreases the phase separation temperature of PEO/P (EO-b-DMS) blends. Figure 25 shows the experimental measured phase transition temperatures under pressure for the compositions that showed in figure 23b as solid squares. As shown in Figure 25, the abnormal pressure effects on the ternary system was found, i.e., at low TL concentration of this system, pressure induces the compatibility, but for high TL concentration, pressure decreases the compatibility of this system.

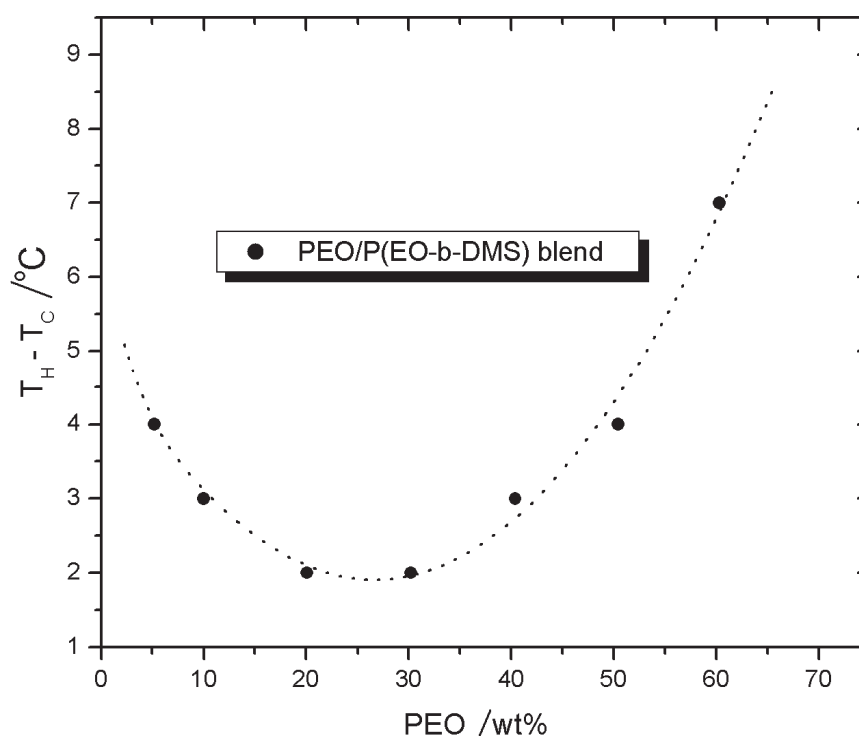


Fig. 25. Pressure dependence of T on T - P plane (the transition temperatures for TL/PEO/P(EO-b-DMS) ternary solutions at indicated temperatures (60 °C (○), 55 °C (△), 45 °C (□), and 35 °C (▽)) and the compositions corresponding to Figure 1b indicated).

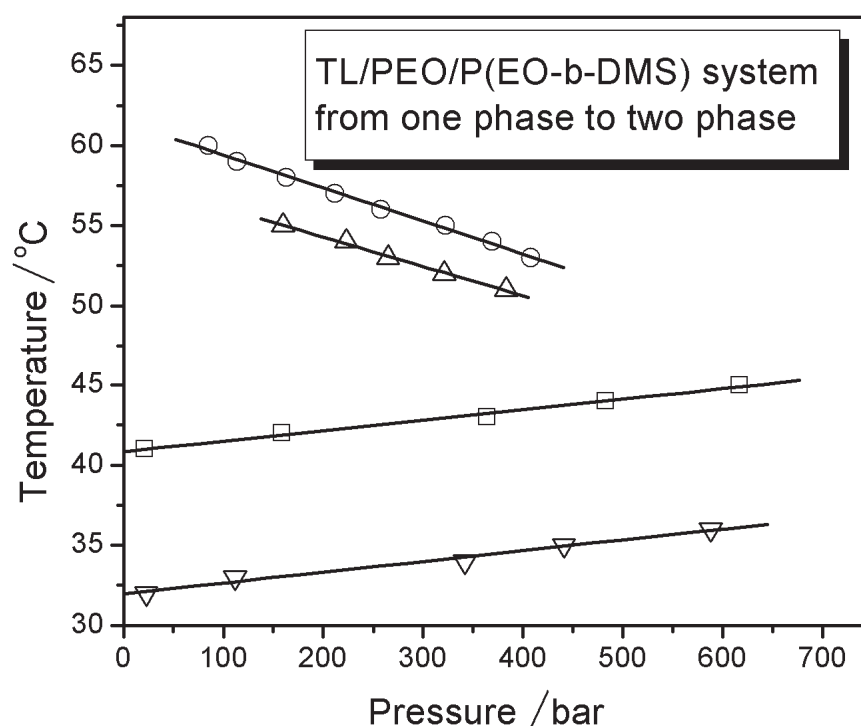


Fig. 26. T_H - T_C vs PEO wt% in binary system (T_H and T_C are the phase transition temperatures of heating and cooling process).

