Mean-field lattice equations of state: 4. Influence of pressure on the phase behaviour of the system polystyrene/cyclohexane

L. van Opstal*
DSM Research, PO Box 18, 6160 MD Geleen, The Netherlands

and R. Koningsveld†
Polymer Institute ΣΠ, Waldfeuchtstraat 13, 6132 HH Sittard, The Netherlands
(Received 29 March 1990; revised 5 August 1991; accepted 1 October 1991)

The pressure dependence of the interaction term in the Flory–Huggins–Staverman expression for the free enthalpy of mixing can be introduced with the aid of general thermodynamic relations. The peculiar pressure influence on the phase behaviour of the system polystyrene/cyclohexane, where the sign of $(\delta T/\delta p)_c$ at the critical point changes upon an increase of pressure and molar mass of polystyrene, is taken as a test case for this semi-phenomenological (SP) model and for a modified form of the mean-field lattice-gas (MFLG) model published earlier. The SP model performs very well in describing one part of the phase diagram and in predicting another part. The MFLG model in contrast only represents data for polystyrene samples of different molar mass separately if one of the parameters for the mixture is made a function of the hole concentration. A simultaneous description for all samples is only qualitative even though the interaction term is made a highly complicated concentration function.

(Keywords: equation of state; behaviour; blends)

INTRODUCTION

Partial miscibility is an important phenomenon in polymer engineering. Liquid–liquid phase separation may occur during solution or bulk polymerization and is an essential feature of e.g. polymer fractionation. A very useful expression for the free enthalpy of mixing was independently derived a long while ago by Staverman and Van Santen[1], Huggins[2] and Flory [3] on the basis of a rigid lattice model. It deals quite successfully with a number of properties of polymer systems, e.g. liquid–liquid equilibrium and three-phase separation at ambient pressure (1 bar‡)[4].

Pressure, however, does not always play a negligible role in polymer manufacture. For instance, solution polymerization of ethylene in hydrocarbons usually proceeds at elevated pressures, and the synthesis does not seldom interfere with liquid–liquid phase separation. As a result, highly viscous phases are formed which may jeopardize smooth operation.

The situation indicates the need for molecular models which include the influence of pressure. The Simha–Somcynski model[5] refers to a quasi-lattice with sites either vacant or occupied by a segment. The Lennard–Jones–Devonshire cell potential was replaced by a square-well, introduced by Prigogine. The scaled equation of state was applied to liquid argon[6] and was used to study a number of liquid polymers near their glass temperatures[7].

The Flory 'equation of state' theory[8] describes the disruption in the local liquid structure which results from mixing two fluids having different packing densities or free volume. As a consequence excess volumes and, thereby, the influence of pressure are taken into account. The model predicts the effect of pressure on thermodynamic properties in a qualitative fashion.

In recent years, equations of state based on the model of a compressible lattice containing randomly distributed vacant sites have been suggested by a number of authors[9–12]. Two of these[11] recognized that the introduction of some empirical parameters cannot be avoided if quantitative agreement between theory and observation is to be obtained. This mean-field lattice-gas (MFLG) model has been applied quite successfully to gas–gas demixing[12] and the solubility of solids in supercritical solvents[13].

Here we also want to consider another approach, namely a semi-phenomenological (SP) treatment. It is based on the rigid lattice model where the pressure dependence of the interaction function is defined with the aid of classical thermodynamic relations of general validity. The applicability of this treatment as well as the MFLG model is tested on the complex phase behaviour of the system polystyrene/cyclohexane (PS/CH).

The calculations were performed with a parameter estimation computer program developed at DSM Research.

---

* Present address: UIA, Universiteitsplein 1, B-2610 Wilrijk, Belgium
† To whom correspondence should be addressed
‡ 1 bar = 1 × 10^5 Pa

0032-3861/92/163433-12

THE SP TREATMENT

The SP treatment is based on the rigid lattice model and combines simple molecular considerations with general classical relationships in order to describe the influence of pressure and temperature on phase behaviour.

The Flory–Huggins–Staverman (FHS) expression for ΔG, the Gibbs free enthalpy of mixing for n_1 moles of solvent and $\sum n_{2i}$ moles of a polydisperse polymer is:

$$\Delta G/(N_\phi RT) = (\phi_1/m_1)\ln\phi_1 + \sum_i (\phi_{2i}/m_{2i})\ln\phi_{2i} + g\phi_1\phi_2 \qquad (1)$$

The interaction term is represented by g, ϕ_1 and $\phi_2 = \sum \phi_{2i}$ are concentration variables and $N\phi$ is the total amount of lattice sites. Further, m_i denotes the relative number of segments per molecule of species i.

Application of a strictly regular approximation[14] where the number of contacts is estimated by surface areas rather than by the number of molecules[15], leads to a closed expression for $g(\phi_2, T)$:

$$g = a + \frac{b}{1 - c\phi_2} \qquad (2)$$

The quantity b is related to the difference between the interaction free enthalpy of unlike and like neighbours. Presuming that Δc_p, the change in specific heat upon mixing, is linearly dependent on the temperature it follows from

$$(\partial\,\Delta H/\partial T)_\mathrm{P} = \Delta c_\mathrm{P}$$

$$(\partial\,\Delta S/\partial T)_\mathrm{P} = \Delta c_\mathrm{P}/T$$

that the temperature dependence of b can be written as[16]:

$$b = b_0 + b_1/T + b_2 T + b_3 \ln T \qquad (3)$$

The parameter c is defined as $c = 1 - s_2/s_1$, where s_1 and s_2 are the molecular surface areas of solvent molecules and polymer segments, respectively. These areas can be calculated using Bondi's group estimation method[17]. Finally, a is an empirical entropy parameter.

Standard methods yield the spinodal and the critical condition[18–20]:

$$\text{spinodal} \qquad \frac{1}{\phi_1} + \frac{1}{\bar{m}_\mathrm{w}\phi_2} = 2\left[a + \frac{b(1-c)}{(1-c\phi_2)^3}\right] \qquad (4)$$

$$\text{critical point} \qquad \frac{1}{\phi_1^2} - \frac{\bar{m}_\mathrm{z}}{\bar{m}_\mathrm{w}^2\phi_2^2} = 6\,\frac{b(1-c)c}{(1-c\phi_2)^4} \qquad (5)$$

where $\bar{m}_\mathrm{w}$ and $\bar{m}_\mathrm{z}$ represent the mass- and centrifuge-average segment numbers, respectively.

The entropy correction term in equation (2) is usually treated as a constant but it can be shown that, in fact, a should be expected to be concentration dependent[21]. The zero-order approach [equations (1)–(3)] is inconsistent because it combines entropy of mixing terms based on identical coordination numbers with an expression for the internal energy of mixing arising from a contact-statistical treatment[15]. Correction with the aid of Silverberg's procedure[22] redefines a and b_0 in equations (2) and (3), respectively:

$$a = 2z_{11}\ln(1 - c\phi_2)/(1 - c\phi_2) \qquad (6)$$

$$b_0 = -z_{11}\ln(z_{01}z_{10}/z_{00}) \qquad (7)$$

where z_{ij} represents the number of nearest neighbours j of repeat units i. This procedure demonstrates that a must be expected to depend on concentration. Instead of using the expressions for a and b_0 as such, we often find it useful to relax their precise definitions. Thus, we leave b_0 as an adjustable parameter and write for a:

$$a = a_0 + a_1\phi_2 + a_2\phi_2^2 + \cdots \qquad (8)$$

The pressure dependence of constants like b in the FHS theory can be defined using thermodynamic relationships, namely:

$$\Delta V^\mathrm{E} = (\partial\,\Delta G/\partial p)_{T,n_1} \qquad (9)$$

$$\alpha = (1/V)(\partial V/\partial T)_p \qquad (10)$$

$$\beta = -(1/V)(\partial V/\partial p)_T \qquad (11)$$

where ΔV^E is the excess volume, and α and β are the thermal expansion coefficient and the isothermal compressibility, respectively. Integration of equations (10) and (11) at constant α and β, respectively, leads to an exponential dependence of V on p and T:

$$V = V_0^*\,\mathrm{e}^{\alpha(T-T_0)}\,\mathrm{e}^{-\beta p} \qquad (12)$$

In equation (12) V_0^* is the volume of the system at zero pressure and some reference temperature T_0. Assuming that α and β are independent of p and T, respectively, $\Delta V^\mathrm{E} = V_\mathrm{m} - \sum \phi_i V_i$ and α and β are representative for the pure components as well as for the mixture, we can express the excess volume as:

$$\Delta V^\mathrm{E} = \Delta V_0^*\,\mathrm{e}^{\alpha(T-T_0)}\,\mathrm{e}^{-\beta p}\phi_1\phi_2 \qquad (13)$$

Combining equations (1), (9) and (13) and integration in p yields the general form of $g(p, T)$. When the exponential terms are expanded in power series and truncated after the quadratic term, the interaction function can be written as

$$g = \left(\frac{A + BT + CT^2}{T}\right)(D + Ep + Fp^2) \qquad (14)$$

According to equation (14) we may expect each coefficient in the strictly regular approximation for g to depend on both pressure and temperature.

