Mean-Field Lattice Equations of State. 3. Modeling the Phase Behavior of Supercritical Gas-Polymer Mixtures

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ABSTRACT: The mean-field lattice gas (MFLG) model of Kleintjens et al. is used to predict the solubility of atactic poly(methyl methacrylate) (PMMA) in supercritical carbon dioxide (CO_2). The necessary material parameters are found via fitting the unary MFLG equations against literature $P-V-T$ data for the pure components and to binary sorption data at temperatures between 315 and 341.2 K. Subsequent predictions of sorption at temperatures of 298.2 and 461.53 K are in excellent agreement with published data, thus demonstrating the large useful temperature range of the model. Dilute solution binodals and spinodals are calculated and compared to oligomer solubility data measured using a flow-through apparatus. The model underestimates oligomer solubility in all cases, possibly due to the breakdown of the mean-field approximation in very dilute polymer solutions and to the assumption that high molecular weight polymer is insoluble in CO_2, which was made to facilitate parameter fitting. An examination is also made of the system polystyrene (PS)-CO_2, despite the scarcity of literature sorption data for use in the determination of the binary parameters. The trends are similar to those found for PMMA-CO_2. Not surprisingly, CO_2 is a better solvent for PMMA than for PS. Considerations are made toward further improvements in the model.

Introduction

Supercritical fluids (SCF) are often used as process fluids in the food, pharmaceutical, and petroleum industries.[1] Recently there has been increased interest in using these types of fluids to extract and/or process polymers.[2,3]

Supercritical gas-polymer mixtures present special problems for those interested in modeling their phase behavior. Generally, solubility of low molecular weight solids in supercritical gases is modeled using a cubic equation of state, such as the modified van der Waals,[4,5] Peng-Robinson, or Soave modifications of the Redlich-Kwong expression.[6] In the modeling of the partitioning of material between phases during phase separation in solid-supercritical gas mixtures, it is often assumed that the solute-rich phase is pure solute. Thus the fugacity of this phase can be described using the solute vapor pressure and the Poynting correction, eliminating the need for a complete description of the solute $P-V-T$ properties (the fugacity of the gas is calculated using the EOS). This approach, while effective in describing low molecular weight crystalline solid solubility in supercritical gases, is inappropriate for modeling amorphous polymer-gas phase behavior (particularly high molecular weight polymer) because, more often than not, the reverse of the aforementioned assumption is true. The solute-rich phase usually consists of highly swollen polymer while the SCF-rich phase is extremely dilute. Provided that the T_g of the polymer has been sufficiently suppressed due to the presence of the gaseous diluent, the system should be treated as one involving liquid-liquid equilibrium, rather than liquid-solid, as described below. However, polymer solution theories such as the Flory-Huggins model do not account for changes in free volume and consequently will not accurately model the phase behavior of gas-polymer mixtures.[7] Models that use a cell representation for changes in volume, such as Flory's equation of state, can accurately predict the $P-V-T$ properties of polymers but will underestimate the compressibility of supercritical gases[8] and thus can give poor predictions below approximately 200 atm. In addition, Raetzsch et al.[9] have shown that it is necessary to incorporate a temperature dependence for the material parameters in this model to obtain a good description of polymer-supercritical gas phase behavior.

Mean-field lattice models, in which holes, or vacancies, have been introduced to simulate the effect of changes in volume, have been used successfully to model aspects of polymer solution phase behavior,[10-12] including the case where the solvent is a supercritical gas.[13] The major drawback to these models is that, due to their mean-field basis, the large fluctuations in polymer segment density owing to the isolated nature of polymer coils in dilute solutions are neglected,[14] leading to an underestimation of the number of polymer segment-segment interactions at low polymer concentrations. Thus, determination of binary interaction parameters via fitting of a mean-field lattice model to dilute polymer solution data could introduce considerable error into subsequent predictions.

In this paper the mean-field lattice gas (MFLG) model of Kleintjens et al.[15,17] is used to model the phase behavior of atactic poly(methyl methacrylate) (PMMA)-CO_2 and polystyrene (PS)-CO_2 mixtures at temperatures above the critical point of the gas. In order to avoid problems concerning the breakdown of the mean-field approximation in very dilute polymer solutions, the binary interaction parameters were determined by fitting the MFLG model equations to equilibrium swelling results for the two gas-polymer mixtures. To facilitate the modeling procedure, the SCF-rich phase for these situations was assumed to be essentially pure and the polymer-rich phase was assumed to be an equilibrium liquid, i.e., above its

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Table I
Thermodynamic Relationships for Binary Mixtures for the Mean-Field Lattice Gas (MFLG) Model

binary equation of state

$$-p = \frac{1}{v_0}\left(\frac{\partial \Delta A}{\partial n_0}\right)_{T,n_1,n_2}$$

binodal

$$\mu_i = \mu'_i, \quad i = 0, 1, 2$$

$$\mu_i = \left(\frac{\partial \Delta A}{\partial n_1}\right)_{T,n_j}$$

spinodal

$$J_{\mathrm{sp}} = \begin{vmatrix} A_{11} & A_{12} \\ A_{12} & A_{22} \end{vmatrix} = A_{11}A_{22} - A_{12}A_{21} = 0$$

where

$$A_{ij} = \frac{\partial^2 \Delta A}{\partial \phi_i \partial \phi_j}$$

critical condition

$$\begin{vmatrix} \dfrac{\partial J_{\mathrm{sp}}}{\partial \phi_1} & \dfrac{\partial J_{\mathrm{sp}}}{\partial \phi_2} \\ A_{21} & A_{22} \end{vmatrix} = \frac{\partial J_{\mathrm{sp}}}{\partial \phi_1}A_{22} - \frac{\partial J_{\mathrm{sp}}}{\partial \phi_2}A_{21} = 0$$

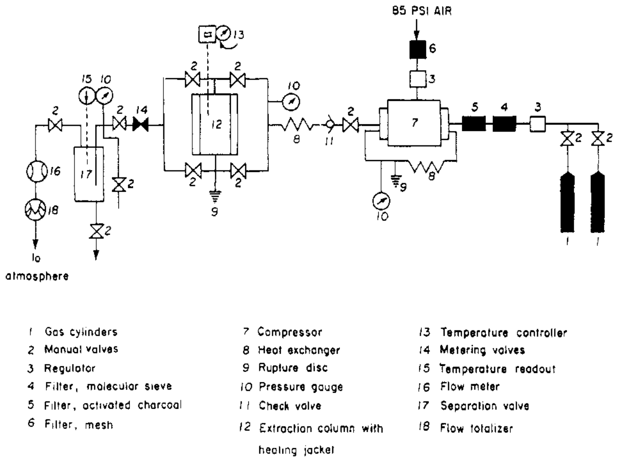

Figure 1. Supercritical fluid extraction unit flow diagram.

Table II
MFLG Material Parameters for Poly(methyl methacrylate) and Carbon Dioxide and for the PMMA–CO$_2$ Mixture

param	CO$_2$	PMMA	zero-order model PMMA–CO$_2$
m	1.31	3.13[a]	
α	0.91498	-9.0493	
g_{10}	-2.519	13.96	
g_{11}	1144.1	3111.2	
γ	-1.2010	-1.286	
α_m			4.2339
g_{m0}			8.9138
g_{m1}			440.6

[a] Segments per monomer unit.

glass transition. The binary interaction parameters are therefore dependent only on the composition of the polymer-rich phase, whose composition is in the range where the mean-field approximation is expected to be valid.

Theory

MFLG Model. The fundamentals of the MFLG model have been described previously.[15-17] A brief summary follows.

The MFLG model envisions a compressible fluid as an equilibrium mixture of segments and holes on a three-dimensional lattice, where the segments and holes are permitted to have different contact surface areas and, therefore, different numbers of nearest neighbors. The internal energy of mixing of holes and segments is calculated using regular solution theory using surface fractions instead of volume fractions. The entropy of mixing is assumed to follow the Flory–Huggins–Staverman expression. Just as a pure component in the context of the MFLG model is represented as an equilibrium pseudobinary (holes and segments), a binary mixture becomes a pseudoternary. The equation for the MFLG Helmholtz free energy of a binary mixture is derived as

$$\begin{aligned}\frac{\Delta A}{N\phi RT} = {} & \phi_0 \ln \phi_0 + \frac{\phi_1}{m_1}\ln \phi_1 + \frac{\phi_2}{m_2}\ln \phi_2 + \\ & \phi_1\phi_1\left(\alpha_1 + \frac{\beta_1}{(1-\gamma_1\phi_1-\gamma_2\phi_2)}\right) - O(\phi_1) + \\ & \phi_0\phi_2\left(\alpha_2 + \frac{\beta_2}{(1-\gamma_1\phi_1-\gamma_2\phi_2)}\right) - O(\phi_2) + \\ & \phi_1\phi_2\left(\alpha_m + \frac{\beta_m}{(1-\gamma\phi_1-\gamma_2\phi_2)}\right) \end{aligned} \quad (1)$$

with

$$\gamma_i = 1 - \sigma_i/\sigma_0 \qquad \beta_i = g_{i0} + g_{i1}/T$$

where the ϕ's are the volume fractions of the holes and segments, the g_{i1}'s are the various segment–segment interaction energies, and the σ_i's are the contact surface areas of the holes and segments. The α's and g_{i0}'s are, in the zero-order MFLG model, purely empirical parameters. The two terms $O(\phi_i)$ are required because ΔA refers to the difference in free agency between a mixture of type 1 segments, type 2 segments, and holes and the initial state's type 1 segments plus holes and type 2 segments plus holes. However, since these terms vanish during the derivations of the binary equation of state, binodal, spinodal, and critical point, they need not be discussed further.

The binary equation of state (EOS), binodal, spinodal, and critical conditions are calculated in the usual way as given in Table I.[18,19] The complete set of equations outlined in Table I can be found in ref 15. The volume fractions (ϕ's) can be related to quantities commonly measured on phase separation, such as weight fraction, ω_1, and solution density, ρ_{sol}, by eqs 2–4 where $c_i =$

$$\phi_1 = \frac{(1-\phi_0)c_1\omega_1}{c_1\omega_1 + c_2\omega_2} \quad (2)$$

$$\phi_2 = \frac{(1-\phi_0)c_2\omega_2}{c_1\omega_1 + c_2\omega_2} \quad (3)$$

$$\rho_{\mathrm{sol}} = (\phi_1/c_1 + \phi_2/c_2)(1/v_0) \quad (4)$$

m_i/M_i and v_0 is the molar lattice site volume, which is assumed to remain constant for all substances. The equations in Table I are used to model the distribution of components during a phase separation. As mentioned in the Introduction, in mixtures of gases and polymers,

Table III
Average Errors in Fitting MFLG Equations to Data on Poly(methyl methacrylate) and Carbon Dioxide

		VLE data			
				density, %	
compd	no. of points	temp, K	vapor pressure, %	vapor	liquid
CO_2	15	0.6	1.2	0.5	2.25

	critical point				equation of state		
compd	temp, K	pressure, %	density, %	no. of points	pressure, %	temp, K	density, %
CO_2	1.7	0.1	7.7	66	1.0		4.9
PMMA				40			0.03

the concentration of one phase, in this case the SCF-rich phase, is often essentially pure (i.e., no polymer dissolves in the gas at low pressure). Equilibrium is properly described by a "swelling" binodal, i.e.

$$\mu_0 = \mu_0'(p = p') \tag{5}$$

and

$$\mu_1 = \mu_1' \tag{6}$$

The μ_i's are the chemical potentials of the solvent segments and the holes in the pure (gas) phase and are therefore calculated using the pure-component MFLG free energy expressions.[15,16] The μ_i''s are the chemical potentials of the holes and the solvent segments while mixed with the polymer segments and are consequently found using the appropriate equations from Table I. The MFLG equations governing gas absorption by polymers are therefore

$$\ln(\phi_0'/\phi_0) = \Delta[\phi_1(1 - 1/m_1) + \phi_1(1 - \phi_0)\alpha_1 + \phi_1\beta_1(Q - \phi_0)/Q^2] + \phi_2(1 - 1/m_2) + \phi_2(1 - \phi_0)\alpha_2 + \phi_2\beta_2(Q - \phi_0)/Q^2 - \phi_1\phi_2(\alpha_m + \beta_m/Q^2) \tag{7}$$

and

$$(1/m_1)\ln(\phi_1'/\phi_1) = \Delta[\phi_1(1 - 1/m_1) + \phi_0(1 - \phi_1)\alpha_1 + \phi_0\beta_1(Q - \phi_1(1 - \gamma_1))/Q^2] + \phi_2(1 - 1/m_2) - \phi_0\phi_2(\alpha_2 + \beta_2(1 - \gamma_1)/Q^2) + \phi_2(1 - \phi_1)\alpha_m + \phi_2\beta_m(Q - \phi_1(1 - \gamma_1))/Q^2 \tag{8}$$

where

$$\beta_1 = g_{10} + g_{11}/T$$
$$\beta_2 = g_{20} + g_{21}/T$$
$$\beta_m = g_{m0} + g_{m1}/T$$
$$Q' = 1 - \gamma_1\phi_1'$$
$$Q = 1 - \gamma_1\phi_1 - \gamma_2\phi_2$$

and $\Delta(x)$ refers to the difference in the value of x of the polymer-rich and SCF-rich phases, or $x - x'$.

Because the MFLG model assumes an equilibrium distribution of holes and segments, eqs 7 and 8 (and indeed, all of the MFLG expressions) apply only to polymer liquids. Therefore, the absorption of a gas by a polymer below its glass transition will be described more accurately by models that account for the nonequilibrium nature of the polymer specific volume below T_g, such as the dual-mode concept.[20]

Computer Fitting Procedure. Determination of the adjustable parameters for the zero- and first-order MFLG models as well as the solution of the coupled equations needed to forecast phase behavior was carried out using the parameter estimation program (PEP), developed at Dutch State Mines (DSM) Research and employed on the University of Massachusetts Engineering Computer Center's DEC Vax cluster. The PEP finds the values of the parameters, λ_j, which are solutions to the minimization problem[21]

minimize

$$\sum_{i=1}^{n}(x_i - x_i^{\circ})^T\Omega^{-1}(x_i - x_i^{\circ}) \tag{9}$$

subject to the constraints

$$f(x_i, \lambda_j) = 0 \tag{10}$$

where the x_i's are the calculated data points, the x_i°'s are the true values, and Ω is the error variance matrix. The constraints are the appropriate equations from Table I in the implicit form, as shown in eq 10. All variables are therefore assumed to have been measured with some error. The errors, or tolerances, from which Ω is calculated are assumed to be random in nature and are set using suggested values from the literature. The best values for the parameters, therefore, are those that fit the surface represented by the constraints (eq 10) to the data x_i° such that the sum of the squares of the distance between x_i°'s and their projections onto the surface is minimal. The distances, $x_i - x_i^{\circ}$, are weighted by the corresponding tolerances, or errors. The problem is solved iteratively for the λ_j using a Gauss–Newton type of algorithm.

Experimental Section

Solubility measurements of polymers in supercritical gases were made using a Fluitron Supercritical Extraction Unit (Fluitron, Inc., Ivyland, PA), a flow diagram of which is shown in Figure 1. Solute is suspended in the flow-through column in a porous, cellulose Soxhlet extraction thimble. Gas is charged to the column to the required pressure after which the system is allowed to equilibrate for approximately 3 h. During this time the pressure and temperature can be maintained to within ±3 bar and ±0.5 K, respectively. The extraction unit is rated for use at pressures up to 2000 bar and temperatures to 150 °C. Following equilibration, the metering valve is opened and the compressor reactivated to maintain pressure during the extraction. As the gas expands through the metering valve, the solute is recovered in the collection vessel, which contains an organic solvent that is known to readily dissolve the polymer under study, in this case toluene. (Use of this organic solvent facilitates removal of the solute from the collection vessel.) A run is continued until the equivalent of 300 cm^3 (3 times the column volume) has been extracted. Following the transfer of the polymer solution from the collection vessel to a flask, the toluene is removed by evaporation and vacuum treatment and the amount of solute is measured gravimetrically. Blank runs involving only the toluene were made in order that impurities in the solvent not be mistaken for dissolved polymer. The volume of the gas expended during the run is recorded by the totalizer and is converted to a weight basis using the literature value for the density. The solubility is taken to be the total amount of solute extracted over two runs divided by the total amount of gas expended during those runs.

Narrow molecular weight polystyrene and poly(methyl methacrylate) standards were obtained from Pressure Chemical Co., Pittsburgh, PA. Nominal molecular weights are 2000 for the

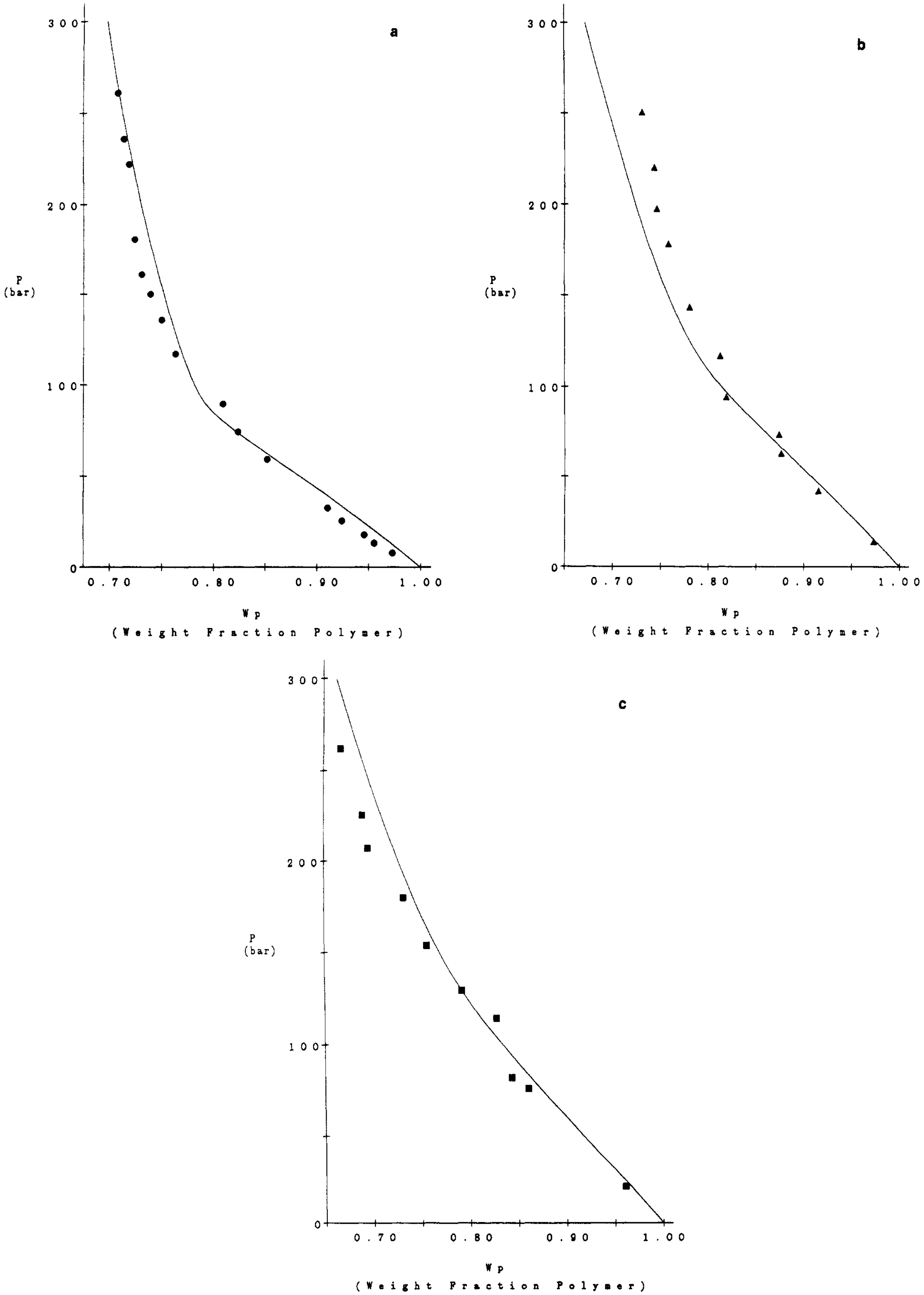

Figure 2. MFLG model (—) description of CO_2 sorption by 33 200 MW PMMA compared to data by Liau and McHugh[22] at (a) $T = 315$ K [●], (b) $T = 331.3$ K [▲], and (c) $T = 341.1$ K [■].

polystyrene ($M_w/M_n < 1.06$) and 7000 and 24 300 for the PMMA's ($M_w/M_n = 1.15$ and 1.10, respectively). Linde bone dry CO_2, obtained from the Merriam-Graves Corp., West Springfield, MA, and Fisher Scientific spectrograde toluene (T-330) were used as received.

Results and Discussion

Poly(methyl methacrylate)–Carbon Dioxide. The sorption behavior of CO_2 by atactic PMMA has been reported by Liau and McHugh.[22] Liau measured the vol-

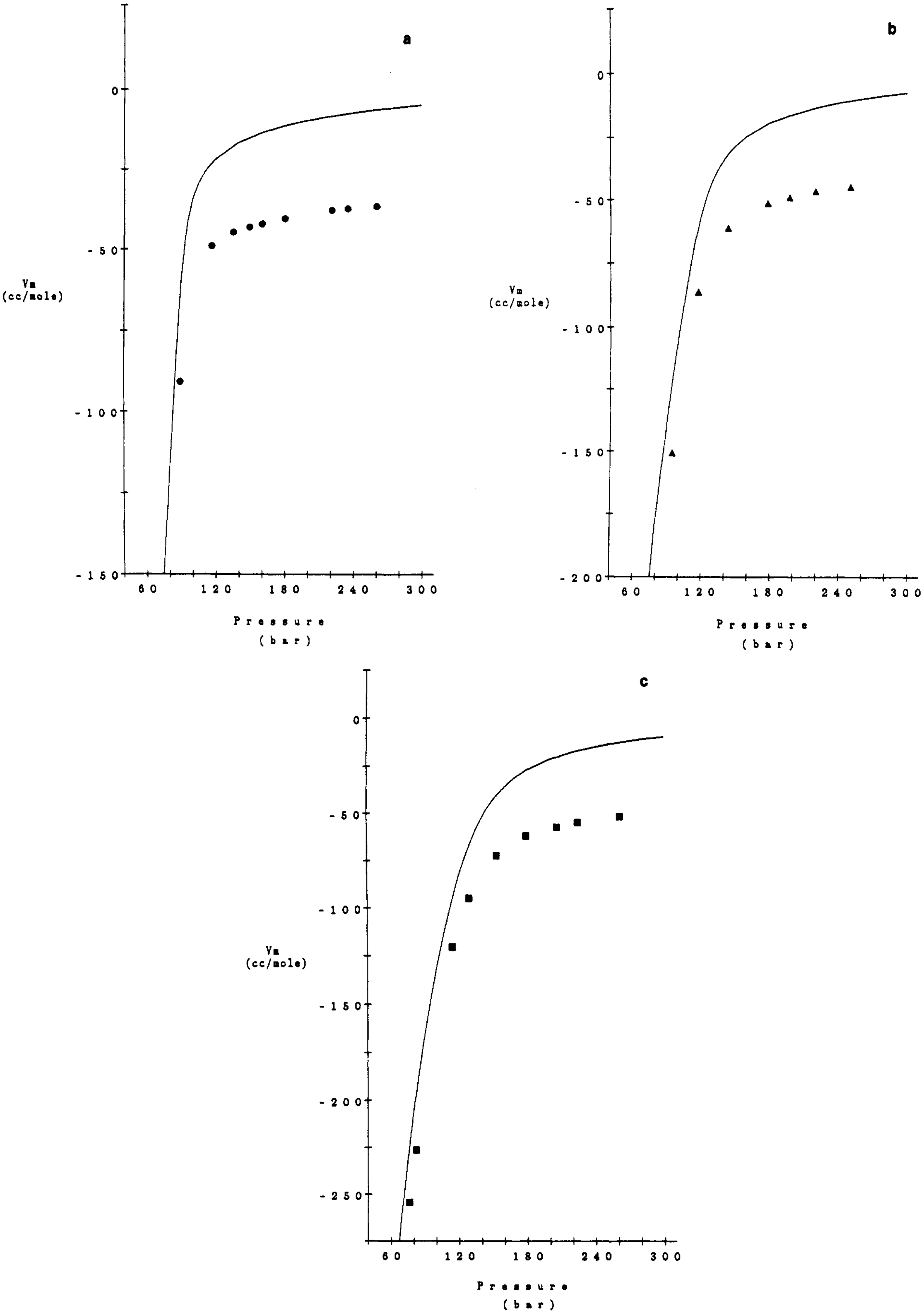

Figure 3. MFLG model (—) prediction of volume change on mixing compared to values calculated from data of Liau and McHugh[22] at (a) $T = 315$ K [●], (b) $T = 331.3$ K [▲], and (c) $T = 341.2$ K [■].

ume change of the polymer upon swelling by the gas, as well as the equilibrium weight fraction CO_2 absorbed, at three temperatures over an extensive range in pressure. The volume change on mixing (excess volume) can be calculated from the combination of the swelling and sorption results using

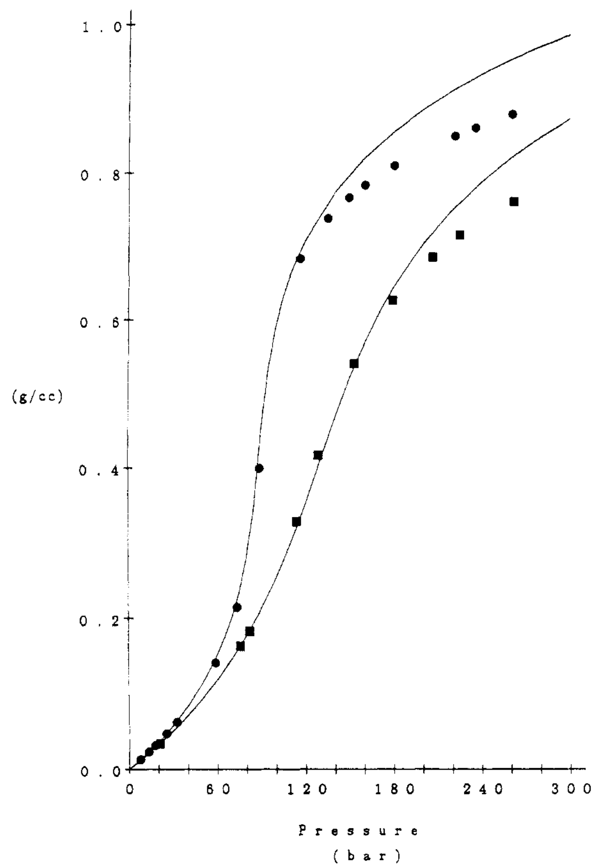

Figure 4. Prediction of CO_2 density by the MFLG model (—) compared to data at T = 315 K (●) and T = 341.2 K (■).

$$\Delta V_m = \frac{\left[\frac{S}{\rho_p} - \left(\frac{1-w_p}{w_p}\right)\frac{1}{\rho_{CO_2}}\right]}{\frac{1}{M_p} + \left(\frac{1-w_p}{w_p}\right)\frac{1}{M_{CO_2}}} \qquad (11)$$

where S is the fractional increase in volume upon swelling, ρ_i and M_i are the densities and molecular weights of the gas and polymer, and w_p is the weight fraction polymer.

Determination of the zero-order MFLG pure-constituent parameters for PMMA and CO_2 has been discussed previously.[23-25] A summary of these results is shown in Tables II and III. The sorption data were used with the model equations governing such behavior (eqs 7 and 8) to find the necessary binary parameters. Results for the three isotherms are shown in parts a-c of Figure 2. The model correctly predicts that the isotherms will intersect, a phenomenon observed in many gas-polymer mixtures.[26,27] The average error in the predicted weight fraction over all three isotherms is 1.6%.

The ΔV_m's derived from Liau's measurements and those predicted by the MFLG model are compared in parts a-c of Figure 3. Although the form of the model description is correct, the predicted ΔV_m's are too positive, particularly at higher pressures. This is a result of both an overestimation of the pure CO_2 density (Figure 4) and an overestimation of the change in volume of the polymer due to swelling by the gas.

To test the useful temperature range of the model, predictions of sorption of CO_2 by PMMA using the binary parameters found above were made at T = 461.53 K and T = 298.2 K and compared to measurements by Durrill et al.[28] and Berens.[29]

The experimental data at 461.53 K are in the form of a Henry's law constant, which is the slope of the sorption-pressure curve at low pressures, and are given in units of cubic centimeters (at standard temperature and pressure) per gram of PMMA. Therefore, to compare the model prediction with the experimental result, eqs 7 and 8 and the model parameters from Table II were used to calculate sorption versus pressure (up to 20 bar) at T = 461.53 K. The results were converted to a cubic centimeter (STP) versus grams of PMMA basis and then linearized using a standard regression procedure to find the slope. The calculated result, 0.326, is greater than the experimental value of 0.260, but the agreement is reasonable considering the high temperature at which the prediction was made.

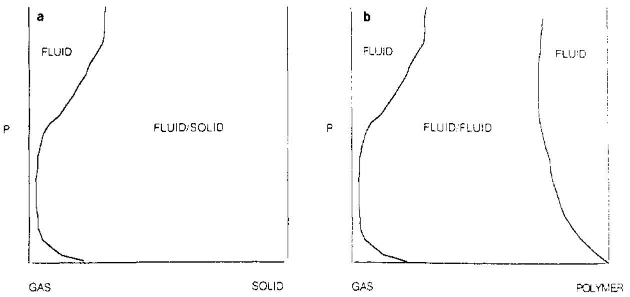

Figure 5. Representation of supercritical fluid phase behavior: (a) ideal fluid-solid mixture, (b) fluid-polymer mixture.

Berens measured the sorption by PMMA of liquid CO_2 at its vapor pressure at 298 K. Prediction of sorption under these conditions requires the solution of equations for three-phase equilibrium (liquid-liquid-vapor), or

$$\mu_0^V = \mu_0^L = \mu_0^P \text{ (two independent equations)} \qquad (12)$$

$$\mu_1^V = \mu_1^L = \mu_1^P \text{ (two independent equations)} \qquad (13)$$

$$\frac{-pv_0}{RT} = \frac{\mu_0^V}{RT}$$

where the μ_i^i are the chemical potentials of the holes and CO_2 segments in the vapor, liquid, and swollen polymer phases. Thus, there are five independent equations for the five unknowns; pressure, CO_2 liquid and vapor densities, weight fraction CO_2 absorbed by the polymer, and the density of the swollen polymer phase. The calculated amount of CO_2 absorbed by the PMMA, 25.6 g of CO_2/g of PMMA, is within experimental error of the measured value, 27.0 ± 2.0 g of CO_2/g of PMMA.

The binodal and spinodal equations, in conjunction with the equation of state, were used to predict the pressure dependence of the composition of the SCF-rich phase in solutions of PMMA in CO_2, given the binary parameters found above. Parts a and b of Figure 5 show qualitatively the type of phase behavior to be expected in dilute solutions in supercritical fluids. In Figure 5a is shown the phase boundary of a hypothetical supercritical fluid-solid mixture at a temperature below the critical point of the heavy constituent. In the PMMA-CO_2 system, the shape of the dilute phase boundary is similar although a second curve appears at the concentrated end of the diagram because the polymer is swollen by the supercritical fluid. The model predictions and data are shown in parts a-d of Figure 6 (the binodal at M = 24 300 (T = 313.2 K) is predicted to lie at concentrations less than 1×10^{-8} and therefore does not appear in the figure). The binodals, which should approximate the solubility, are greatly underestimated by the model, despite a reasonable estimation of the shape of the curve.

The underestimation of the binodals is likely due to several factors. First, in the determination of the adjust-

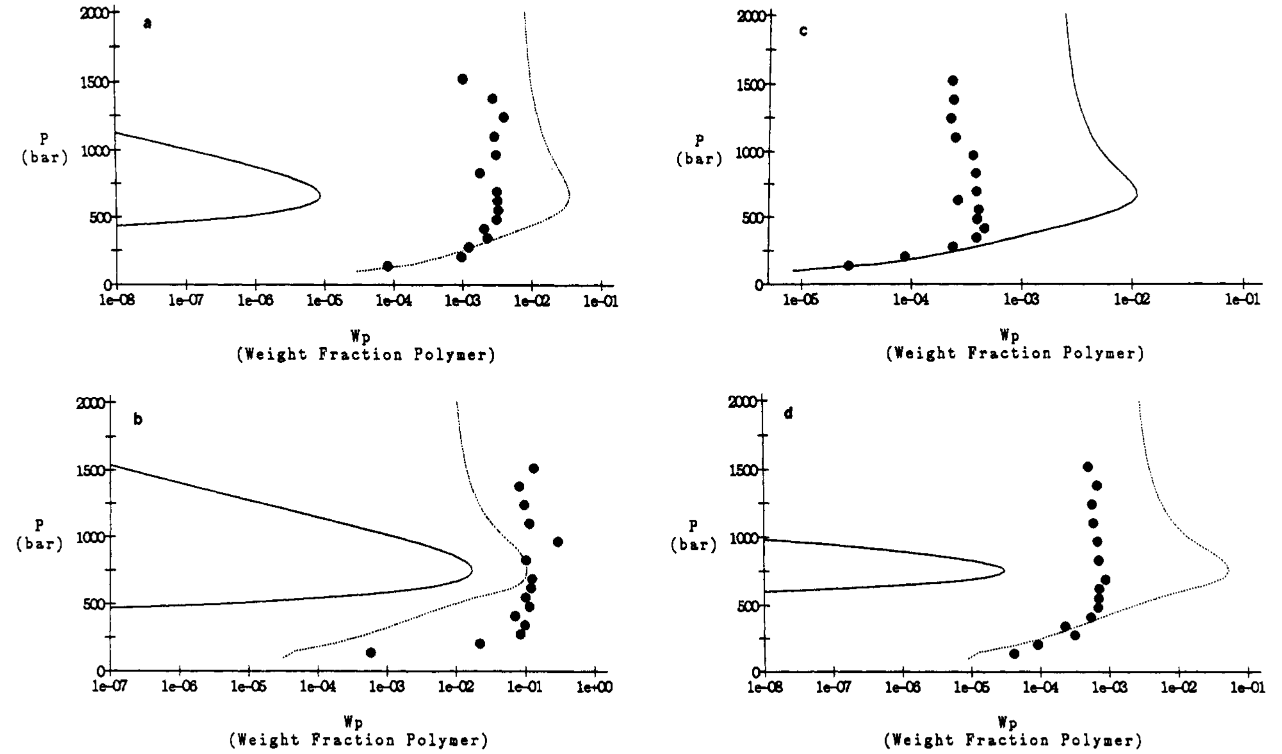

Figure 6. Predictions of MFLG binodal (—) and spinodal (···) compared to PMMA solubility in CO_2 data (●) at (a) M_n = 7000, T = 313.2 K, (b) M_n = 7000, T = 333.2 K, (c) M_n = 24 300, T = 333.2 K, and (d) M_n = 24 300, T = 333.2 K.

able parameters using Liau's sorption data, it was assumed that the SCF-rich phase during the equilibrium swelling of the 33 200 MW PMMA was essentially pure CO_2. On the basis of the experimental solubility results using the 24 300 MW PMMA, this may not be so. Koningsveld[24] has shown that this type of mistake can create significant errors in subsequent phase boundary predictions. Second, as mentioned in the Introduction, mean-field lattice models do not account for the large fluctuations in monomer segment density in dilute polymer solutions (due to the isolated nature of the individual polymer coils) and consequently do not usually predict dilute polymer solution data accurately. Finally, problems in the predicted shape of the binodal curves are partially due to the errors in the prediction of the excess volume at higher pressures.

Polystyrene–CO_2. Determination of the polystyrene parameters was accomplished via fitting of the MFLG model's equations of state against P–V–T data at five molecular weights ranging from 2000 to 125 000.[23] The average error between calculated and actual density is 0.12% for the 117 data points used for the parameter fit.

Sorption data on the PS–CO_2 binary are relatively scarce. The binary parameters for the model were determined by fitting the sorption equations against Henry's law region data at several temperatures.[20,28] Due to the lack of volume of mixing data (solution densities were set to the density of pure PS and assigned a tolerance of 10% during fitting), α_m could not be determined with any confidence and was consequently set equal to zero.

The material parameters for PS and the PS–CO_2 binary are shown in Table IV. The error between calculated and actual Henry's law constants is less than 0.1%.

The predicted sorption at T = 298 K, 5.7 g of CO_2/g of PS, is much lower than the measured value[29] of 13.5. The large error in this prediction, as compared to the corresponding calculation for PMMA–CO_2, is due to both the ambiguity in the binary parameters owing to the scarcity of sorption data and to the distinct possibility that polystyrene, under these conditions (CO_2 vapor at 298.2 K), is in the glassy state. Because the MFLG model is predicted on an equilibrium distribution of segments and holes, it is not rigorously applicable to nonequilibrium materials such as polymer glasses. Sorption of gases by glasses is better represented by a model of the dual-mode variety.[20]

Table IV
Material Parameters for Polystyrene (PS) and a PS–CO_2 Mixture Using the MFLG Model

param	polystyrene	polystyrene–CO_2
m	3.7[a]	
α	–6.8354	
g_{10}	10.157	
g_{11}	2318.7	
γ	–1.0889	
α_m		0
g_{m0}		–0.8022
g_{m1}		1285.1

[a] Segments per monomer unit.

The predictions of the dilute solution behavior of PS–CO_2 are shown in parts a and b of Figure 7. The trends are similar to those found for PMMA–CO_2, although, not surprisingly, it appears that CO_2 is a much better solvent for PMMA than for PS. Unlike the PMMA–CO_2 system, the approximation made during the determination of the binary parameters, that high molecular weight polymer does not dissolve in the gas over the pressure range of the sorption data, holds quite well for the PS–CO_2 binary.[30]

Conclusions

The MFLG model produces an accurate description of the sorption of supercritical CO_2 by atactic PMMA in the concentration region where the mean-field approximation is expected to be valid. When the binary parameters found by fitting the appropriate model equations to the literature sorption data at temperatures between 315 and 341.2 K are used, accurate predictions of sorption have been made at temperatures of 298.2 and 461.53

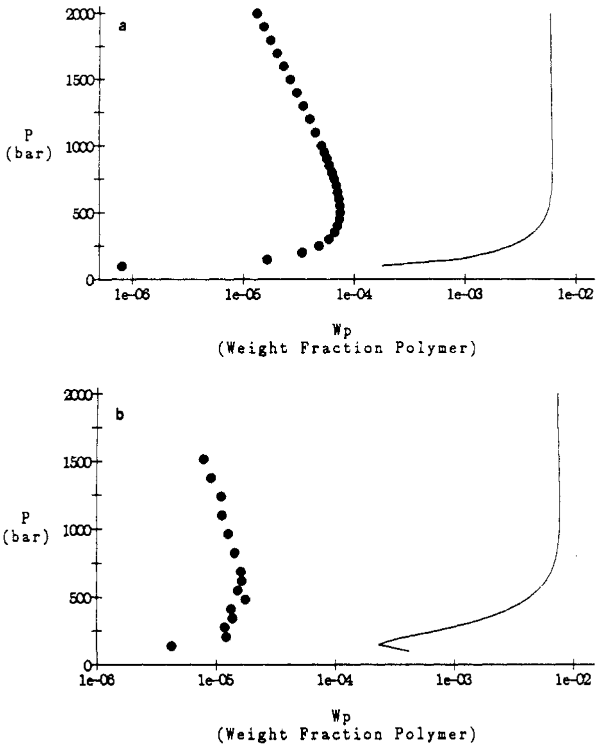

Figure 7. Predictions of the MFLG model (—) spinodals compared to PS solubility in CO_2 data at (a) M_n = 2000, T = 313.2 K, smoothed data (●) of Bowman,[30] and (b) M_n = 2000, T = 353.2 K, data (●).

K, thus demonstrating the large useful temperature range of the model. Predictions of the volume change on mixing, while displaying the proper trends versus temperature and pressure, show deviations from the data at high pressure.

In general, though correctly describing the effects of temperature, pressure, and molecular weight on dilute solution phase behavior, the model greatly underestimates the solubility of PMMA in CO_2. This is due both to the assumptions made during the determination of the binary parameters (that no 33 200 MW PMMA dissolves in CO_2 up to pressures of 300 bar) and to the breakdown of the mean-field approximation in very dilute polymer solutions.

The predictions in the PS–CO_2 system were made using a minimal amount of data during the fitting procedure. Despite this, the model solubility predictions qualitatively describe the dilute solution behavior but, as in the PMMA–CO_2 binary, underestimates the solubility. Not surprisingly, CO_2 is a much better solvent for PMMA than for PS.

Clearly, dilute polymer solutions present a problem for the model in its present form. A number of authors have attempted to bridge the gap between dilute and concentrated polymer solution thermodynamics.[31–36] Of these, the bridging theories of Koningsveld et al. and Irvine and Gordon, the cell model by Sanchez and Lohse, and the field theoretical approach of Muthukumar seem to be the most readily adaptable to a lattice model such as the MFLG since each of these builds from an existing mean-field approach.

Another source for potential improvement to the model is the nature of the empirical parameters α and g_{i0}. In a derivation of a variation of the MFLG model,[17,24,37] it has been shown that these parameters are at least partially due to deviations of the entropy of mixing from the simple Flory–Huggins relation, owing to the different contact surface areas of the segments and holes. The empirical parameters are redefined in this variation as functions of the surface areas and ϕ_0. The modified model produces better descriptions of the volume of mixing and equilibrium vapor pressure, i.e., quantities that would intuitively depend on ϕ_0 but cannot equal the MFLG model description of the temperature dependence of phase behavior in the gas–polymer systems.[37]

Deviations from the regular solution approximation used to calculate the internal energy of mixing can also be considered. Recently, Kumar et al.[38] used the Panayiotou–Vera equation of state, modified to allow for specific interactions and thus non-mean-field nearest-neighbor concentrations, to model the distribution of polystyrene oligomers between a SCF-rich and polymer-rich phase. Through algebraic manipulation, it can be shown[23] that the Panayiotou–Vera equation of state represents a specific case of the MFLG equation of state, that is, when α is zero. Given this similarity between the Panayiotou–Vera and MFLG models and the reasonably good description of oligomeric polystyrene solubility in supercritical ethane by the P–V model, it is certainly possible that inclusion of specific interactions in the derivation of the MFLG model could lead to a more accurate concentration or temperature dependence of the binary interaction parameters. However, results for liquid systems such as polystyrene–cyclohexane and polystyrene–toluene[37] have shown that whereas use of the quasi-chemical approximation in conjunction with the MFLG model will improve the description of the mixture phase behavior, the problem concerning accurate modeling of both the solvent-rich and polymer-rich phases is not fully resolved.

Finally, fitting of a large variety of both liquid and gaseous P–V–T data to the MFLG equation of state indicates that, in the context of the model, one segment equals approximately two C–C bonds. Thus it could be beneficial to convert the model to a group contribution basis[39] possibly using molecular parameters such as those by Bondi[40] to evaluate the contact surface areas of the various groups.

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Rheology of Ordered and Disordered Symmetric Poly(ethylenepropylene)–Poly(ethylethylene) Diblock Copolymers

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ABSTRACT: A series of poly(ethylenepropylene)–poly(ethylethylene) (PEP–PEE) diblock copolymers, containing 55% by volume PEP, and the corresponding PEP and PEE homopolymers have been investigated by dynamic mechanical spectroscopy. The ordered and disordered states are characterized by qualitatively different low-frequency rheological properties in close agreement with previous reports on this subject. This paper addresses three aspects of such behavior in the vicinity of the order–disorder transition: identification of the microphase-separation transition temperature, T_{MST}, evaluation of fluctuation effects, and characterization of the ordering kinetics. We identify T_{MST} based on the distinct discontinuity in G' ($\omega \ll \omega_c'$) and G'' ($\omega \ll \omega_c''$) that accompanies the order–disorder transition; $\omega_c' \cong 3\omega_c'' \ll \tau_d^{-1}$ delineates the beginning of the phase-state-dependent low-frequency regime where τ_d is the conventional single-chain longest relaxation time. Above and below T_{MST} the rheological properties are complex for $\omega < \omega_c$ (e.g., failure of time–temperature superposition), owing to the presence of composition fluctuations. In the disordered state these effects are evident 50 °C beyond T_{MST}. The magnitude of these fluctuation effects is underpredicted by recent theory, although the relative fluctuation contributions to the dynamic elastic and loss moduli are in quantitative agreement with theory. Quenching experiments from slightly above to just below T_{MST} reveal a ca. 10 °C region within which the ordering process can be followed rheologically. On the basis of the temporal evolution of G' ($\omega \ll \omega_c'$) following such temperature quenches, we conclude that the ordering process is governed by heterogeneous (secondary) nucleation.

I. Introduction

Block copolymer rheology has been shown in the past to be strongly dependent on morphology, which can be divided into two general categories. The ordered, or microphase-separated, state refers to the familiar periodically arranged spherical, cylindrical, lamellar, or bicontinuous double-diamond structures,[1] while the disordered state is spatially homogeneous. These two thermodynamic regimes are separated by the order–disorder transition (ODT), also referred to as the microphase separation transition (MST); here we use these expressions interchangeably. In all known block copolymers the segment–segment interaction parameter, χ, is linear with inverse temperature, thus producing a disordered material at sufficiently high temperatures. This situation is analogous to UCST behavior in binary polymer mixtures. Below the MST temperature (T_{MST}) block copolymers exist in the ordered state. We presently describe a detailed study of the dynamic mechanical properties of a nearly symmetric (f = 0.55) set of model poly(ethylenepropylene)–poly(ethylethylene) diblock copolymers, denoted PEP–PEE, both above and below T_{MST} where f corresponds to the volume fraction of the PEP block.

Nearly all previous investigations aimed at elucidating the relationships between rheology and morphology for block copolymers have relied upon materials composed of polystyrene and/or polydiene blocks, includ-

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