With the reservations concerning the critical polymer concentration, indicated in the figure 23a, figure 26 was constructed from the phase diagram of PEO/P(EO-b-DMS) binary mixtures as shown in figure 23a by plotting the (T_H - T_C) vs. 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 the (T_H - T_C) was considered as the critical composition of this binary system.

The pressure effects on the demixing temperatures of polymer containing binary system and ternary system are shown in figure 27. Figure 27a shows the slopes of isopleths (dT/dP) in reference (Jiang et al, 2002) vs. 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 27b shows the slopes of isopleths (dT/dP) in figure 25 vs. TL concentration for TL/PEO/P(EO-b-DMS) ternary solutions. The pressure effect on the ternary system where TL=0 is according to the results from figure 26 and figure 27a, which is the pressure effect on the critical composition of PEO/P(EO-b-DMS) binary mixtures. Figure 27b shows a 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 (Imre et al, 2001).

The influence of pressure can be deduced by calculating the pressure coefficient (dT_{cr}/dP) of the critical solution temperature, which given by (Wolf & Blaum, 1977):

$$dT_{cr} / dP \cong T \Delta V_m / \Delta H_m \quad (34)$$

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 equation (Ma, 1982) 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 eq. 2 and 34. 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 FH theory through the addition of free volume), shows that to leading order for binary mixtures (Sanchez & Lacombe, 1976):

$$\Delta V_m = \phi(1 - \phi)\{4\chi - [(\epsilon_{11} - \epsilon_{22}) / RT]^2\} \quad (35)$$

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 the 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 Foreman and Freed using the lattice cluster model (Horst, 1995; Horst & Wolf, 1992). According to figure 27b and equation 35, 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 the information on the pressure effects on χ parameter for this system, i.e., with the increasing of TL in this system, χ parameter increases from small to large.

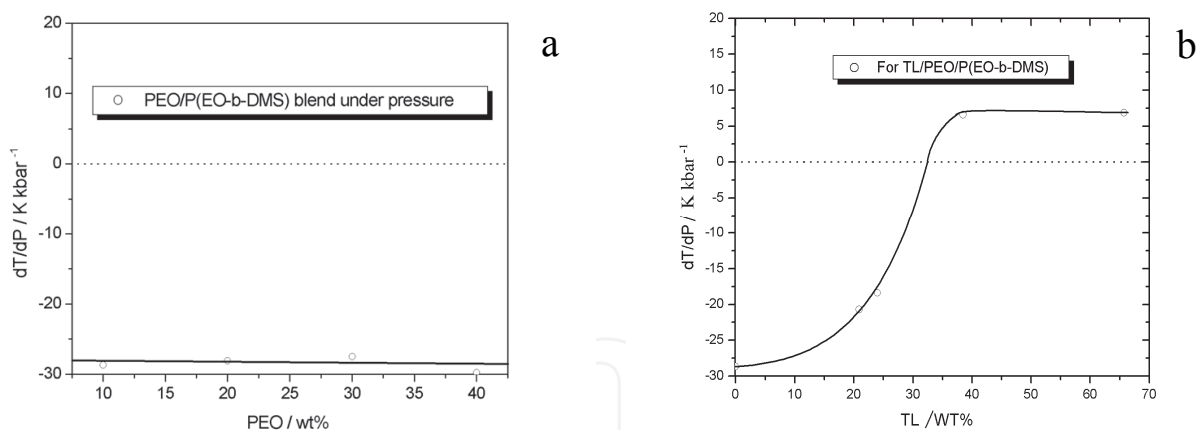


Fig. 27. Pressure dependence of the transition temperatures (dT/dP) vs referred composition(a: for binary mixtures; b: for ternary solutions).

