Macromolecules **1997,** *30,* 4882−4886

Phase Equilibria of Polypropylene with Compressed Propane and Related Systems. 1. Isotactic and Atactic Polypropylene with Propane and Propylene

P. D. Whaley, H. H Winter, and P. Ehrlich*

Department of Polymer Science, University of Massachusetts, Amherst, Amherst, Massachusetts 01003

Received October 21, 1996; Revised Manuscript Received May 16, 1997[⊗]

ABSTRACT: Cloud-point pressures of two isotactic polypropylene samples (iPP-1 and iPP-2) of different molecular weight and of a high molecular weight atactic polypropylene (aPP) in propane were measured, as well as solid−supercritical fluid (S-SCF) equilibria for the crystalline isotactic samples. The lower critical end point (LCEP) for the aPP sample lies at 6 °C. The second critical endpoint of iPP-1 (M_w = 29 000, M_w/M_n = 2.0), which is defined as the intersection of the 3-phase line starting at the triple-point of the polymer with the liquid−vapor critical locus, is estimated to lie at about 109 °C, 175 bar, and 15 wt % polymer; that of iPP-2 (M_w = 290 000, M_w/M_n = 4.4)is estimated to lie at about 130 °C, 250 bar, and 7.5 wt % polymer. The pressure−temperature ($P-T$) phase boundaries separating two fluid phases from a single supercritical phase (cloud-point isopleths) were determined at several polymer concentrations to 160 °C and show a positive slope throughout. Pressure−composition plots (cloud-point isotherms) are shown for 135, 145, and 155 °C to 20 wt % polymer. An aPP−propylene isopleth near the critical composition is roughly parallel to that for aPP−propane, but it occurs at a slightly higher pressure. The locus of lower critical solution temperatures originating at the LCEP of aPP−propane can be made to fit the Sanchez−Lacombe lattice−fluid theory, after allowing both the energy and volume adjustment parameters to be temperature-dependent.

Introduction

Polypropylene (PP), like polyethylene (PE), forms a supercritical (sc) solution with propane in all proportions beyond a cloud-point pressure and at temperatures high enough to prevent formation of a crystalline polymer phase.[1] At lower pressures vapor−liquid equilibrium exists. The solubility of crystalline polymer, in this case isotactic polypropylene (iPP), in the sc solvent becomes vanishingly small at temperatures not far below that where infinite miscibility is attained. The 3-dimensional phase model for the binary system, a perfect fraction of iPP with propane, is of the same type as that of PE−propane,[2] showing solid−sc fluid (S−SCF) and liquid−vapor (L−V) equilibria, as well as a univariant solid−liquid−vapor (S−L−V) equilibrium. Atactic polypropylene (aPP) with propane does not crystallize. Its critical liquid−vapor (L−V) locus does not terminate in a critical end point, usually referred to as the second critical end point,[3] where crystalline polymer coexists with a critical phase, as in PE−propane or in iPP−propane, but extends downward in temperature to a lower critical end point (LCEP), virtually on the vapor pressure curve of pure propane. The system aPP−propane thus conforms to the behavior of what has been termed a type V system, i.e. one that possesses a single, unbroken critical locus, extending from the LCEP toward the critical point of the solute.[4,5]

The L−V as well as S−SCF equilibria for PP−propane that define the system's phase diagram will be reported in this paper, and an attempt will be made to model the LCEP and the temperature−pressure (T,P) behavior of the critical locus according to the lattice−fluid theory of Sanchez and Lacombe.[6−9] The phase equilibria of some more complex mixtures, related to PP−propane, will be reported in the following paper.

Experimental Section

Materials. Propane (CP Grade, 99.0+ minimum purity) was obtained from Merriam-Graves and was used as received. Two samples of isotactic polypropylene, iPP-1 and iPP-2, and one sample of atactic polypropylene, aPP, were used in these studies. M_w and M_w/M_n for these samples were 29 000 and 2.0; 290 000 and 4.4; and 400 000 and 2.0, respectively. All three samples were free of stabilizers and other additives. The iPP samples contained less than 2 wt % xylene solubles (aPP). This iPP was used as received. The aPP sample was filtered while in toluene solution, with the toluene subsequently removed by vacuum-stripping.