The SP treatment has previously been shown to be successful in describing cloud-point curves (CPC) at different pressures and predicting cloud points at pressures beyond the range of the measurements for the system linear polyethylene/ethylene[23].

THE MFLG MODEL

In the zero-order MFLG model[11–13,21,24] a two-component system is represented by a pseudo-ternary mixture of holes and occupied sites. The Helmholtz free energy, ΔA, of mixing n_0 vacant sites, $m_1 n_1$ sites occupied by molecules 1 and $m_2 n_2$ sites by molecules 2 contains—besides the pure component parameters—three extra parameters for the mixture and reads:

$$\Delta A/(N_\phi RT) = \phi_0\ln\phi_0 + (\phi_1/m_1)\ln\phi_1 + (\phi_2/m_2)\ln\phi_2 + g_1\phi_0\phi_1 + g_2\phi_0\phi_2 + g_{12}\phi_1\phi_2 \qquad (15\mathrm{a})$$

where

$$g_i = a_i + b_i/Q$$

$$g_{12} = a_{12} + b_{12}/Q$$

$$b_i = b_{i,0} + b_{i,1}/T$$
$$b_{12} = (b_{12,0} + b_{12,1}/T)(1 - c_1)(1 - c_2)$$
$$Q = 1 - c_1\phi_1 - c_2\phi_2$$

The site fractions of vacant and occupied sites by molecules 1 and 2 are represented by ϕ_0, ϕ_1 and ϕ_2, respectively. They are related by

$$\phi_2 = \frac{\mathrm{d}_2 w_2(1 - \phi_0)}{\mathrm{d}_1 w_1 + \mathrm{d}_2 w_2} \qquad (15\mathrm{b})$$

where $d_i = m_i/M_i$ and m_i, M_i and w_i are the number of sites occupied by one molecule, the molar mass and the mass fraction of species i, respectively. Further, $b_{i,1}$ and $b_{12,1}$ denote the interaction between like and unlike segments, respectively, and RT has its usual meaning.

The disparity in size and shape is introduced in the MFLG model by means of $c_i = 1 - s_i/s_0$ where s_0 and s_i are the surface area of holes and segments i, respectively. The parameters for the pure components or constituents, can be calculated from pVT data. Parameters for the mixture can be obtained from any thermodynamic information on the mixed system.

In a first approximation Staverman's contact number statistics[21] (see above) assigns a physical significance to the empirical entropy corrections a_i, a_{12}, $b_{i,0}$ and $b_{12,0}$ for the mixture

$$\begin{aligned} a_i &= (2z_{ii} \ln Q)/Q \\ b_{i,0} &= -z_{ii} \ln z \\ a_{12} &= 2z_{00}Q^{-1}(1 - c_1)(1 - c_2) \ln Q \\ b_{12,0} &= -z_{00} \ln(z_{12}z_{21}/z_{00}^2) \end{aligned} \qquad (16)$$

where z_{ij} represents the number of nearest neighbours j of repeat units i.

Standard thermodynamic procedures lead to the equation of state (EOS), the spinodal and critical conditions and the equations for equilibrium between the two phases. The equations for the zero- and first-order MFLG model are given in references (13) and (24), respectively.

POLYSTYRENE/CYCLOHEXANE

Over the years a large number of experimental and theoretical investigations on the system PS/CH have been carried out. Since the pressure influence on phase behaviour is the main issue here we focus on this aspect only.

Saeki *et al.*[25] measured critical points and CPC for different anionic PS samples ($\bar{M} = 37$–$1450\ \mathrm{kg\ mol^{-1}}$) for pressures between 1 bar and 50 bar. They found that the value of $(\delta T/\partial p)_\mathrm{c}$ for low molar masses of PS ($\bar{M} = 37\ \mathrm{kg\ mol^{-1}}$) is positive while it is negative for higher molar masses. A qualitative prediction of the experimental results by use of Patterson's and Flory's theories was obtained which do not reproduce the positive value of $(\delta T/\delta p)_\mathrm{c}$ for low molar masses.

The viscosity of a polymer solution often breaks down when a homogeneous system is brought into a two-phase region. Using this phenomenon Wolf and Geerissen[26] investigated the pressure dependence of the demixing temperatures of solutions of PS ($\bar{M} = 600\ \mathrm{kg\ mol^{-1}}$, $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} \leqslant 1.1$) up to pressures of 300 bar. These authors drew attention to the influence of small amounts of impurities on the demixing temperatures of polymer systems. This was shown for PS solutions in cyclopentane samples of different origin. It was observed that the location of the CPC is lowered by ~3°C when 'Fluka purum' (>99.9%) is used instead of 'Merck Uvasol' (>99.9%). In relation to this it is known that small amounts of water (up to 1%) change the location of spinodals for PS/CH by ~5°C[27]. It is clear that the task of modelling can become quite arduous because of minute amounts of contamination. *Figure 1* plots a number of CPC at 1 bar taken from various literature sources[25,26,28,29] for PS/CH. It is seen that the miscibility gap for $\bar{M} = 670\ \mathrm{kg\ mol^{-1}}$ (ref. 25) is located below that for $\bar{M} = 600\ \mathrm{kg\ mol^{-1}}$ (ref. 26). This inconsistency is probably due to the presence of contamination.

In addition to a CPC at 1 bar, Wolf and Geerissen[26] reported a pressure of optimum miscibility for a solution of 6.0 wt% PS (near-critical) in CH at ~120 bar. This means that the value of $(\delta T/\partial p)_\mathrm{c}$ changes from negative to positive with increasing pressure (*Figure 2a*).

Schulz and Lechner[30,31] measured the second virial coefficient A_2 for PS ($\bar{M} = 100\ \mathrm{kg\ mol^{-1}}$, $\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} \leqslant 1.1$) in CH using light scattering at pressures from 0 to 800 bar at intervals of 200 bar and at temperatures of 40, 45 and 50°C. They observed a pressure dependence of A_2, $(\delta A_2/\delta p)$, which is negative at 40°C and positive at 45 and 50°C. Such behaviour of $(\delta A_2/\delta p)$ as a function of temperature points to excess volumes which are negative at 45 and 50°C and positive at low temperatures. This conclusion seems to be in conflict with the observations of $(\delta T/\delta p)_\mathrm{c}$ and ΔV^E. The value of $(\delta T/\delta p)_\mathrm{c}$ indicates for high molar masses ($\bar{M} > 100\ \mathrm{kg\ mol^{-1}}$) a negative ΔV^E and for low molar masses a positive value near the temperature of demixing (<35°C)[25,26]. Further, Hocker *et al.*[32] and Wolf[33] measured negative values for ΔV^E for $\bar{M} = 51\ \mathrm{kg\ mol^{-1}}$ at 25°C and for $\bar{M} = 0.6$–$670\ \mathrm{kg\ mol^{-1}}$ at 28°C, respectively.

Extrapolating their data on A_2 to 0, Schulz and Lechner determined the θ temperature at 0, 200 and

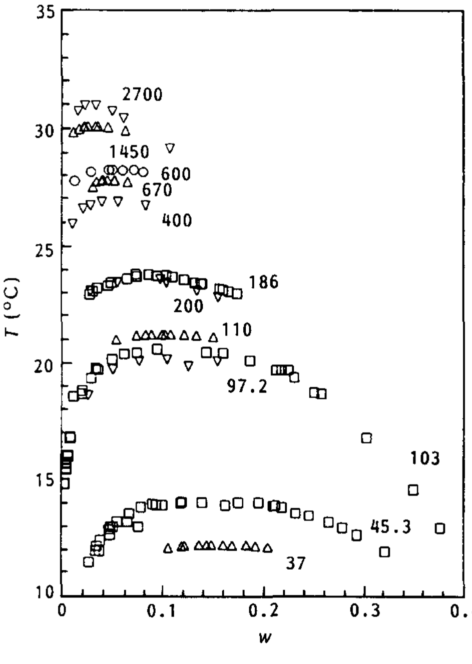

Figure 1 Comparison of experimental cloud points at ambient pressure for PS/CH for the indicated molar masses of PS (in kg mol^{-1}) taken from several literature sources: (△) reference 25; (□) reference 29; (▽) reference 28; (○) reference 26. w = weight fraction of PS