The same as classic thermodynamics, polymer thermodynamics is function of pressure, temperature and composite. But in many cases, pressure effects on polymer thermodynamics was neglected, because polymer thermodynamics were often studied under atmosphere. The classic theory of polymer thermodynamics is Flory-Huggins hard lattice theory. In this theory, the hard lattice is incompressible. A rigorously incompressible system should be unaffected by pressure. However, since experimental results show that the critical temperature for polymer demixing system is strongly affected by pressure, it is clear that polymer containing systems show significant departures from this ideal limit. We wish

above introduction would give readers a rough draft on the thermodynamics of polymer containing systems.

6. Acknowledgements

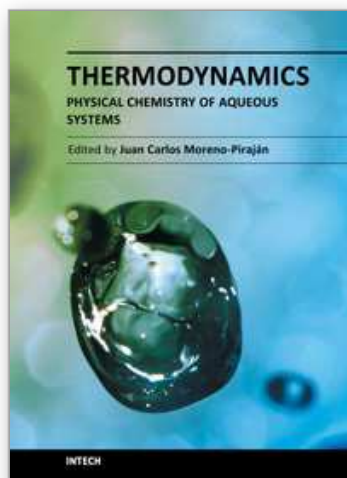
This work is supported by the National Natural Science Foundation of China (20974077 · 51073157) and subsidized by the Special Funds for National Basic Research Program of China (2010CB631102). We appreciated helpful discussion provided by Prof. Lijia An (Changhun Institute of Applied Chemistry) and Prof. Bernhard A. Wolf (Mainz University).

7. References

- An et al. 1997, Pressure dependence of the miscibility of poly(vinyl methyl ether) and polystyrene: Theoretical representation, *J Chem. Phys.* Vol.107, No.7, PP. 2597-2602.
- An & Wolf, 1998, Combined effects of pressure and shear on the phase separation of polymer solutions, *Macromolecules*, Vol.31, No. 14, PP. 4621-4625.
- Beiner et al. 1998, Pressure-induced compatibility in a model polymer blend, *Physical Review Letters*, Vol. 81, No. 3, PP. 594-597; 2002, Strong isotopic labeling effects on the pressure dependent thermodynamics of polydimethylsiloxane/polyethylmethysiloxane blends, *J. Chem. Phys.*, Vol. 116, No. 3, PP.1185-1192.
- Blaum & Wolf, 1976, Generation of true cosolvency by pressure - solubility limits of high molecular-weight polystyrene in mixtures of acetone and diethyl-ether, *Macromolecules*, Vol. 9, No. 4, PP. 579-582.
- Bruhat, 1930, *Chaleur Ind.*, 11, 263.
- de Loos et al. 1983, Fluid phase-equilibria in the system polyethylene + ethylene .1. systems of linear polyethylene + ethylene at high-pressure, *Macromolecules*, Vol. 16, No. 1, PP. 111-117.
- Dudowicz & Freed, 1995, Pressure-dependence of polymer fluids - application of the lattice cluster theory, *Macromolecules*, Vol. 28, No. 19, PP. 6625-6641; 2006, Entropy theory of polymer glass formation revisited, I. General formulation, *J. Chem. Phys.*, Vol. 124, No. 6, PP. 064901.
- Flory, 1953, *Principle of Polymer Chemistry*; Cornell University Press: Ithaca, NY, Chapter 12.
- Geerissen et al. 1985, Continuous fractionation and solution properties of PVC. 3. Pressure-dependence of the solubility in single solvents, *Makromol. Chem.*, Vol. 186, No. 4, PP. 769-776
- Hajduk et al., 1995, High-pressure effects on the disordered phase of block-copolymer melts, *Macromolecules*, Vol. 28, No. 21, PP. 7148-7258; 1996, High-pressure effects on the order-disorder transition in block copolymer melts, *Macromolecules*, Vol. 29, No. 5, PP. 1473-1481
- Hammouda & Bauer, 1995, compressibility of 2 polymer blend mixtures, *Macromolecules*, Vol. 28, No. 13, PP. 4505-4508; 1997, Small-angle neutron scattering from pressurized polyethylbutylene/ polymethylbutylene blends, *Macromolecules*, Vol. 30, No. 18, PP. 5572-5574