Methods and Apparatus. A variable-volume view cell mounted in an air oven, as described elsewhere,[2] was used to measure the iPP−propane phase equilibria. The appearance of a second fluid phase upon a decrease in pressure, or its disappearance upon a pressure increase, was determined over a suitable temperature range for a series of constant composition mixtures (cloud-point isopleths). The S−SCF transition was found by determining the temperature at which the last trace of solid disappeared upon slow heating. Pressure−composition diagrams (cloud-point isotherms) were constructed from the cloud-point isopleths at selected temperatures. The apparatus was equipped with a jacket for circulation of a cooling fluid to obtain equilibrium data with aPP, which required measurements below room temperature.

Results

Figures 1 and 2 show cloud-point isopleths and S−SCF transitions for iPP-1 and iPP-2 in propane, respectively. The critical compositions, which may be assumed to be constant over the temperature range investigated, were determined by noting the composition at which the two fluid-phase volumes at the cloud-point equaled one another. These compositions were determined to an accuracy of about ±1 wt % for iPP-1 and ±2 wt % for iPP-2. The second critical end point, C_2, is then determined by the intersection of the critical cloud-point isopleth with the S−SCF transition for the critical composition. Since both these lines are only weakly dependent on composition in the neighborhood of the

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

S0024-9297(96)01545-8 CCC: $14.00

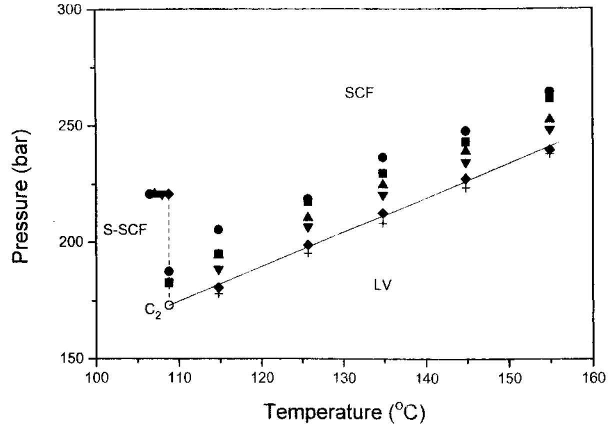

Figure 1. Cloud-point isopleths and S−SCF transitions for iPP-1−propane. The solid line represents the critical L = V locus. (■) 1 wt % polymer; (●) 5 wt %; (▲) 7.5 wt %; (▼) 10 wt %; (◆) 15 wt %; (+) 20 wt %. ○ represents the second critical endpoint, C_2. (SCF is a single supercritical phase, LV denotes liquid−vapor equilibrium, S−SCF denotes a two-phase region of solid polymer and a supercritical phase).

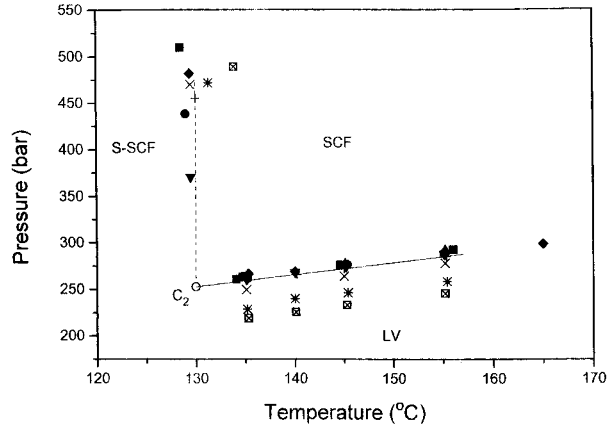

Figure 2. Cloud-point isopleths and S−SCF transitions for iPP-2−propane. The solid line represents the critical L = V locus. (■) 1 wt % polymer; (●) 2 wt %; (▲) 3 wt %; (▼) 4 wt %; (◆) 5 wt %; (+) 7.5 wt %; (×) 10 wt %; (*) 15 wt %; (× in a box) 20 wt %. ○ represents the second critical end point, C_2. (SCF is a single supercritical phase, LV denotes liquid−vapor equilibrium, S−SCF denotes a two-phase region of solid polymer and a supercritical phase).

Table 1. Location of Second Critical End Point, C_2, for iPP-1 and iPP-2, in Propane

	P (bar)	*T* (°C)	critical polymer wt fraction
C_2(iPP-1)	175	109	0.15
C_2(iPP-2)	250	130	0.075

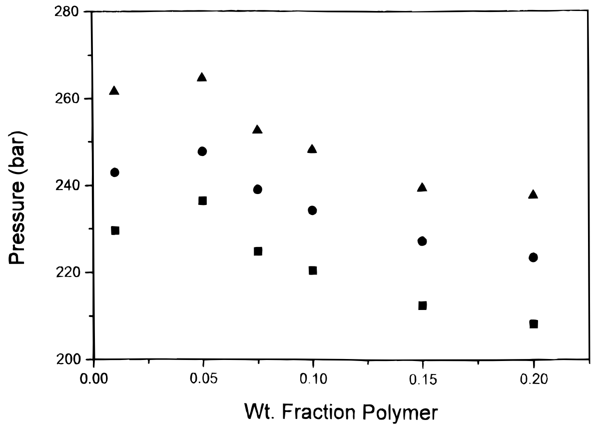

Figure 3. Cloud-point isotherms for iPP-1−propane. (■) 135 °C; (●) 145 °C, (▲) 155 °C.

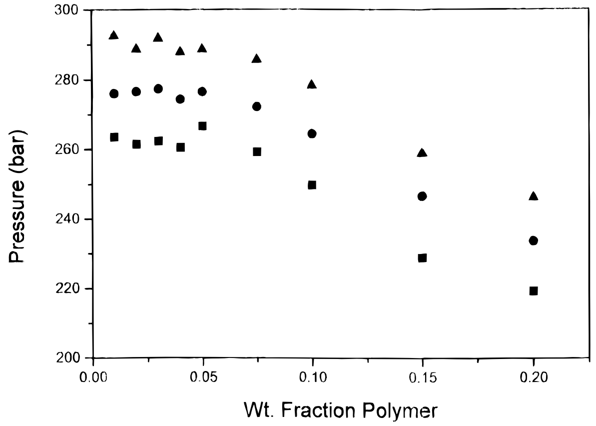

Figure 4. Cloud-point isopleths for iPP-2−propane. (■) 135 °C, (●) 145 °C, (▲) 155 °C.

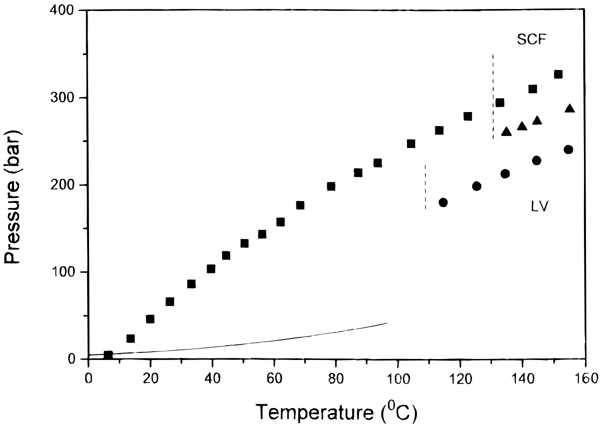

Figure 5. Cloud-point isopleths for aPP−propane compared to iPP−propane: (■) aPP at 2 wt %; (●) iPP-1 at 15 wt %; (▲) iPP-2 at 7.5 wt %. (SCF denotes a single supercritical phase, and LV denotes liquid−vapor equilibrium. The dashed lines represent the upper temperature limits for the formation of crystalline polymer in iPP-1 and ipp-2.

critical composition, the pressure and temperature coordinates of C_2 can be estimated with reasonable accuracy, in spite of some uncertainty in the critical composition. The coordinates of C_2, estimated in the manner indicated, are given in Table 1. Cloud-point isotherms for several temperatures are shown in Figures 3 and 4.

The availability of high molecular weight amorphous polypropylene made it possible to observe cloud points at temperatures where solid formation and the termination of the critical line at C_2 make this impossible with iPP. Cloud-point isopleths for a 2 wt % aPP solution, which represent lower critical solution temperatures (LCSTs), could be traced to the temperature 6 °C, where a vapor phase of essentially pure propane appears (Figure 5). Again, because of the insensitivity of the cloud-point pressure to composition in this range, the 2% isopleth must lie very close to the critical one, and its terminus at 279 K represents a good estimate for the LCEP of high molecular weight aPP with propane. Comparison of the isopleths of Figure 5, taking into account molecular weight, shows that the effect of tacticity on fluid phase equilibria must be small.

We also present data for the 2 wt % isopleth of aPP with propylene (Figure 6). It lies at somewhat higher pressures than the propane isopleth. Similarly, cloud-point isopleths for polyethylene−ethylene lie at higher

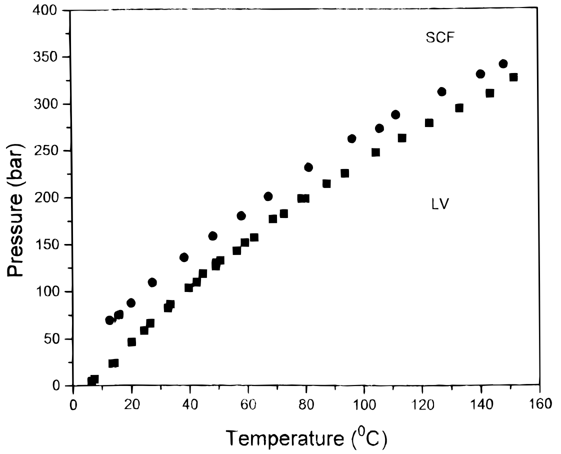

Figure 6. Cloud-point isopleths for aPP–propylene compared to aPP–propane: aPP at 2 wt % (■) in propane and (●) in propylene. (SCF denotes a single supercritical phase, and LV denotes liquid–vapor equilibrium.)

pressures than those for polyethylene–ethane.[10] There is a weak suggestion of a possible upswing in the propylene isopleth at its low-temperature end, which is of interest in connection with the classication of binary phase diagrams according to the method of Scott and van Konynenburg,[4,5] based on solutions to the van der Waals equation. According to the classification of Scott and van Konynenburg,[4,5] aPP–propane is a type V mixture, represented by an unbroken critical line extending from an LCEP toward the critical point of the solute. This type of behavior is expected for a mixture of two members of a homologous series. aPP–propylene, on the other hand, might be an example of a transition toward a type IV system, which also possesses an upper critical end point (UCEP) and a critical line representing upper critical solution temperatures (UCSTs) emanating from it. As the miscibility of polymer and solvent decreases in such mixtures, the two critical lines can merge, eliminating the miscibility window along the vapor pressure curve between the UCEP and the LCEP.[11,12]. The aPP–propylene system may be of the latter type. We will show in the following paper that aPP with mixed solvent systems (propane with low molecular weight alcohols) is a type IV system, which can have separate, as well as merged, UCST–LCST loci.[13]

Modeling the LCST Locus

Successful semiquantitative calculations of LCST and merged UCST–LCST loci were made over 20 years ago by Patterson and co-workers[11,14] and by Chen and Radosz,[12] on the basis of the Patterson–Flory approach.[15] Later, Chen and Radosz[16,17] used the statistical associating fluids theory (SAFT) to analyze these types of critical lines. They were able to match theory and experiment for ethylene–propylene copolymers, using an empirical interaction term that was molecular-weight-dependent. We choose for our model the Sanchez–Lacombe theory, whose authors have also provided a broadly-based set of reference (characteristic) parameters for solvents[6,8] and polymers.[8] We follow that approach. The Sanchez–Lacombe (SL) lattice–fluid theory is particularly suitable for use with nonpolar systems and, like other thermodynamic theories, more successful in predicting critical conditions than cloud-point isotherms. Furthermore, it is much easier to make a successful prediction of an LCEP than a UCEP.[8] We therefore use the theory in an attempt to locate the LCSTs in P, T space.

Table 2. Sanchez–Lacombe Equation of State Parameters

fluid	T^* (K)	P^* (MPa)	ρ^* (kg/m^3)
propane[a]	371.0	314.0	690.0
isotactic polypropylene (iPP)[b]	771.0	281.0	852.0

[a] Sanchez and Lacombe, ref 8. [b] Rodgers and Sanchez, ref 24

Using the recommended mixing rules,[7,9] several authors have calculated the P and T coordinates of critical lines, using only one of two adjustment parameters, ζ for the energy or δ for the volume, and allowing these to be T-dependent.[18–23] These two adjustment parameters describe the deviation of the cross term for the energy interaction ϵ_{12} from the geometric mean and that of the cross term for the volume v_{12} from the arithmetic mean, respectively.

In our calculations, we have used the SL equation of state (EOS) in its limiting form for polymer occupying an infinite number of lattice sites, r

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + \tilde{\rho}] = 0 \qquad (1)$$

where $\tilde{\rho}$, $\tilde{T}$, and $\tilde{P}$ represent the reduced density, temperature, and pressure of a mixture of given composition. The characteristic parameters of the pure components are given in Table 2.[8,24] Those for the mixture must be calculated from the mixing rules for the corresponding molecular parameters ϵ^*, v^*, and r. They are

$$\epsilon^* = \sum_i \sum_j \phi_i \phi_j \frac{v_{ij}^* \epsilon_{ij}^*}{v^*} \qquad v^* = \sum_i \sum_j \phi_i \phi_j v_{ij}^* \qquad \frac{1}{r} = \sum_i \frac{\phi_i}{r_i} \qquad (2)$$

The relations between the molecular and EOS parameters are

$$\epsilon^* = k\mathrm{T}^*, \quad v^* = \frac{k\mathrm{T}^*}{\mathrm{P}^*}, \quad r = \frac{\mathrm{MP}^*}{k\mathrm{T}^*\rho^*} = \frac{\mathrm{M}}{\rho^* v^*} \qquad (3)$$

The SL equation for the chemical potential, μ_i, is[21]

$$\mu_i = R\mathrm{T}\left[\ln(\phi_i) + \left(1 + \frac{r_i}{r}\right)\right] + r_i\left\{-\rho\left[\frac{2}{v^*}\left(\sum_{j=1}^{c}\phi_j v_{ij}^*\epsilon_{ij}^* - \epsilon^*\sum_{j=1}^{c}\phi_j v_{ij}^*\right)\right] + \mathrm{P}\tilde{v}\left[2\sum_{j=1}^{c}\phi_j v_{ij}^* - v^*\right] + R\mathrm{T}\tilde{v}\left[(1 - \tilde{\rho})\ln(1 - \tilde{\rho}) + \frac{\tilde{\rho}}{r_i}\ln\tilde{\rho}\right]\right\} \qquad (4)$$

where the ϕ_i are the volume fractions, M is the molecular weight, and c is the number of components in the system. Together with the conditions for a critical point,

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}\phi_1} = \frac{\mathrm{d}^2\mu_1}{\mathrm{d}\phi_1{}^2} = 0$$

and the phase stability criteria,

$$\frac{\mathrm{d}\mu_1}{\mathrm{d}\phi_1} > 0; \quad \frac{\mathrm{d}\mu_2}{\mathrm{d}\phi_2} > 0$$

eq 4 was used to calculate the spinodals, binodals, and

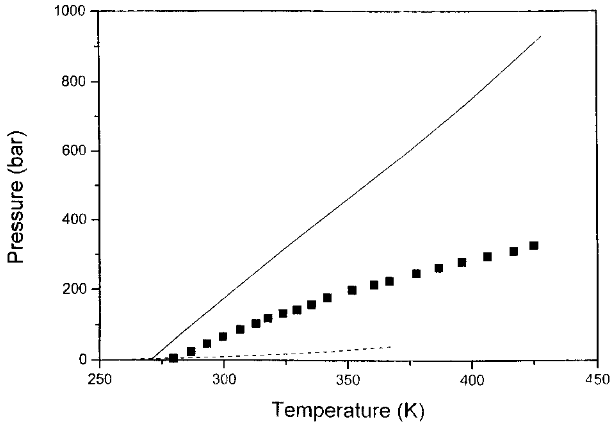

Figure 7. Sanchez–Lacombe model prediction for no parameter adjustment ($\delta = 0.0$, $\zeta = 1.0$), (—) compared to the experimental cloud-point isopleth for aPP–propane (■). Vapor pressure of propane (– – –)

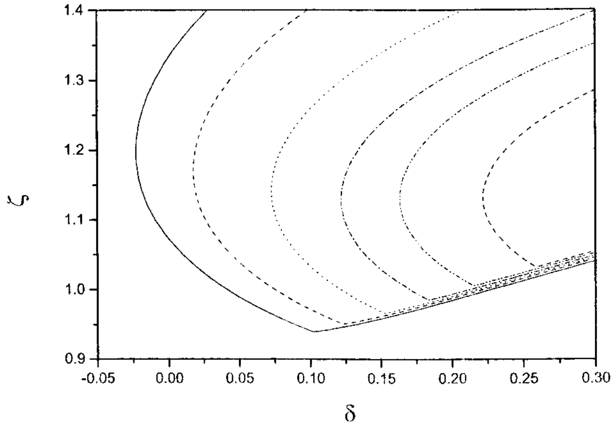

Figure 8. δ–ζ solution sets for aPP–propane.

critical points with the help of a computer program based on a graphical procedure proposed by Lacombe and Sanchez (Figure 3 of ref 7). For details see ref 25. We consider here only the calculation of critical points in the form of the LCST locus in P, T, since the cloud-point isotherms of this multicomponent system are not expected to match the binodals of the pseudobinary system.

A comparison of the calculated LCST locus with the experimental 2 wt % cloud-point isopleth for aPP–propane, without adjustment of the mixing rules for energy and volume ($\zeta = 1$, $\delta = 0$) is shown in Figure 7. The deviation between the theoretical and experimental curves increases with increasing temperature. It was found that making an adjustment to only one of the mixing rules does not lead to agreement. The qualitative solutions allowing both parameters to vary from their nonadjusted values are shown in Figure 8. While an infinite set of solutions is possible, the calculated pressure dependence of the chemical potential based on them shows that only solutions in the nonlinear part of the figure are stable.[25] Other values of δ and ζ tend to predict a second two-phase region at pressures not greatly in excess of the cloud-point pressure. No such lower critical solution pressure was observed. We pick the set of values corresponding to the minimum value of δ. This leads to the T-dependence of the two adjustment parameters shown in Figure 9 and the satisfactory match of calculated and experimental data shown in Figure 10.

We have examined the question whether a variation in the characteristic parameters of the pure components would dispense with the need for the substantial empirical and temperature-dependent adjustment of the mixing rules that is indicated in Figure 7. In the case of propane such a variation might seem justified, since the characteristic parameters were chosen on the basis of the vapor pressure data,[8] while many of the fluid-phase equilibria were measured at temperatures above the critical point of propane. We found that a reasonably good fit of supercritical P–V–T data[26] is obtainable with the parameters listed in Table 2. While a small change in these parameters improves the fit somewhat when the supercritical region is singled out, the mismatch between the experimental and the calculated critical loci is not affected significantly. This is also true if an adjustment of the characteristic parameters of aPP is made, for which there is less justification, since the calibration was made in the temperature range where our phase equilibria experiments were carried out. We consequently see no alternative to a temperature-dependent adjustment of the correction terms $\delta \neq 0$ and $\zeta \neq 1$, if the entire section of the critical locus encompassed by our data is to be represented by the Sanchez–Lacombe lattice-fluid theory.

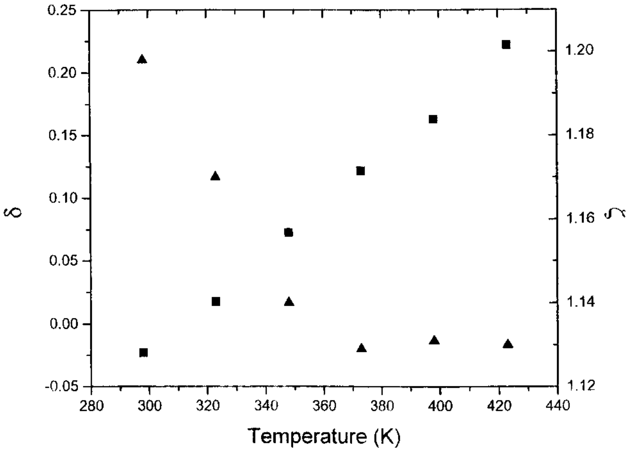

Figure 9. δ (■) vs ζ (▲) solutions at minimum δ for atactic polypropylene–propane.

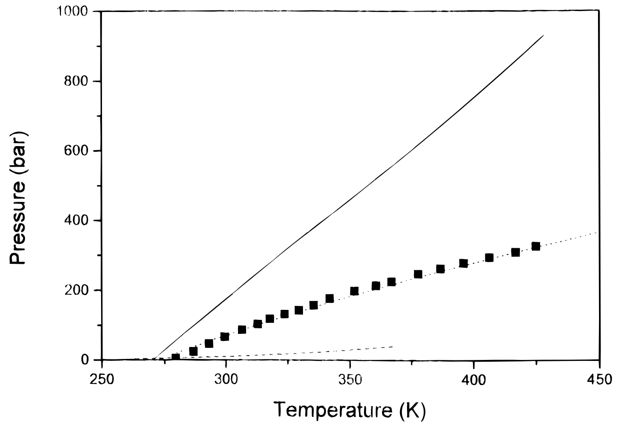

Figure 10. SL model prediction for no parameter adjustment ($\delta = 0.0$, $\zeta = 1.0$) (—) and minimum δ approach, (···) as compared to the experimental cloud-point isopleth for the aPP–propane (■). Vapor pressure of propane (– – –).

Conclusions

The phase equilibria of the system iPP–propane resemble those of crystalline PE with propane in that a high-temperature region, where a supercritical solution separating into two fluid phases upon lowering the pressure impinges upon lowering the temperature on a region where a single fluid phase of virtually pure propane coexists with crystalline polymer at all pressures greater than the vapor pressure of propane. However, while the slope of the L = V critical locus, which for crystalline polymer exists only for temperatures greater than that of C_2, is weakly negative in PE–propane, it is strongly positive in iPP–propane, giving rise to LCST-type behavior. The availability of high molecular weight amorphous aPP allowed us to trace the L = V locus below C_2 to the LCEP on the solvent's vapor pressure line at 6 °C. We note the small displacement to higher pressures of the critical line of a PP–propane compared to that of the slightly lower molecular weight iPP-2–propane. This is as expected, if tacticity has only a small effect on the cloud-point pressure.

The broad temperature range over which the L = V locus has been measured allows a more rigorous test of the Sanchez–Lacombe theory than in previous work. While the prediction of the LCEP is quite satisfactory, use of both adjustment parameters, ζ and δ, must be made, and both must be allowed to be temperature-dependent. We have chosen to minimize δ, which seemed more acceptable in meeting criteria of phase stability and which is also more consistent with theory than alternative choices.[27] The failure to reproduce a large section of the L = V locus according to the Sanchez–Lacombe theory without arbitrary adjustment of parameters is not unexpected. Related treatments, such as the Flory–Patterson approach,[15,28] have been successful only in predicting the LCEP and its initial slope[11] In the case of iPP and ethylene–propylene copolymers with linear and branched alkanes in the range C-5 to C-9, a failure to correlate the LCEPs with those of PE was attributed to the failure to account for correlations of molecular order between solvent and solute, shown to persist to high temperatures.[29] It is possible that this type of ordering is a contributor to the limitations of the uncorrected lattice–fluid theory observed here.

Acknowledgment. The financial support through NSF Grant 9202541 is gratefully acknowledged. We appreciate the gifts by Dr. H. Turner of Exxon of the iPP-1 and aPP samples and by Dr. Jean News of Himont of the iPP-2 sample.

References and Notes

(1) Whaley, P. D.; Winter, H. H.; Ehrlich, P. *Proceedings of the 3rd International Symposium on Supercritical Fluids*, Brunner, G., Perrut, M., Eds.; Oct. 17–19, Strasbourg, Tome 1; ISSF94: Strasbourg, France, 1994; p 149.
(2) Condo, P. D.; Colman, E. J.; Ehrlich, P. *Macromolecules* **1992**, *25*, 750.
(3) Koningsveld, R.; Kleintjens, L. A.; Diepen, G. A. M. *Ber. Buns.-Ges. Phys. Chem.* **1984**, *88*, 848.
(4) Scott, R. L.; van Konynenburg, P. H. *Discuss. Faraday Soc.* **1970**, *49*, 87.
(5) Rowlinson, J. S., Swinton, F. L. *Liquids and Liquid Mixtures*; Butterworths: London, Boston, 1982; Chapter 6.
(6) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352.
(7) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2568.
(8) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(9) Sanchez, I. C.; Lacombe, R. H. *J. Macromol. Sci., Phys.* **1980**, *B17*, 565.
(10) Ehrlich, P.; Kurpen, J. J. *J. Polym. Sci., Part A* **1963**, *1*, 3217.
(11) Zeman, L.; Patterson, D. *J. Phys. Chem.* **1972**, *76*, 1214.
(12) Chen, S. J.; Radosz, M. *Macromolecules* **1992**, *25*, 3089.
(13) Whaley, P. D.; Winter, H. H.; Ehrlich, P. *Macromolecules* **1997**, *30*, 4887 (the following paper in this issue).
(14) Zeman, L.; Biros, J.; Delmas, G.; Patterson, D. *J. Phys. Chem.* **1972**, *76*, 1206.
(15) Patterson, D. *Rubber Chem. Technol.* **1967**, *40*, 1.
(16) Chen, J. C.; Economou, I. G.; Radosz, M. *Macromolecules* **1992**, *25*, 4987.
(17) Chen, J. C.; Economou, I. G.; Radosz, M. *Fluid Phase Equilib.* **1993**, *83*, 391.
(18) Hasch, B. M.; Meilchen, M. A.; Lee, S.; McHugh, M. A. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 1365.
(19) Hash, B. M.; Lee, S.; Watkins, J. J.; Krukonis, V. J. *Polymer* **1993**, *34*, 2554.
(20) Haschets, C. W.; Shine, A. D. *Macromolecules* **1993**, *26*, 5052.
(21) Meilchen, M. A.; Hasch, B. M.; McHugh, M. A. *Macromolecules* **1991**, *24*, 4874.
(22) Xiong, Y.; Kiran, E. *Polymer* **1994**, *35*, 4408.
(23) Xiong, Y., Kiran, E. *J. Appl. Polym. Sci.* **1995**, *55*, 1805.
(24) Rodgers, P. A.; Sanchez, I. C. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 273.
(25) Whaley, P. D. Ph.D. Dissertation, University of Massachusetts, 1996.
(26) Younglove, B. A.; Ely, I. F. Thermophysical properties of fluids. II. Methane, ethane, propane, isobutane and normal butane. *Phys. Chem. Ref. Data* **1987**, *16* (4).
(27) Personal Communication from Prof. I. C. Sanchez.
(28) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7.
(29) Charlet, G.; Delmas, G. *Polymer* **1981**, *22*, 1181.

MA961545+