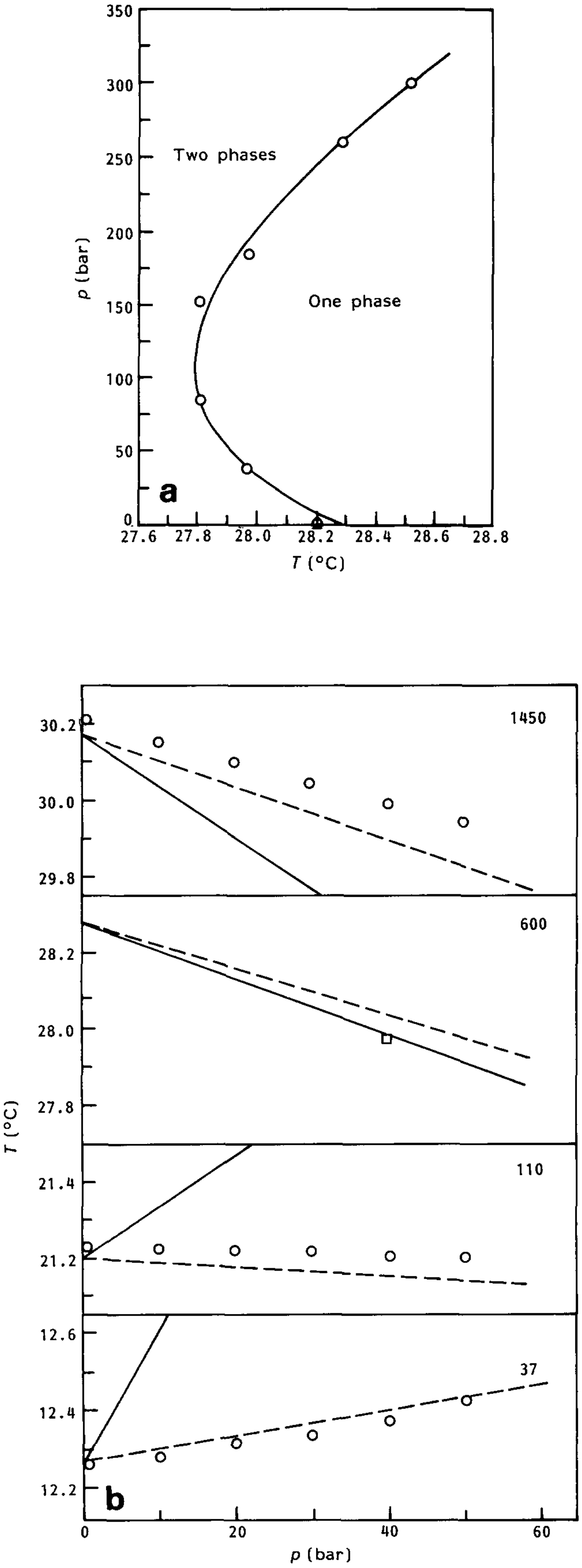

Figure 2 (a) Critical temperatures as a function of pressure calculated with the SP treatment [equation (17), fit A] for a PS sample of molar mass of 600 kg mol^{-1} and compared to experimental data[26]. (b) Critical temperatures as a function of pressure calculated with the SP treatment [equation (17) and with the parameter values in *Table 2*, columns A (——) and B (– – –)] for the indicated molar masses of PS (in kg mol^{-1}). Experimental data from references 25 (○) and (26) (□), respectively

Table 1 Molar masses and pressure ranges studied

$\bar{M}$ (kg mol^{-1})	Pressure range (bar)	Ref.
37	1-50	25
110	1-50	25
600	1-300	26
1450	1-50	25

400 bar to be 36, 38 and 40°C, respectively. This means that the value of $(\delta A_2/\delta p)$ is positive which seems to be quite unexpected in view of the experimental $(\delta T/\delta p)_c$ values.

We now investigate the descriptive power of the SP approach and the MFLG model with regard to the dependence of the consolute states on pressure and molar mass in PS/CH. It is assumed that the PS/CH systems can be considered to represent practically binary solutions. The molar mass distributions are narrow and are ignored here.

The reader is referred to reference 34 for a more extensive discussion of the results presented here.

SP treatment

In a first attempt (fit A) the combined upper critical solution temperature (*UCST*) data of Saeki *et al.*[25] at 1 bar and Wolf and Geerissen[26] at 1–300 bar were described with the binary analogues of equations (4) and (5). Only those PS samples were considered on which the influence of pressure was determined experimentally. In view of the discrepancy in *Figure 1* (see above) the data for $\bar{M} = 670$ kg mol^{-1} were not considered (*Table 1*). The critical mass fractions, w_c, were identified with the top of the CPC. For Wolf and Geerissen's data the value of 6.0 wt% PS was assigned to w_c for all pressures. Volume fractions were used as the concentration variables. They were calculated from the mass fraction on the basis of volume additivity.

Other concentration variables have been used but descriptions of critical data and predictions of thermodynamic properties (e.g. ΔV^E, binodal and spinodal curves) did not change much; only parameter values changed drastically[34].

In order to obtain a fair description of the data it was found to be necessary to define the temperature and pressure dependence of b in equations (4) and (5) as

$$b = b_0 + b_1/T + b_2T \tag{17a}$$

$$b_0 = b_{0,0} + b_{0,1}p + b_{0,2}p^2 \tag{17b}$$

$$b_1 = b_{1,0} + b_{1,1}p \tag{17c}$$

The remaining parameters c and a were treated as constants. Fit A, thus contains 10 floating parameters and their values are listed in *Table 2* (column A).

A pressure of optimum miscibility could be reproduced (*Figure 2a*). Fit A was then used to predict values for $(\delta T/\delta p)_c$. Positive as well as negative values for low and high molar masses, respectively, are predicted surprisingly well although no quantitative agreement is obtained (*Figure 2b*). Inclusion of Saeki *et al.*'s data[25] at elevated pressures in the fit considerably improved the description (fit B, *Figure 2b* and *Table 2*, column B).

Since fit B is an improvement in representing the pressure dependence on the phase behaviour of the system in hand it was used to predict some thermodynamic properties.

Table 2 SP treatment. Values for the parameters in equations (17a)–(17c)

	A	B
$b_{0,0}$	−0.65234	−0.67199
$b_{0,1}$ (bar^{-1}) ($\times 10^{-2}$)	−0.11662	−0.02085
$b_{0,2}$ (bar^{-2}) ($\times 10^{-7}$)	0.42768	0.29395
$b_{1,2}$ (K)	346.86	323.95
$b_{1,2}$ (K bar^{-1})	0.34818	0.06052
$b_{1,2}$ (K^{-1}) ($\times 10^{-2}$)	0.28058	0.24977
a	−0.65433	−0.46242
c	0.13834	0.16368
s_2/s_1	0.769	0.746
s_2/s_1 (Bondi)	0.895	0.895

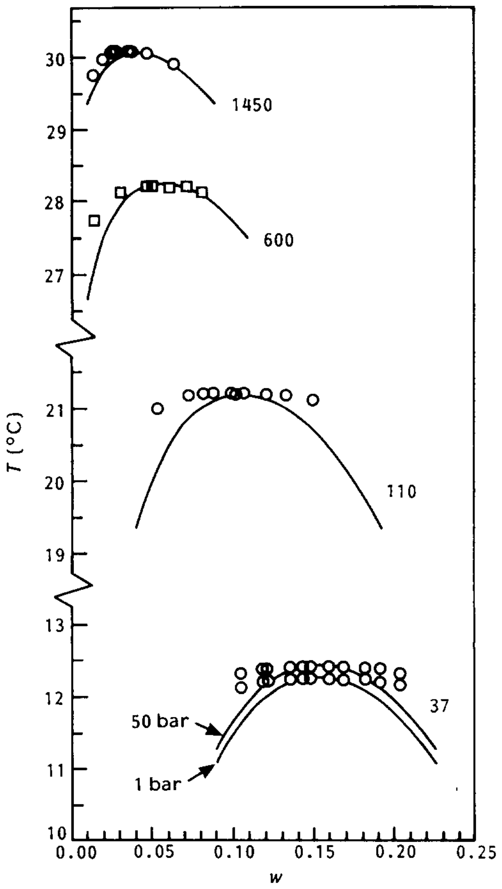

Figure 3 Theoretical binodals (——) in the SP treatment [predicted with equation (17) and with the parameter values in *Table 2*, column B] for the indicated molar masses of PS (in kg mol^{-1}) at 1 bar. Experimental cloud points from references 25 (○) and 26 (□), respectively

The θ temperature, at which $A_2 = 0$, can be calculated from

$$A_2 = 1/2 - \chi_1$$

$$\chi_1 = \left(g - \phi_1 \frac{\delta g}{\delta \phi_2} \right)_{\phi_2 = 0}$$

or

$$[(1/2) - a - b(1 - c)]_{T=\theta} = 0 \qquad (18)$$

Computed values for $\delta\theta/\delta p$ are much lower than those observed[31] and exhibit an optimum at 180°C which has not been reported. Further, at 1 bar, $\theta = 33$°C which agrees with the values from Shultz–Flory plots.

In *Figures 3* and *4* some predicted binodals and spinodals, respectively, are plotted for several molar masses of PS and pressures (1 and 50 bar) and compared to observed data[25,35,36]. As is usually found[37] both spinodals and binodals bend too steeply at small PS concentrations. The ΔV^{E} can be easily computed from

$$\frac{\Delta V^{\mathrm{E}}}{N_\phi RT} = \phi_1 \phi_2 (\partial g/\partial p)_{T,n_i} \qquad (19)$$

Combining equations (17) and (19) results in

$$\Delta V^{\mathrm{E}} = T\phi_1\phi_2(b_{0,1} + 2b_{0,2}p + b_{1,1}/T)(1 - c\phi_2)^{-1} \qquad (20)$$

where the term $N_\phi R$ is not considered since its value is close to unity. It is clear from equation (20) that ΔV^{E} is independent of the molar mass of PS. Further, the experimental values are three times as large as the calculated ones. Yet, they are consistent with the observed $(\delta T/\delta p)_{\mathrm{c}}$ values, e.g. positive values for ΔV^{E} in PS (37 kg mol^{-1})/CH at the demixing temperatures (12°C) are obtained (*Figure 5*).

Knowledge of the specific volume as a function of molar mass of the polymer, temperature and pressure would result in $\Delta V^{\mathrm{E}} = f(M, T, p)$. Such a fitting procedure, however, would complicate the problem. Furthermore it would demand a large amount of experimental pVT data which is not available at present.

One might question the necessity of the linear T term in equation (17a). During fitting the critical data with equation (17) it proved to improve the description especially at higher pressures. This could be explained by the fact that at higher pressures Δc_{p} might change sign. As a result a linear term could become indispensable. Furthermore, it is known that the system PS/CH shows, apart from *UCST*, also lower critical solution temperature (*LCST*) demixing at elevated temperatures of ~230°C. Without a linear T term one cannot describe (or predict) *LCST* behaviour[38].

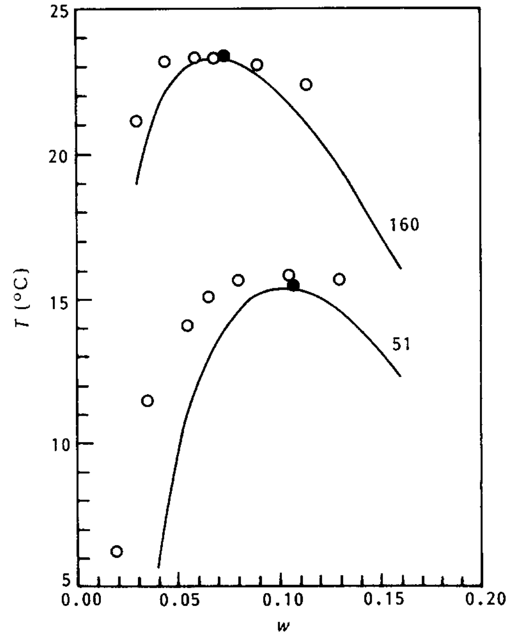

Figure 4 Spinodals for the indicated molar masses of PS (in kg mol^{-1}) at 1 bar predicted with the SP treatment [equation (17) and with the parameter values in *Table 2*, column B] compared to experimental data: (○) spinodal points[37]; (●) critical points[34]

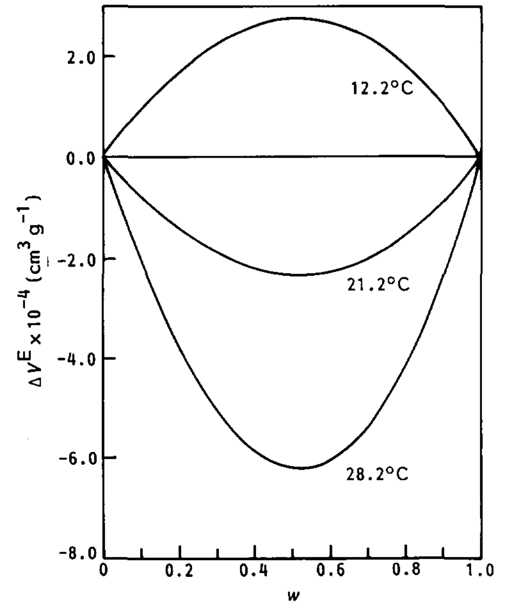

Figure 5 Calculated excess volume in the SP treatment [equation (20) and with the parameter values in *Table 2*, column B] at the indicated temperatures. Experimental values fall outside the plane of drawing

Table 3 SP treatment. Values for the parameters in equations (17) and (21). Simultaneous description of *UCST* and *LCST* consolute points (see text)

$b_{0,0}$	-0.35404
$b_{0,1}$ (bar^{-1})	-0.82047×10^{-2}
$b_{0,2}$ (bar^{-2})	0.30646×10^{-7}
$b_{1,0}$ (K)	258.11
$b_{1,1}$ (K bar^{-1})	1.2405
$b_{2,0}$ (K^{-1})	0.16465×10^{-2}
$b_{2,1}$ (K^{-1} bar^{-1})	0.13539×10^{-4}
a	-0.30471
c	0.18954

LCST consolute states were predicted with the parameter values from *Table 2* (column B). The calculated critical temperatures were 50–60°C too low, even when allowance was made for the fact that at temperatures of 230°C the vapour pressure of CH cannot be ignored. Saturation pressures at demixing temperatures were determined by interpolation of the data by Young[39].

Since the prediction of lower critical demixing temperatures is not altogether unsatisfactory, an attempt was made to describe *UCST* and *LCST* behaviour simultaneously. Therefore, fit B was extended with *LCST* critical data by Saeki *et al.*[28] and the vapour pressure of CH was taken into account. It was to be expected that b_2 in equation (17a) would have to be made pressure dependent:

$$b_2 = b_{2,0} + b_{2,1}p \qquad (21)$$

thus introducing an extra parameter.

The parameter values are listed in *Table 3*. It can be seen from *Figures 6* and *7* that the location of the critical conditions and predicted binodals are quite well reproduced. It should be noted that no fit was possible if the saturation pressure of CH was ignored. In *Figure 7* binodals of two molar masses, which were not included in the fit (45.3 and 670 kg mol^{-1}), are also shown. It is seen that theory approaches the observed data quite well.

The Nies' function

Up to now SP treatment has been used to define the pressure dependence of parameters like a, b_0 and b_1 in the FHS theory. Very good results were obtained in describing critical data and predicting miscibility gaps. One should however be careful in defining $g(p, T, \phi_2)$ as was revealed by the calculation of ΔV^E for different g functions[34].

In the following it was investigated whether existing improvements of the FHS model, would lead to improved descriptions.

The higher order entropy term by Huggins, Orr and Guggenheim (HOG)[40] was introduced into the model. The interaction term g in equation (1) is then redefined as

$$g' = \mathrm{HOG} + g$$

$$\mathrm{HOG} = \frac{1}{c}[(1-c)\phi_2 \ln(1-c) - (1-c\phi_2)\ln(1-c\phi_2)] \qquad (22)$$

The adoption of the HOG term had little or no effect on the description of the critical data. Calculated spinodals widened only by ~0.04°C.

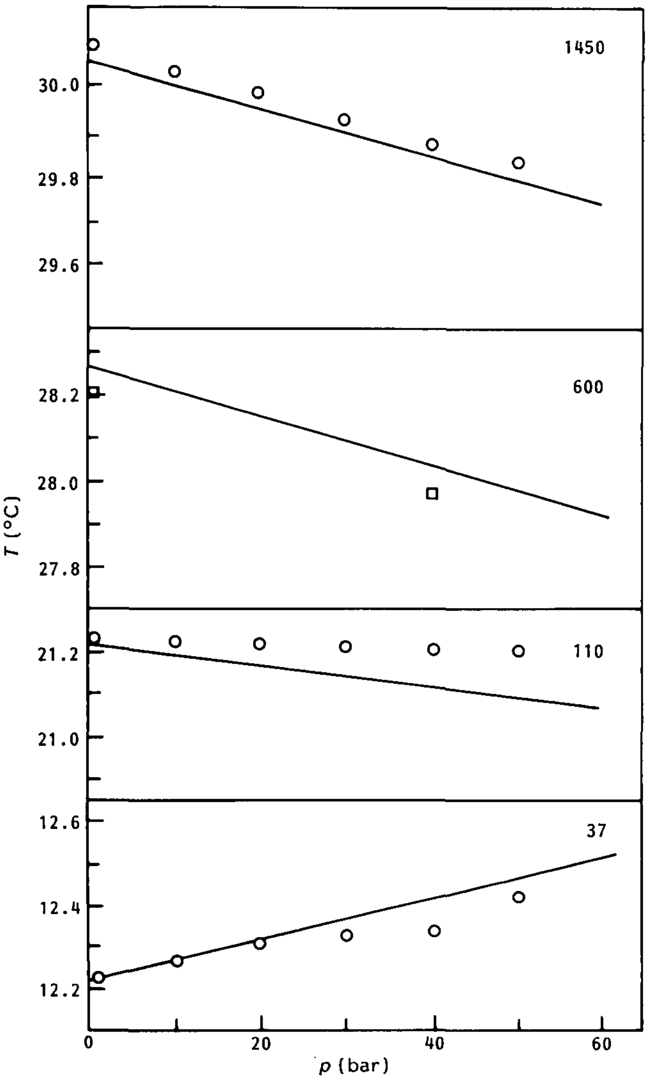

Figure 6 Critical temperatures as a function of pressure calculated with the SP treatment [equations (17) and (21) and with the parameter values in *Table 3*] for the indicated molar masses of PS (in kg mol^{-1}). Experimental data from references 25 (○) and 26 (□), respectively

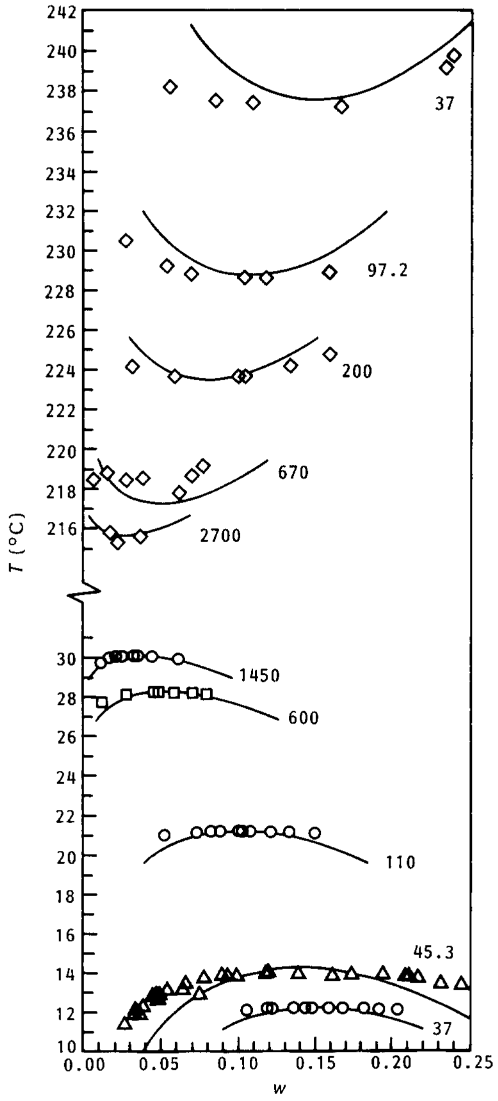

Figure 7 Theoretical binodals (——) of the *LCST* and *UCST* type predicted with the SP treatment [equations (17) and (21) and parameter values in *Table 3*] for the indicated molar masses of PS (in kg mol^{-1}) at 1 bar. Experimental cloud points from references 25 (○), 26 (□), 28 (◇) and 29 (△), respectively

Another improvement was suggested by Koningsveld *et al.*[37]. It takes the experimental finding into account that during phase separation a concentrated and dilute phase are formed.

We find that the choice of the excluded volume function $h(z)$ is very critical[37]. Use of the FKO function leads to an irrational shape of the spinodal at PS concentrations below 2 wt%. On the other hand, Stockmayer's expression for $h(z)$ does not have that disadvantage (see also ref. 34).

Since a theoretical expression for ΔG covering both concentration regimes did not lead to quantitative descriptions[37] Nies *et al.*[40,41] developed an empirical ΔG expression, based on the bridging function:

$$g = g^*P + g^c \tag{23a}$$

It reads

$$\Delta G/(N_\phi RT) = \mathrm{FHS} + \phi_1\phi_2(A_G + g^*P + g^c) \tag{23b}$$

where

$$\mathrm{FHS} = \phi_1 \ln \phi_1 + (\phi_2/m_2)\ln \phi_2$$

$$A_G = (A_0 + A_1/m_2) + (A_2 + A_3/m_2)(T - \theta)$$

$$P = \exp(-\lambda_0\sqrt{m_2}\,\phi_2)$$

$$g^c = (B_0 + B_1/T)(1 - c\phi_2)^{-1}$$

$$g^* = [g_1 + g_2(T - \theta)](T - \theta)[1 - (1/m_2)]/m_2$$

and λ_0 is an adaptable parameter.

With this equation, binodal points at 1 bar for PS/CH are covered in a very satisfactory manner (*Figure 8*), albeit at the cost of a large number (10) of empirical parameters. Here it was tried to transfer this excellent description to higher pressures making g pressure dependent. The most obvious way was defining B_0 and B_1 in equation (23) to be quadratic in p

$$B_i = B_{i0} + B_{i1}p + B_{i2}p^2 \tag{24}$$

which increases the number of parameters to 14.

The parameters $B_{01}, \ldots, B_{12}$ in equation (24) were adjusted to all critical data in *Table 1* at 1 bar fixing all the remaining parameter values given in reference 40. The parameter values are given in *Table 4*. In *Figure 9* it can be seen that $(\delta T/\delta p)_c$ values are in close agreement with experimental values. A binodal predicted for $\bar{M} = 37$ kg mol^{-1} at 50 bar is plotted in *Figure 10* and agrees very well with the observed data[25] in contrast to the binodal predicted with fit B.

The ΔV^E is negative for $T < 13.0$°C. The calculation is thus consistent with observations on $(\delta T/\delta_p)_c$ and ΔV^E. None of the 'simpler' SP treatments lead to this degree of agreement.

MFLG treatment

Beckman[42] has studied the system PS/CH with the zero-order MFLG model. He adjusted the three

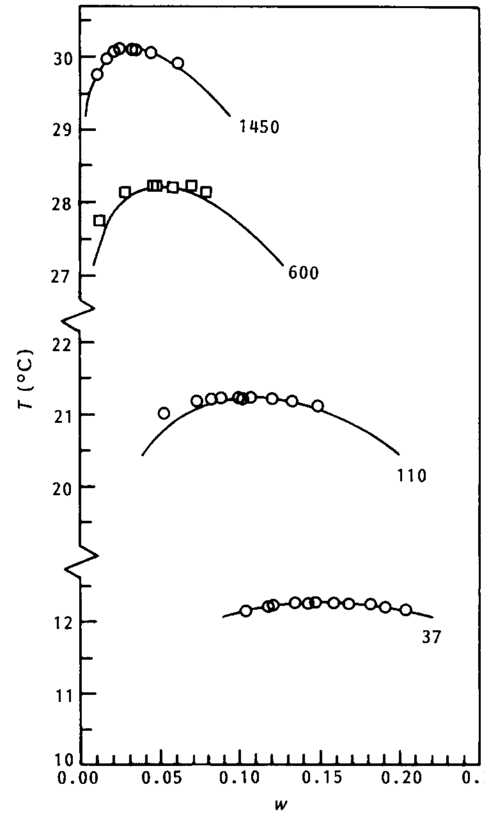

Figure 8 Predicted binodals (——) for the indicated molar masses of PS (in kg mol^{-1} in the rigid lattice model calculated with the semi-empirical interaction function of Nies *et al.*[40]. Experimental cloud points from references 25 (○) and 26 (□), respectively

Table 4 SP treatment. Values for the parameters in equations (23) and (24)

$B_{0,1}$ (bar^{-1})	-0.21163×10^{-3}
$B_{0,2}$ (bar^{-2})	-0.14547×10^{-5}
$B_{1,0}$ (K bar^{-1})	0.60546×10^{-1}
$B_{1,2}$ (K bar^{-2})	0.45138×10^{-3}

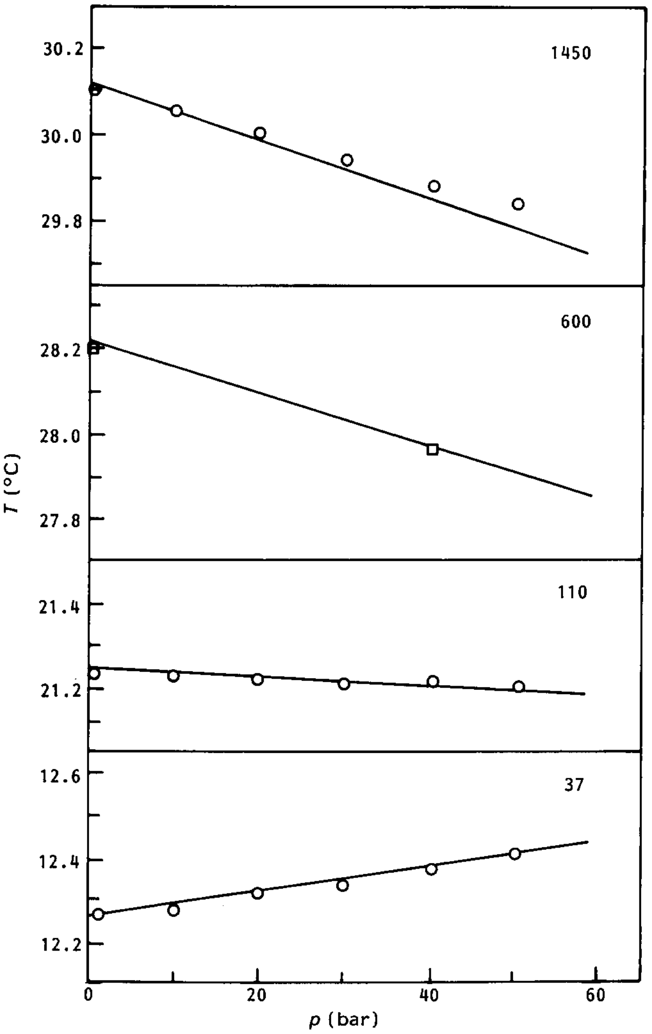

Figure 9 Critical temperatures as a function of pressure calculated with the SP treatment [equations (23) and (24) and with the parameter values in *Table 4*] for the indicated molar masses of PS (in kg mol^{-1}). Experimental data from references 25 (○) and 26 (□), respectively

parameters for the mixture in equation (15) to spinodal points at 1 bar for different molar masses of PS. We used these parameter values to predict consolute states at higher pressures. No pressure of optimum miscibility is obtained: the value of $(\delta T/\delta p)_c$ for each molar mass is positive and fairly large. This result is not unexpected since the adjustment of the parameters was confined to data at atmospheric pressure.

Therefore, the parameters for the mixture in the zero order MFLG model were adjusted to the critical data of Saeki *et al.*[25] at 1 bar and Wolf and Geerissen[26] at 1–300 bar (similar to fit A). The parameters for the pure components were taken from reference (42). This procedure fails completely: no fit was possible and we had to resort to higher order MFLG treatments.

Instead of using the first-order MFLG model [equation (16)] in its closed form, we made the parameter a_{12} ϕ_0-dependent. This is allowed since expanding the $\ln Q/Q$ term in equation (16) into a power series of the hole concentration results in

$$a_{12} = a_{12,0} + a_{12,1}\phi_0 + a_{12,2}\phi_0^2 + \cdots \qquad (25)$$

Here the polynomial was truncated after the quadratic term.

Equations for EOS, and spinodal and critical conditions can be found in the Appendix. Again the parameters for the mixture were adjusted to the data in *Table 1* (similar to fit A). The main conclusion is that this version of the MFLG model is capable of representing the influence of pressure on the phase behaviour of one PS sample in CH. The MFLG description of Wolf and Geerissen's data is slightly less good than that in the SP treatment (*Figure 11*). However, predicted binodals are very flat and the critical exponent $(\delta T/\delta m_2^{-1})_c$ is too small. Although a positive value has not been obtained for lower molar masses $(\delta T/\delta p)_c$ increases (becomes less negative) at very low molar masses of PS.

Rather simple MFLG models have so far failed in covering consolute states for PS/CH. It was, however, possible to obtain a qualitative description. Introduction

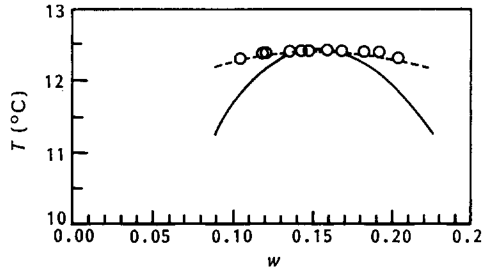

Figure 10 Predicted binodal (– – –) at 50 bar ($\bar{M}$ = 37 kg mol^{-1}) in the SP treatment [equations (23) and (24) and with the parameter values in *Table 4*]: (——) calculated with equation (17) and the parameter values in *Table 2*, column *B*; (○) experimental cloud points[25]

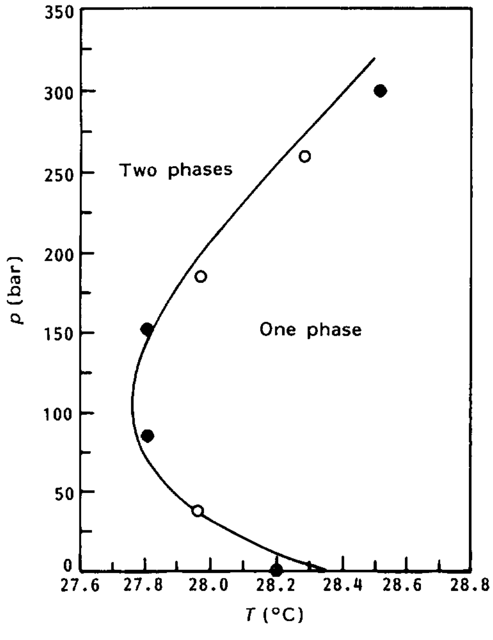

Figure 11 Critical temperatures as a function of pressure calculated with the MFLG model for a PS sample of molar mass of 600 kg mol^{-1} and compared to experimental data (○)^{26} (see text): (+) used in the fit

Table 5 Values for the MFLG parameters for the pure components CH and PS and for their mixture

	CH	PS	PS/CH
m_i	3.9931	3.7013[a]	
c_i	−0.43713	−0.94379	
$b_{0,i}$	0.28334	0.91379	
$b_{1,i}$ (K)	578.07	2158.3	
$a_{i,0}$	−0.08179	−2.484	
$a_{i,1}$	−0.62039	2.8023	
$a_{12,0}$			0.28425
$a_{12,2}$			−3.0095
$b_{12,00}$			0.06510
$b_{12,01}$			1.0224
$b_{12,02}$			−0.33737
$b_{12,10}$ (K)			−5.5952
$b_{12,11}$ (K)			−361.35
b_{12} (K^{-1})			-0.3653×10^{-2}

[a] Per chemical repeat unit

of a large amount of semi-empirical parameters for the mixture and re-examination of the parameters for the pure components were inevitable.

First of all inspection of the fit procedure of Beckman[42] for CH showed that the parameters for CH were adjusted to data outside the temperature range of interest (10–30°C). Therefore, the parameters were recalculated using some additional data by Wisotski and Wurflinger[43] and Jonas *et al.*[44]. Furthermore since both ends of the concentration scale should be described properly, a_i was made linearly dependent on ϕ_0:

$$a_i = a_{i0} + a_{i1}\phi_0 \tag{26}$$

This procedure was repeated for PS. The parameter values are listed in *Table 5*.

Further, a large number of parameters on a semi-empirical basis had to be introduced. A 'trial and error' procedure yielded the following equation for g_{12} in equation (15)

$$g_{12} = a_{12}\phi_0 + (b_{12,0}\phi_0 + b_{12,1}\phi_0/T + b_{12,2}T)Q^{-1} \tag{27}$$

with

$$b_{12,0} = b_{12,00} + b_{12,01}\phi_0 + b_{12,02}\phi_0^2$$

$$b_{12,1} = b_{12,10} + b_{12,11}\phi_0$$

$$a_{12} = a_{12,0} + a_{12,2}\phi_0^2$$

This procedure defining $b_{12,0}$ and $b_{12,1}$ as a function of ϕ_0 resembles the SP treatment. In the MFLG models no justification can be found[45] why $b_{12,1}$ and $b_{12,0}$ should depend on ϕ_0. One could argue that the interaction between like and unlike segments changes with the reciprocal volume and, as a consequence, with the hole fraction.

The parameters in equation (27) have been estimated using the critical data of references 25 and 26 in *Table 1* (similar to fit B). The values are listed in *Table 5*. The agreement between theory and observation is only qualitative (*Figures 12* and *13*). The value for $(\delta T/\delta p)_c$ changes sign from positive to negative upon an increase in molar mass, as it has been observed, but the agreement is very poor compared to the prediction with Nies *et al.*'s g function[40] which contains fewer parameters than the version of the MFLG model used here (14 *versus* 22 in the MFLG model). *LCST* demixing is predicted by the MFLG model at ~150°C lower than the measured temperatures.

In the MFLG model ΔV^E is calculated using the EOS and equation (28):

$$\Delta V^E = V_m - w_1 V_1 - w_2 V_2 \tag{28}$$

where w_1 represents the weight fraction of component i.

In *Figure 14* ΔV^E values at 28°C for different molar masses of PS are compared to experimental data[32,33]. For large molar masses ΔV^E is more or less independent of the molar mass. For short chain lengths the calculated ΔV^E is slightly positive at low concentrations. Further, values for ΔV^E approximate Flory's value but their absolute values are too small compared to Wolf's data.

In view of these results it seems neither worth while nor practical to try and further extend the MFLG model.

DISCUSSION AND CONCLUSIONS

The SP and MFLG models were developed along similar lines and are based on a mean-field lattice approach. The enthalpy of mixing is in both cases calculated using Staverman's concept[15] of interacting molecular surface areas of segments and molecules.

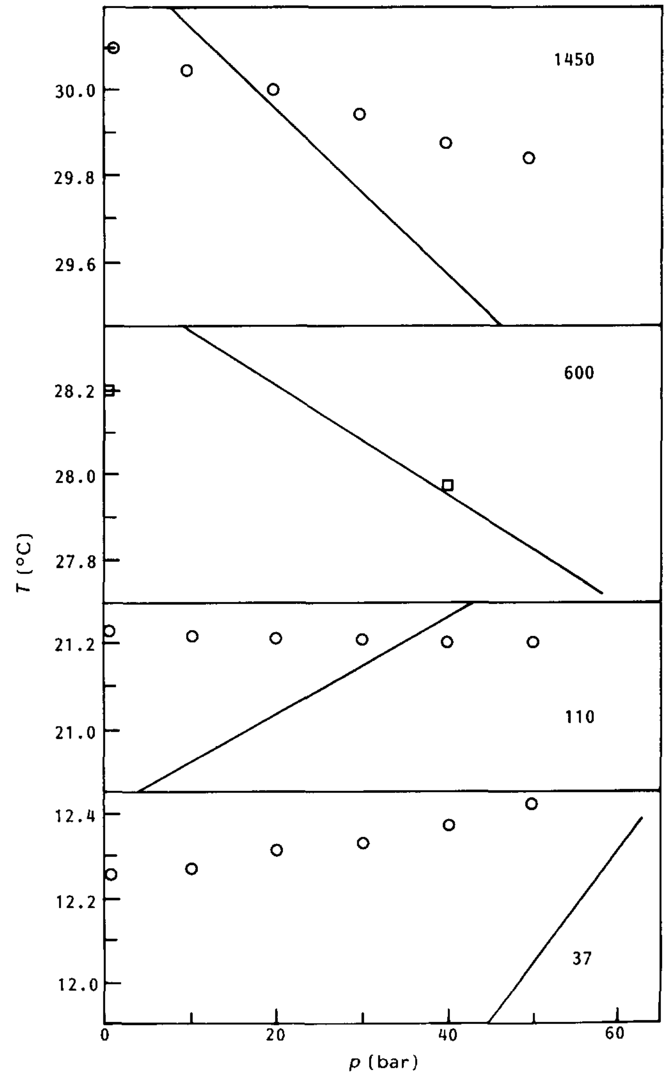

Figure 12 Critical temperature as a function of pressure calculated with the MFLG model [equations (25)–(27) and with the parameter values in *Table 5*] for the indicated molar masses of PS (kg mol^{-1}). Experimental data from references 25 (○) and 26 (□), respectively

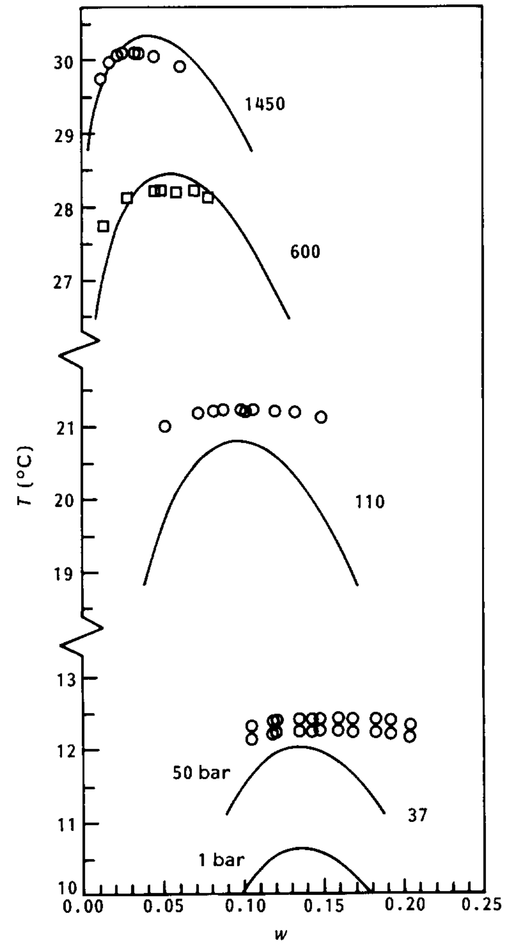

Figure 13 Theoretical binodals (——) in the MFLG model predicted with equations (25)–(27) and with the parameter values in *Table 5*, for the indicated molar masses of PS (in kg mol^{-1}) at 1 bar. Experimental cloud points from references 25 (○) and 26 (□), respectively

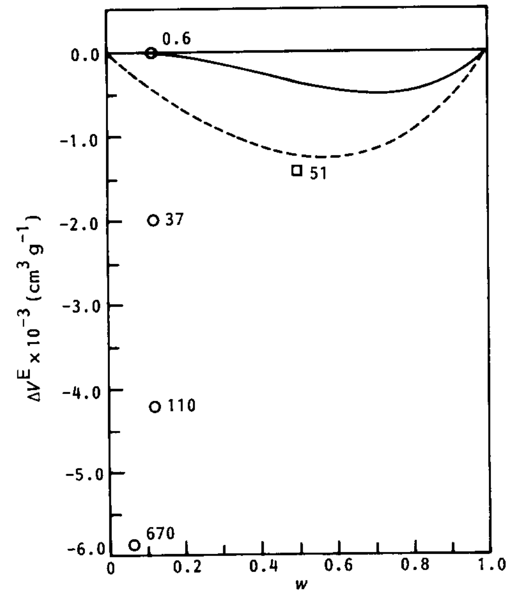

Figure 14 Comparison of experimental excess volumes and those predicted by the MFLG model at 28°C [equations (25)–(29) and with the parameter values in *Table 5*): (——) $\bar{M} = 0.6$ kg mol^{-1}; (– – –) $\bar{M} = 670$ kg mol^{-1}. Calculated curves for molar masses of 37, 110 and 670 kg mol^{-1} coincide. Experimental data at the indicated molar masses of PS and at 25°C (□)[32] and 28°C (○)[33]

In the MFLG model, however, empty sites or holes are introduced into the two-component rigid lattice which, effectively, play the role of a third component. This results in an extra parameter. The concentration of segments 1 and 2 and holes are related through equation (15b). In the SP model volume fractions were assumed to be independent of pressure and molar mass. Furthermore in the MFLG model parameters for the pure components have to be adjusted to experimental data such as V/L equilibria. This information is not always available over a broad p–T range.

In the SP approach the variation of some parameters [b_0 and b_1 in equation (3)] with pressure was defined using general relationships. When this pressure dependence is determined by critical data at 1–300 bar for one PS sample in CH it correctly predicts the change in sign of $(\delta T/\delta p)_{\text{c}}$ on going from low to high molar masses of PS. A near-quantitative covering of all data could be reproduced.

As easily as good results with the SP model were obtained so was it difficult for the MFLG model. The pressure-phase behaviour relation for one PS sample could be very well represented if a_{12} is made ϕ_0-dependent. A very complex interaction function [equation (28)] had to be applied and led to qualitative results only. Perhaps it should not be a surprise that a highly complicated concentration dependence of g_{12} on ϕ_0 was found. Phenomenological thermodynamics yields the following relation between the critical temperature and pressure[46]

$$\left(\frac{\partial \ln T}{\partial p}\right)_{\text{c}} = \frac{(\partial^2 \Delta V^{\text{E}}/\partial x^2)_{\text{c}}}{(\partial^2 \Delta H^{\text{E}}/\partial x^2)_{\text{c}}} \tag{29}$$

where the subscript c indicates the critical point. For *UCST*s ($\Delta H^{\text{E}} > 0$) the denominator is negative. If there is an extremum in temperature[26] then $(\delta \ln T/\delta p)_{\text{c}}$ is zero and $\Delta V^{\text{E}}(x)$ possesses a point of inflection. In the case of PS/CH, it should, therefore, be expected that theoretical expressions may become quite complex.

As a result of the definition of the interaction function ΔV^{E} in the SP model is independent of the molar mass of the polymer. In the MFLG model ΔV^{E} is a function of the molar mass of PS through equation (15b). The effect is too small, however, and quickly vanishes with increasing chain length. Only at very small segment numbers does ΔV^{E} change drastically and eventually change sign. The values for ΔV^{E} in the SP model are about five times smaller than the values calculated with the MFLG model at 28°C.

Binodals predicted at different pressures using both models were in reasonable agreement with experiment though too narrow. A modified form of the SP treatment which takes the bridging theory into account, covers binodal (and spinodal points) at ambient pressure (1 bar) extremely well. This semi-empirical model could be transferred to higher pressures within the SP treatment.

It was mentioned in the Introduction that conclusions made from the second virial coefficient data by Schulz and Lechner[31] on the one hand and the data by Saeki *et al.*[25] on the other seem to be in conflict. Using the SP model (fit B) the positive value of $(\delta T/\delta p)_\theta$ could be reproduced only at higher pressures (> 150 bar). Furthermore calculated θ values were too low but agree with θ temperatures obtained from Shultz–Flory plots. Calculated ΔV^{E} are negative at high temperatures (>17°C) which is inconsistent with data by Schulz *et al.*, but consistent with observed ΔV^{E} data.

The question remains, however, as to how accurately ΔV^{E} values can be determined[47]. This brings us to the question whether ΔV^{E} values can be used to determine model parameters and as a result provide information on the demixing of a polymer solution. The SP treatment cannot be applied since experimental data on ΔV^{E} would only supply some of the parameters [see equation (20)]. It would be necessary to obtain additional information (e.g. spinodals). For the MFLG model the situation is somewhat different. Using the EOS and equation (29) all parameters for the mixture could be determined only if sufficient information is available, i.e. over a wide temperature and pressure range. Furthermore one should have accurate descriptions of the *pVT* data for both components in the $p-T$ region of interest.

It can be concluded that the SP model is a promising approach for a consistent study of the pressure dependence of phase relations in polymer solutions. It has the advantage over the MFLG model that no parameters for the pure components are needed.

ACKNOWLEDGEMENTS

The authors are indebted to Professor B. A. Wolf (Mainz) for kindly supplying the experimental data on the excess volume, to Dr E. Nies (Eindhoven) for calling their attention to reference 31 and to Dr L. A. Kleintjens (DSM) for stimulating discussions. L. van Opstal thanks DSM for a PhD grant (Universitaire Instelling Antwerpen).

REFERENCES

1 Staverman, A. J. and Van Santen, J. M. *Rec. Trav. Chim.* 1941, **60**, 76; Staverman, A. J. *Rec. Trav. Chim.* 1941, **60**, 640

2 Huggins, M. L. *J. Chem. Phys.* 1941, **9**, 440; *Ann. NY Acad. Sci.* 1942, **43**, 1

3 Flory, P. J. *J. Chem. Phys.* 1941, **9**, 660; 1942, **10**, 51

4 Koningsveld, R. and Staverman, A. J. *Kolloid.-Z. Z. Polym.* 1966, **210**, 151; 1967, **220**, 31

5 Simha, R. and Somcynski, T. *Macromolecules* 1969, **2**, 343

6 Jain, R. K. and Simha, R. *J. Chem. Phys.* 1980, **72**, 4909

7 Simha, R. and Wilson, P. J. *Macromolecules* 1973, **6**, 908

8 Flory, P. J., Orwoll, A. and Vrij, J. A. *J. Am. Chem. Soc.* 1964, **86**, 3507

9 Frenkel, J. 'Kinetic Theory of Liquids', Oxford University Press, London, 1946

10 Sanchez, I. C. and Lacombe, R. H. *J. Phys. Chem.* 1976, **80**, 2352

11 Kleintjens, L. A. and Koningsveld, R. *Colloid Polym. Sci.* 1980, **258**, 711

12 Kleintjens, L. A. and Koningsveld, R. *J. Electr. Chem.* 1980, **127**, 2352

13 Van der Haegen, R., Koningsveld, R., Kleintjens, L. A. and van Opstal, L. *Fluid Phase Eq.* 1988, **43**, 1

14 Guggenheim, E. A. 'Mixtures', Clarendon, Oxford, 1952

15 Staverman, A. J. *Rec. Trav. Chim.* 1937, **56**, 885; *PhD Thesis*, University of Leiden, 1938

16 Koningsveld, R. and Staverman, A. J. *J. Polym. Sci. A2* 1968, **6**, 325

17 Bondi, A. *J. Phys. Chem.* 1968, **68**, 441

18 Gibbs, J. W. 'Collected Works', Vol. I, Yale University Press, 1948

19 Stockmayer, W. H. *J. Chem. Phys.* 1949, **17**, 588

20 Koningsveld, R., Chermin, H. A. G. and Gordon, M. *Proc. R. Soc.* 1970, **A319**, 331

21 Koningsveld, R. in 'Integration of Fundamental Polymer Science and Technology' (Eds L. A. Kleintjens and P. J. Lemstra), Elsevier, London, 1985, p. 3

22 Silverberg, A. *J. Chem. Phys.* 1968, **48**, 2835

23 Koningsveld, R., Diepen, G. A. M. and Chermin, H. A. G. *Rec. Trav. Chim.* 1966, **85**, 504

24 Beckman, E., Porter, R. S. and Koningsveld, R. *J. Phys. Chem.* 1987, **91**, 6429

25 Saeki, S., Kuwahara, N., Nakata, M. and Kaneko, M. *Polym. J.* 1975, **16**, 445

26 Wolf, B. A. and Geerissen, H. *Colloid Polym. Sci.* 1981, **259**, 1214

27 Gordon, M. personal communication, 1988

28 Saeki, S., Kuwahara, N., Konno, S. and Kaneko, M. *Macromolecules* 1973, **6**, 246

29 Hashizume, J., Teramoto, A. and Fujita, H. *J. Polym. Sci.* 1981, **19**, 1405

30 Schulz, G. V. and Lechner, M. *J. Polym. Sci. A2* 1970, **8**, 1885

31 Schulz, G. V. and Lechner, M. in 'Light Scattering from Polymer Solutions' (Ed. M. B. Huglin), Academic Press, New York, 1971, Ch. 12, p. 17

32 Hocker, H., Shih, H. and Flory, P. J. *Trans. Faraday Soc.* 1971, **67**, 2275

33 Wolf, B. A. personal communication, 1989

34 van Opstal, L. *PhD Thesis* Antwerp, 1991

35 Koningsveld, R., Kleintjens, L. A. and Shultz, A. R. *J. Polym. Sci. A2* 1970, **8**, 1261

36 Scholte, T. G. *J. Polym. Sci. A2* 1971, **9**, 1553

37 Koningsveld, R., Stockmayer, W. H., Kennedy, J. W. and Kleintjens, L. A. *Macromolecules* 1974, **7**, 73

38 Delmas, G., Patterson, D. and Somcynski, T. *J. Polym. Sci.* 1962, **57**, 79

39 Young, S. *Sci. Proc. R. Soc. (Dublin)* 1910, 374

40 Nies, E., Koningsveld, R. and Kleintjens, L. A. *Progr. Coll. Polym. Sci.* 1987, **71**, 2

41 Koningsveld, R., Kleintjens, L. A. and Nies, E. *Croatica Chem. Acta* 1987, **60**, 53

42 Beckman, E. J. *PhD Thesis* University of Massachusetts, 1987

43 Wisotzki, K. D. and Wurflinger, A. *J. Phys. Chem. Solids* 1982, **43**, 13

44 Jonas, J., Haska, D. and Huang, J. G. *J. Phys. Chem.* 1980, **84**, 109

45 Koningsveld, R., Kleintjens, L. A. and Leblans-Vinck, A.-M. *J. Phys. Chem.* 1987, **91**, 6423

46 Rehage, G. *Z. Naturforsch.* 1955, **10a**, 300

47 Koningsveld, R. and Kleintjens, L. A. *Acta Polym.* 1988, **9**, 342

APPENDIX

The equation of state is in the MFLG model defined as[11–13]

$$-p = (\partial\, \Delta A/\partial V)_{T,n_1} \tag{A1}$$

Combination of equations (15), (26) and (A1) results in

$$-\frac{pv_0}{RT} = \ln \phi_0 + \sum_i [1 - (1/m_i)]\phi_i + (1 - \phi_0)\sum_i a_i\phi_i + (Q - \phi_0)Q^{-2}\sum_i b_i\phi_i - (a_{12} + b_{12}Q^{-2})\phi_1\phi_2 + (a_{12,1} + 2a_{12,2}\phi_0)\phi_1\phi_2 \tag{A2}$$

The equilibrium condition between two phases is given by

$$\Delta\mu_k^{\mathrm{l}} = \Delta\mu_k^{\mathrm{v}} \tag{A3}$$

and

$$\Delta\mu_k = (\partial\, \Delta A/\partial n_k)_{T,n_{i\neq k}} \tag{A4}$$

Substitution of equations (15) and (26) into equation

(A4) and rearrangement yields

$$\begin{aligned}\Delta\mu_k/(m_kRT) &= (1/m_k)\ln\phi_k - [1-(1/m_k)]\\ &\quad + \sum_i^2 [1-(1/m_i)]\phi_i\\ &\quad - \phi_0\sum_i^2 a_i\phi_i + g_k\phi_0 + g_{12}\phi_k\\ &\quad - (1-c_k)Q^{-2}\left(\phi_0\sum_i^2 b_i\phi_i + b_{12}\phi_1\phi_2\right)\\ &\quad - (a_{12,0}+2a_{12,0}\phi_0+3a_{12,2}\phi_0^2)\phi_1\phi_2\end{aligned}\tag{A5}$$

The spinodal and critical condition are defined as[11–13]

$$J_{\mathrm{SP}} = F_{11}F_{22} - F_{12}^2 = 0\tag{A6}$$

and

$$J_{\mathrm{C}} = (\partial J_{\mathrm{SP}}/\partial\phi_1)F_{22} - (\partial J_{\mathrm{SP}}/\partial\phi_2)F_{12} = 0\tag{A7}$$

respectively, where

$$F_{hk} = \partial^2 F/\partial\phi_h\,\partial\phi_k\tag{A8}$$

$$\begin{aligned}&= 1/\phi_0 + \delta_{hk}/(m_h\phi_h) - g_h - g_k - \sum_i^2 (g_{i,h}+g_{i,k})\phi_i\\ &\quad + \phi_0(g_{h,k}+g_{k,h}) + \phi_0\sum_i^2 g_{i,hk}\phi_i + g_{12}(1-\delta_{hk})\\ &\quad + g_{12,k}\phi_k + g_{12,h}\phi_h\\ &\quad + g_{12,hk}\phi_1\phi_2\end{aligned}\tag{A9}$$

$$\begin{aligned}F_{hkl} &= \partial^3 F/\partial\phi_h\,\partial\phi_k\,\partial\phi_l\\ &= 1/\phi_0^2 - \delta_{hkl}/(m_h\phi_h^2)\\ &\quad - (g_{k,h}+g_{l,h}+g_{h,k}+g_{l,k}+g_{h,l}+g_{k,l})\\ &\quad - \sum_i^2 (g_{i,kh}+g_{i,hl}+g_{i,kl})\phi_i\\ &\quad + \phi_0(g_{h,kl}+g_{k,hl}+g_{l,hk}) + \phi_0\sum_i^2 g_{i,hkl}\phi_i\\ &\quad + 2g_{12,1}(1-\delta_{hkl})\\ &\quad + 2g_{12,kl}\phi_k + g_{12,hl}\phi_h\\ &\quad + g_{12,hkl}\phi_1\phi_2\end{aligned}$$

and where

$$F = \Delta A$$

$$g_{i,hkl}\ldots = \partial^\omega g_i/\partial\phi_h\,\partial\phi_k\,\partial\phi_l\,\partial\ldots = (\omega!)b_i\prod_i^\omega c_iQ^{-(\omega+1)}$$

$$g_{ij,hkl}\ldots = \partial^\omega g_{ij}/\partial\phi_h\,\partial\phi_k\,\partial\phi_l\,\partial\ldots = (\omega!)b_{ij}\prod_i^\omega c_iQ^{-(\omega+1)}$$

$$\delta_{xy} = \begin{cases}1 & x = y\\ 0 & x \neq y\end{cases}$$

$$\delta_{xyz} = \begin{cases}1 & x = y = z\\ 0 & \text{otherwise}\end{cases}$$