- Horst, 1995, Calculation of phase-diagrams not requiring the derivatives of the gibbs energy demonstrated for a mixture of 2 homopolymers with the corresponding copolymer, *Macromol. Theory Simul.*, Vol. 4, No. 3, PP. 449-458
- Horst & Wolf, 1992, Calculation of the phase-separation behavior of sheared polymer blends, *Macromolecules*, Vol. 25, No. 20, PP. 5291-5296
- Hosokawa et al. 1993, Coexistence curve of polystyrene in methylcyclohexane .7. coexistence surface and critical double point of binary-system in t-p-phi space, *J. Chem. Phys.*, Vol. 98, NO. 12, PP. 10078-10084
- Imre, 2001, On the effect of pressure on the phase transition of polymer blends and polymer solutions: Oligostyrene-n-alkane systems, *Phys. Chem. Chem. Phys.*, Vol. 3, No. 6, PP. 1063-1066
- Janssen et al. 1993, Pressure-dependence of the flory-huggins interaction parameter in polymer blends - a sans study and a comparison to the flory-orwoll-vrij equation of state, *Macromolecules*, Vol. 26, No. 21, PP. 5587-5591; 1995, Coil and melt compressibility of polymer blends studied by sans and pvt experiments, *Macromolecules*, Vol. 28, No. 7, PP. 2555-2560
- Jiang et al. 2002, Pressure-induced compatibility in PEO/P(EO-b-DMS) polymer mixtures, *Macromolecules*, Vol. 35, No. 15, PP. 5727-5730
- Koningsveld & Staverman, 1968, liquid-liquid phase separation in multicomponent polymer solutions .2. critical state, *J. Polym. Sci., Part A*, Vol. 6, No. 2, PP. 325-347
- Konowalow, 1903, The critical area of solutions and the appearance of opalescence, *Ann. Physik.*, Vol. 10, No. 2, PP. 360-392
- Kumar, 2000, Pressure effects on the thermodynamics of polymer blends, *Macromolecules*, Vol. 33, No. 14, PP. 5285-5291
- Lacombe & Sanchez, 1976, Statistical thermodynamics of fluid mixtures, *J. Phys. Chem.*, Vol. 80, No. 23, PP. 2568-2580
- Lefebvre et al 1999, Relationship between internal energy and volume change of mixing in pressurized polymer blends, *Macromolecules*, Vol. 32, No. 16, PP. 5460-5462; 2000, Neutron scattering from pressurized polyolefin blends near the limits of metastability, *Macromolecules*, Vol. 33, No. 21, PP. 7977-7989
- Ma, 1982, *Statistical Mechanics*; World Scientific: Singapore
- Madbouly & Wolf, 2002, Equilibrium phase behavior of polyethylene oxide and of its mixtures with tetrahydronaphthalene or/and poly(ethylene oxide-block-dimethylsiloxane), *J. Chem. Phys.*, Vol. 117, No. 15, PP. 7357-7363
- Maderek et al. 1983, High-temperature demixing of poly(decyl methacrylate) solutions in isooctane and its pressure-dependence, *Makromol. Chem.*, Vol. 184, No. 6, PP. 1303-1309; Lower critical solution temperatures of poly(decyl methacrylate) in hydrocarbons, *Eur. Polym. J.*, Vol. 19, No. 10, PP. 963-965
- Patterson & Robard, 1978, Thermodynamics of polymer compatibility, *Macromolecules*, Vol. 11, No. 4, 690-695
- Rabeony et al 1998, Effect of pressure on polymer blend miscibility: A temperature-pressure superposition, *Macromolecules*, Vol. 31, No. 19, PP. 6511-6514
- Rodgers, 1991, Procedure for predicting lower critical solution temperature behavior in binary blends of polymers, *Macromolecules*, Vol. 24, No. 14, PP. 4101-4109
- Rudolf & Cantow, 1995, Description of phase-behavior of polymer blends by different equation-of-state theories .2. excess volumes and influence of pressure on miscibility, *Macromolecules*, Vol. 28, No. 19, PP. 6595-6599

- Sanchez & Balasz, 1989, Generalization of the lattice-fluid model for specific interactions, *Macromolecules*, Vol. 22, No. 5, PP. 2325-2331
- Sanchez & Lacombe, 1976, Elementary molecular theory of classical fluids - pure fluids, *J. Phys. Chem.*, Vol. 80, No. 21, PP. 2352-2362; 1978, statistical thermodynamics of polymer-solutions, *Macromolecules*, Vol. 11, No. 6, PP. 1145-1156
- Schmidt & Maurer, 1998, Pressure-volume-temperature properties and free volume parameters of PEO/PMMA blends, *Polym. Sci. B: Polym. Phys.*, Vol. 36, No. 6, PP. 1061-1080
- Schwahn et al. 1995, ginzburg criterion for the mean-field to 3-dimensional ising crossover in polymer blends, *Phys. Rev. E*, Vol. 52, No. 2, PP. 1288-1291; 1996, Temperature and pressure dependence of the order parameter fluctuations, conformational compressibility, and the phase diagram of the PEP-PDMS diblock copolymer, *Physical Review Letters*, Vol. 77, No. 15, PP. 3153-3156; 2001, Abnormal pressure dependence of the phase boundaries in PEE-PDMS and PEP-PDMS binary homopolymer blends and diblock copolymers, *Macromolecules*, Vol. 34, No. 6, PP. 1694-1706
- Sun et al. 1999, Phase-separation behavior of the system PES/phenoxy: An application of the Sanchez-Lacombe lattice fluid theory, *Macromol. Sci.-Phys.*, Vol. 38, No. 1-2, PP. 67-74
- Tait, 1888, *Physics and Chemistry of the Voyage of H.M.S. Challenger*, Vol. 2, Part 4 HMSO, London
- van Opstal & Koningsveld, 1992, Mean-field lattice equations of state .4. influence of pressure on the phase-behavior of the system polystyrene cyclohexane, *Polymer*, Vol. 33, No. 16, PP. 3433-3444; Mean-field lattice equations of state .5. influence of pressure on liquid liquid-phase behavior of polymer blends, *Polymer*, Vol. 33, No. 16, PP. 3445-3452
- Walsh & Rostami, 1985, Effect of pressure on polymer polymer phase-separation behavior, *Macromolecules*, Vol. 18, No. 2, PP. 216-219
- Wolf & Blaum, Pressure influence on true cosolvency - measured and calculated solubility limits of polystyrene in mixtures of acetone and diethylether , *Makromol. Chem.*, 1976, Vol. 177, No. 4, PP.1073-1088; 1977, dependence of oligomer-oligomer incompatibility on chain-length and pressure .1. oligo-isobutene-oligo-propylene glycol and oligo-styrene-oligo-ethylene glycol, *Journal of Polymer Science: Polymer Symposium*, No. 61, PP. 251-270
- Wolf & Jend, 1977, Possibilities for determination of enthalpies and volumes of mixing from molecular-weight dependence of critical demixing temperatures and pressures, demonstrated for system trans-decahydronaphthalene-polystyrene, *Makromol. Chem.*, Vol. 178, No. 6, PP. 1811-1822; 1979, Pressure and temperature-dependence of the viscosity of polymer-solutions in the region of phase-separation, *Macromolecules*, Vol. 12, No. 4, PP. 732-737
- Zeman et al. 1972, Pressure effects in polymer-solution phase equilibria .1. lower critical solution temperature of polyisobutylene and polydimethylsiloxane or lower alkanes, *J. Phys. Chem.*, Vol. 76, No. 8, PP. 1206-1213
- Zeman & Patterson, 1972, Pressure effects in polymer-solution phase equilibria .2. systems showing upper and lower critical solution temperatures, *J. Phys. Chem.*, Vol. 76, No. 8, PP. 1214-1219



Thermodynamics - Physical Chemistry of Aqueous Systems

Edited by Dr. Juan Carlos Moreno Piraján

ISBN 978-953-307-979-0

Hard cover, 434 pages

Publisher InTech

Published online 15, September, 2011

Published in print edition September, 2011

Thermodynamics is one of the most exciting branches of physical chemistry which has greatly contributed to the modern science. Being concentrated on a wide range of applications of thermodynamics, this book gathers a series of contributions by the finest scientists in the world, gathered in an orderly manner. It can be used in post-graduate courses for students and as a reference book, as it is written in a language pleasing to the reader. It can also serve as a reference material for researchers to whom the thermodynamics is one of the area of interest.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Shichun Jiang and Hongfei Li (2011). Pressure Effects on Thermodynamics of Polymer Containing Systems, Thermodynamics - Physical Chemistry of Aqueous Systems, Dr. Juan Carlos Moreno Piraján (Ed.), ISBN: 978-953-307-979-0, InTech, Available from: <http://www.intechopen.com/books/thermodynamics-physical-chemistry-of-aqueous-systems/pressure-effects-on-thermodynamics-of-polymer-containing-systems>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen