Calculations of the phase diagrams of polyethylene dissolved in supercritical solvents

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Calculations have been made, using the equation of state theory of Flory and coworkers, of the phase diagrams of high density polyethylene and low density polyethylene dissolved in ethylene, and of high density polyethylene dissolved in fluorotrichloromethane. This was done using reduction parameters obtained by fitting the equation of state to data from the literature for ethylene and fluorotrichloromethane and to measured *PVT* data for the polyethylenes. The theory correctly describes the experimental LCST and UCST (lower and upper critical solution temperature) phase diagrams within the uncertainties of the reduction parameters. This was achieved assuming a zero value for the interaction parameters which do not contribute significantly within a realistic range of possible values. The main uncertainties arose from the high sensitivity of the predicted phase diagrams to the values of the reduction parameters of the pure components.

(Keywords: polyethylene; fluorotrichloromethane; ethylene; phase diagram; supercritical fluids; equation of state)

INTRODUCTION

Simple lattice theories do not adequately describe the behaviour of polymers, polymer solutions and mixtures. Various other theories have been developed which allow for the possibility of volume changes. Well known theories are those attributed to Simha and Somcynsky[1], Sanchez and Lacombe[2], and Flory and coworkers[3,4], and of these the last has been most extensively applied.

As a test of free volume theories, solutions of polymers in supercritical solvents have the advantage that in them the effects of volume changes are very pronounced. Most of the data in the literature concerning such solutions concerns polyethylene and especially polyethylene dissolved in ethylene, a common solvent during high pressure polymerization.

Several experimental measurements of the polyethylene/ethylene phase diagram have been reported[5-7] and they show upper critical solution temperatures (UCSTs) over a range of temperatures and pressures in the region of 150°C and 150 MPa. One study[8] noted a large difference between low and high density polyethylene. Other studies have attempted to describe the phase diagrams in terms of theory[9-12]. Some of these studies have concentrated on modified theories which aim to describe the equilibrium sorption of ethylene at relatively low pressures, whereas others concentrate on describing the data close to the critical point. In one study[11] the phase diagram was simulated using the theory of Flory and coworkers, using *PVT* data for the pure components to calculate the reduction parameters. However, these reduction parameters were enforced as empirical expansions in temperature. Another study[12] used the same expressions over a narrow range of conditions close to the critical point to extract constant reduction parameters for a simulation.

Another system for which data is available is the polyethylene/fluorotrichloromethane (FTCM) mixture[13], which shows lower critical solution temperatures (LCSTs) in the region of 150°C and 10 MPa. This system shows an LCST in this region rather than a UCST because the FTCM is much closer to its critical point and is hence more gas-like. A UCST could, however, possibly be found under different conditions of temperature and pressure.

In this paper, we describe the simulation of the phase diagrams for polyethylene/ethylene and polyethylene/FTCM using the equation of state theory of Flory and coworkers. We have used *PVT* data from our own measurements for polyethylene and from the literature for the solvents and used a fit for the reduction parameters over a wide range of temperature and pressure. The theory adequately describes all the data within uncertainties.

THEORY

The phase diagram can be determined if we can calculate the parameters in the equation of state of the components and the mixture. In this case, we used the equation of state of Flory and coworkers[3,4]:

$$\tilde{P}\tilde{v}/\tilde{T}=\tilde{v}^{1/3}/(\tilde{v}^{1/3}-1)-1/\tilde{T}\tilde{v} \qquad (1)$$

where $\tilde{P}$, $\tilde{v}$ *and* $\tilde{T}$ are the reduced variables and

$$\tilde{P}=P/P^*, \qquad \tilde{v}=v/v^*, \qquad \tilde{T}=T/T^* \qquad (2)$$

where P^*, v^* and T^* are the hard core reduction parameters which must be found to characterize the system. To calculate these parameters for a mixture one

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needs to know the parameters of the pure components plus an estimate of the interactions within the mixture given by an interaction parameter X_{12} and an interaction entropy parameter Q_{12}. The chemical potential of mixing is given by

$$\begin{aligned}\Delta\mu_1/RT = {} & \ln\phi_1 + (1-r_1/r_2)\phi_2 \\ & + P_1^* V_1^*/RT\{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3}-1)/(\tilde{v}^{1/3}-1)] \\ & + 1/\tilde{v}_1 - 1/\tilde{v} + \tilde{P}_1(\tilde{v}-\tilde{v}_1)\} + V_1^* X_{12}\theta_2^2/RT\tilde{v} \\ & - V_1^* Q_{12}\,\theta_2^2/R \end{aligned} \qquad (3)$$

where V_1^* is the hard core molar volume and r the number of mers per molecule, which are defined such that r_1/r_2 is the ratio of the hard core molar volumes of the components. A full description of the derivation and use of this equation can be found in the literature[3,4,14,15].

By definition at the binodal curve the two coexistent phases A and B are at equilibrium where

$$\begin{aligned}(\Delta\mu_1)_A &= (\Delta\mu_1)_B \\ (\Delta\mu_2)_A &= (\Delta\mu_2)_B\end{aligned} \qquad (4)$$

and the spinodal, the limit of metastable compositions, is given by

$$\begin{aligned}(\partial/\partial\phi_2)(\Delta\mu_1/RT) = 0 = {} & -1/\phi_1 + (1-r_1/r_2) \\ & + (P_1^* V_1^*/RT_1^*)(-D/(\tilde{v}-\tilde{v}^{2/3})) \\ & + P_1^* V_1^* D/RT\tilde{v}^2 + PV_1^* D/RT \\ & + V_1^* X_{12} 2\theta_2^2\theta_1/RT\,\tilde{v}\theta_1\theta_2 \\ & - V_1^* X_{12} D\theta_2^2/RT\tilde{v}^2 - V_1^* Q_{12} 2\theta_2^2\theta_1/R\phi_2 \end{aligned} \qquad (5)$$

where $D = \partial\tilde{v}/\partial\phi$.

For the pure components the reduction parameters can be obtained from their *PVT* properties. For a mixture, the reduction parameters can be obtained from

$$P^* = P_1^*\phi_1 + P_2^*\phi_2 - \phi_1\theta_2 X_{12} \qquad (6)$$

where ϕ is a segment fraction and θ a site fraction which approximates to a volume fraction, and

$$T^* = P^*/(\phi_1 P_1^*/T_1^* + \phi_2 P_2^*/T_2^*) \qquad (7)$$

Knowing P^* and T^*, we can calculate $\tilde{v}$ from equation (1). The only remaining unknowns are, therefore, the parameters X_{12} and Q_{12}. For a weakly, non-specific, interacting system such as this, the parameters ought to be small. There are ways of estimating them but in this case it is simpler to treat them as variables within a reasonable range. We eventually find that they do not affect our results within the errors caused by uncertainties in other values.

EXPERIMENTAL

Densities of the polymer were measured at room temperature and atmospheric pressure using an autopycnometer (Micromeritics) and approximately 8 g samples. The changes in density as a function of temperature and pressure were measured using a *PVT* apparatus which has been described fully elsewhere[16]. It consists of a sample cell containing about 1–2 g of sample and mercury as a confining fluid. A flexible bellows closes off one end of the sample cell. The expansion and contraction of this bellows under temperature and pressure changes are used to calculate the volume change of the sample cell, making proper allowance for the well known volume change of the mercury. In the isothermal mode, volume readings are obtained at fixed pressure intervals (usually 10 MPa or about 100 kg cm^{-2} apart) at a constant temperature. Following measurements along an isotherm, the temperature is changed by 8–10°C, and the process is repeated. The absolute accuracy of the device is $1\text{–}2\times10^{-3}$ cm^3 g^{-1}. However, volume changes as small as $1\text{–}2\times10^{-4}$ cm^3 g^{-1} can be resolved. A version of this *PVT* apparatus is available as a complete instrument from Gnomix Research, Boulder, CO, USA.

PVT measurements were made on both low density and high density polyethylene. The molecular weights of the polymers were determined by gel permeation chromatography (g.p.c.) relative to polyethylene standards and are shown below:

LDPE	$M_n = 23\,000$, $M_w = 102\,000$
HDPE	$M_n = 24\,000$, $M_w = 89\,000$

RESULTS

The reduction parameters for ethylene were found by fitting *PVT* data to equation (1). The data used[17] was chosen to be between 0 and 150°C and between 20 and 240 MPa. These values are in sharp contrast to those calculated using the same data by other workers, who have calculated much higher numbers. Bonner *et al.*[11] calculated best fits at each isotherm and expressed the reduction parameters as polynomials in *T*. DeLoos[12] performed a fit to a small region of one isotherm and used these values throughout. It is possible to get a good fit over the entire data set with single values for the reduction parameters. The fitting procedure used was an iterative nonlinear least squares fit to the equation of state. Choosing an initial value of v^* we then performed linear regression, minimizing the function S^2 to determine values of P^* and T^*. The quantity S^2 is defined as

$$S^2 = \frac{\sum_i (P_{i,\text{data}} - P_{i,\text{fit}})^2}{N-3}$$

where P_{data} is the measured pressure at a given volume and temperature, P_{fit} is the value of the pressure as determined by the equation of state and N is the number of data points. The value of v^* is then adjusted so as to decrease the value of S^2, and P^* and T^* are recomputed. Iteration of this procedure allows us to determine the values of P^*, T^* and v^* which minimize the sum of squares S^2. The fit obtained is shown in *Figure 1*. The values used in this work are shown in *Table 1* and compared to those of DeLoos and Bonner *et al.*

The reduction parameters for FTCM were found by fitting the *PVT* data from the literature[18]. The data chosen was that lying between 100 and 200°C and between 5 and 13 MPa. The fit is shown in *Figure 2* and the values obtained were: $P^* = 425.9$ MPa, $T^* = 4197.5$ K, $v^* = 0.50232$ cm^3 g^{-1} and $S^2 = 0.023$.

The reduction parameters for polyethylene samples were obtained using data from the pressure dilatometer.

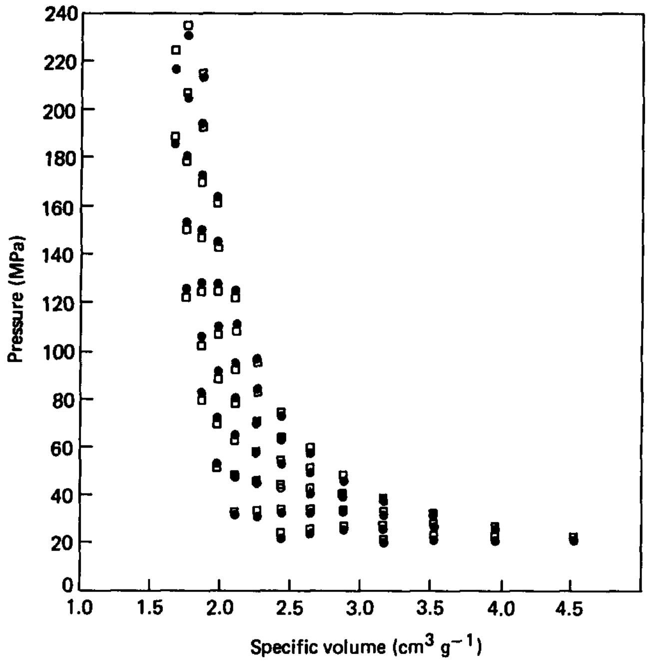

Figure 1 PVT values for ethylene, from reference 17, showing pressures and volumes at isotherms between 9 and 150°C. The experimental points are depicted by ●. For each point a value of the pressure corresponding to that temperature and volume was calculated using the equation of state with reduction parameters giving a best fit. These values are depicted by □

Table 1 Reduction parameters for ethylene

	This work	DeLoos[12]	Bonner *et al.*[11] (T=423.15 K)
P^* (MPa)	334.6	669.19	703.16
T^* (K)	2375.9	2828.0	2998.3
v^* (cm^3 g^{-1})	1.31512	1.25257	1.265
S^2	6.2		

The *PVT* data for low density and high density polyethylene are presented in *Figures 3* and *4*, which also show the fit obtained. Values of the reduction parameters were obtained by fitting equation (1) to the data above the melting transitions and up to 262°C and pressures in the range $10 < P < 200$ MPa. The values obtained are shown in *Table 2*.

The values of S^2 indicate that the equation of state of Flory and coworkers[3,4] is not a perfect fit to the polyethylene data. Values of S^2 in the range 0.1–0.2 correspond to errors in the volume of the order of $1-2\times10^{-4}$ cm^3 g^{-1}, which is the ultimate precision to which the volumes can be measured. Choosing smaller subsets of the main data causes S^2 to approach values consistent with the experimental errors in the data, but the values of the reduction parameters change as a function of temperature and pressure. For the polyethylene samples above, the deviations in the values of the reduction parameters as measured this way are of the order of ±30 MPa in P^*, ±600 K in T^* and ±0.03 in v^*. If one fits the data individually for each isobar and then averages these values as was done by Zoller[18], one also obtains different results.

Using these values and assuming zero values for the interaction parameters, the phase diagram for the low density polyethylene in ethylene was calculated for a series of pressures. Polydispersity (which will not affect the spinodal but will broaden the binodal) was ignored. The results are shown in *Figure 5*. By varying the reduction parameters it is evident that very small differences in reduction parameters can have a substantial effect on the solubility. If P^* is increased by 20 J cm^{-3} or T^* by 100 K the critical temperatures are increased by about 30 K, which is equivalent to about a reduction of 100 atmos (101 J cm^{-3}) in pressure. We also examined the effect of the interaction parameters on the phase diagram and found that a reasonably large range of possible values of ±10 in X_{12} causes only a minimal change in the phase diagram.

The phase diagram of *Figure 5* has been derived with no adjustable parameters other than the interaction terms,

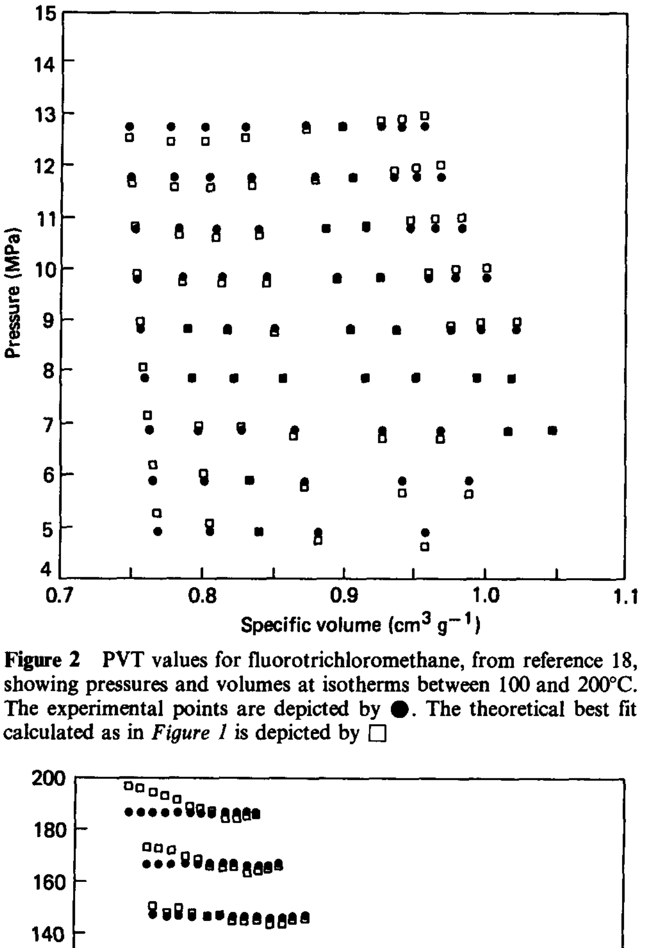

Figure 2 PVT values for fluorotrichloromethane, from reference 18, showing pressures and volumes at isotherms between 100 and 200°C. The experimental points are depicted by ●. The theoretical best fit calculated as in *Figure 1* is depicted by □

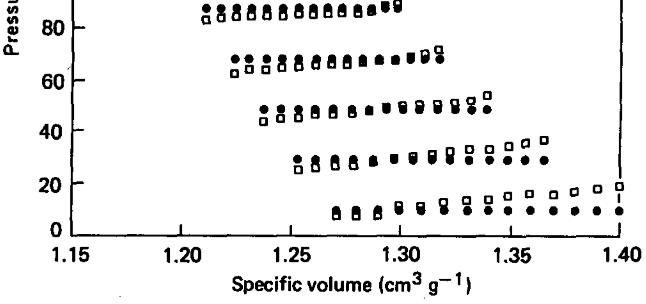

Figure 3 PVT values for low density polyethylene showing pressures and volumes at isotherms between 126°C (above the melting transition) and 258°C. The experimental points, ●, and best fit, □, are as in *Figure 1*

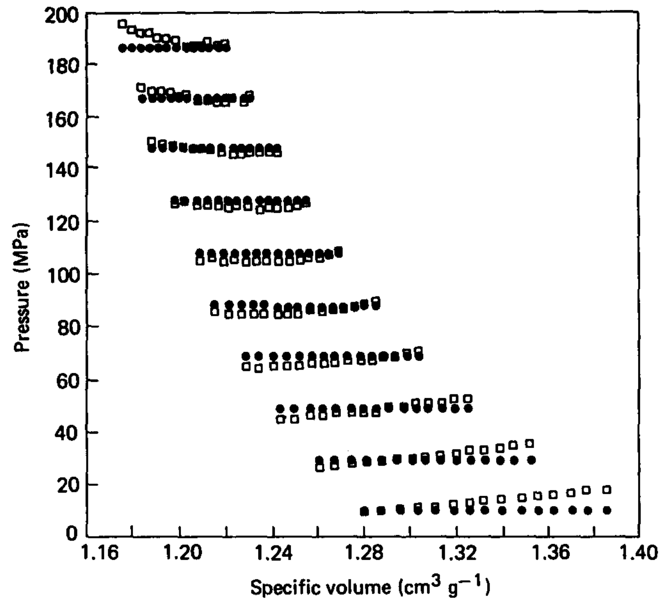

Figure 4 PVT values for high density polyethylene showing pressures and volumes at isotherms between 152°C (above the melting transition) and 262°C. The experimental points, ●, and best fit, □, are as in *Figure 1*

Table 2 Reduction parameters for polyethylene

	Low density polyethylene	High density polyethylene
P^* (MPa)	537.8	516.8
T^* (K)	6653.1	6821.6
v^* ($\mathrm{cm}^3\,\mathrm{g}^{-1}$)	1.00995	1.00758
S^2	12.56	9.25

which have very little effect. It is interesting, therefore, to compare them to some of the published cloud point data. The maxima in the coexistence curve as shown in *Table 3*.

It can be seen that our predictions are well within the reported range. Some of the wide range of scatter in the experimental results could be accounted for by the predicted sensitivity of the phase diagrams to small changes in the state parameters. In particular, the difference between low density and high density polyethylene could be explained on this basis. The differences in solubility observed between high and low density polyethylene (high density, linear appears much less soluble) could be accounted for by the differences in the reduction parameters, given the uncertainties in the values. Using the data for high density polyethylene, one predicts similar phase diagrams to those of *Figure 5* but shifted approximately 20 K higher. Differences in the interaction terms are likely to be small and not likely to be the cause. In practice, one should be very hesitant in predicting the exact phase separation temperature for any given polyethylene since it is likely to be very dependent on the microstructure of the polymer.

The phase diagram for high density polyethylene with FTCM was also simulated, assuming zero values for the interaction parameters. The results are shown in *Figure 6* compared to the measured cloud points from the literature[13]. The theory correctly predicts an LCST, but the predicted phase diagram is approximately 35 K lower than that measured at the minimum. The simulated curves are again not very dependent on the values of the interaction parameters but are very dependent on the values of the reduction parameters of the components. The deviation in the results could be explained by changing the hard-core temperatures by only 2% for example.

CONCLUSION

We have shown that the equation of state theory of Flory and coworkers can be successfully used to describe the

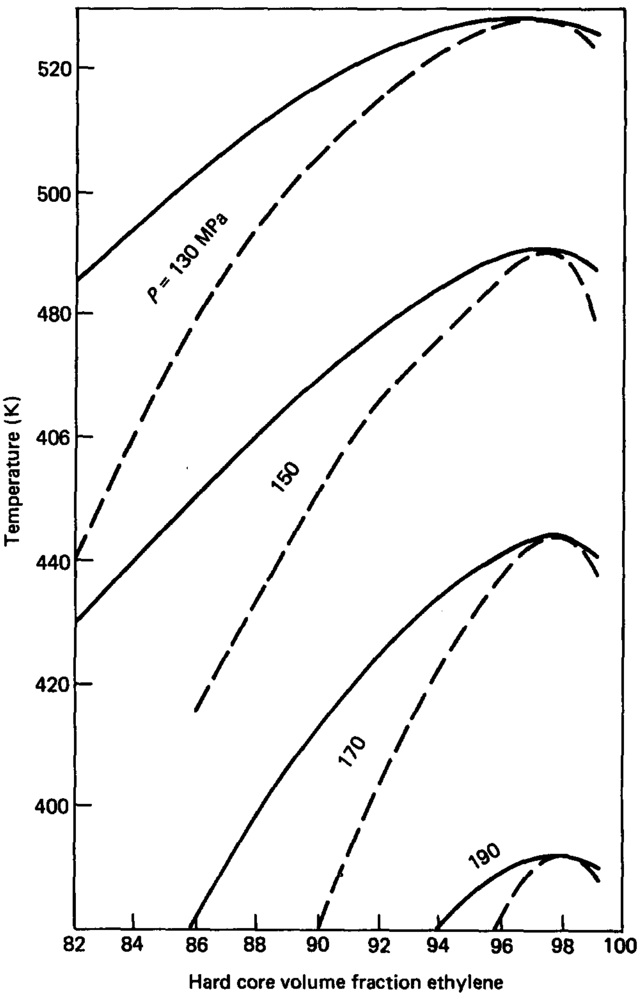

Figure 5 The calculated phase diagrams for low density polyethylene/ethylene mixtures at 130, 150, 170 and 190 MPa showing binodals (———) and spinodals (– – –)

Table 3 Reported values of the maxima in the coexistence curve taken from the literature

	$M_w(\times 10^3)$	$M_n(\times 10^3)$	T (°C)	P (MPa)
Ehrlich[5]	(high, broad)		130	190
			155	170
			200	135
	(low fraction)		130	150
			165	130
Ratzsch[7]	374	27	160	140
	232	11	160	125
	232	11	220	110
	328	30	220	135
Kleintjens[8]				
Branched	54	7	150	150
Linear	55	8.6	150	165
DeLoos[12]	99	56	170	166
(all linear)	99	56	150	180
	8.8	7.6	170	120
	8.8	7.6	130	135

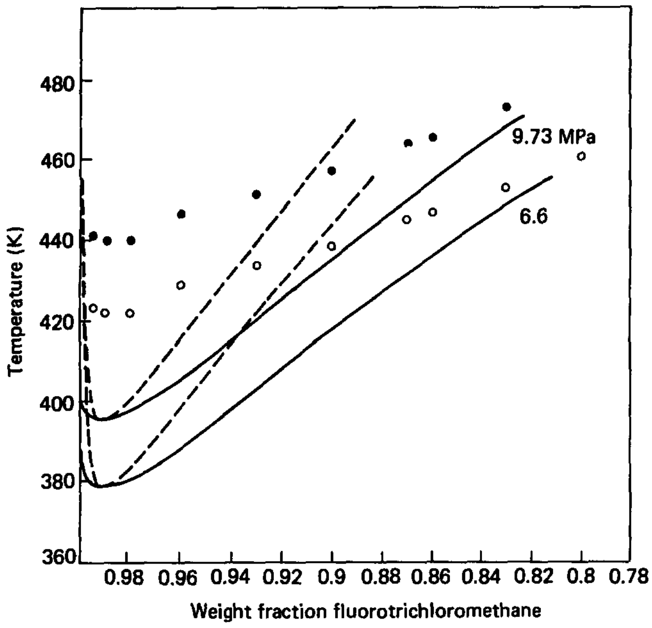

Figure 6 The phase diagram of high density polyethylene/fluorotrichloromethane mixtures at 6.6 and 9.73 MPa. The calculated phase diagrams are shown with binodals (———) and spinodals (– – –). The points are the experimental cloud points from reference 13

phase diagram of polyethylene in both ethylene and fluorotrichloromethane. This can be achieved assuming a zero value for the interaction terms which do not contribute significantly to the results within reasonable values. The main uncertainties arise from the high sensitivity of the predicted phase diagrams to the values of the reduction parameters of the pure components.

REFERENCES

1 Simha, R. and Somcynsky, T. *Macromolecules* 1969, **2**, 342
2 Sanchez, I. C. and Locombe, R. H. *J. Phys. Chem.* 1976, **80**, 2352, 2568
3 Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3567
4 Eichinger, B. E. and Flory, P. J. *Trans. Farad. Soc.* 1968, **65**, 2035
5 Ehrlich, P. *J. Polym. Sci. A3* 1965, **3**, 131
6 Luft, G. and Lindler, A. *Angew. Makromol. Chem.* 1976, **56**, 99
7 Ratzsch, M., Findersen, R. and Sernow, V. S. *Z. Phys. Chem. Leipzig* 1980, **261**, 995
8 Kleintjens, L. A. Dissertation, Essex, 1979
9 Cheng, Y. L. and Bonner, D. C. *J. Polym. Sci. Phys.* 1978, **16**, 319
10 Liu, D. D. and Prausnitz, J. M. *Ind. Eng. Chem. Proc. Res. Dev.* 1980, **19**, 205
11 Bonner, D. C., Maloney, D. P. and Prausnitz, J. M. *Ind. Eng. Chem. Proc. Des. Dev.* 1974, **13**, 91
12 deLoos, T. W. Dissertation, Delft, 1981
13 Anderson, R. D. and Ramano, J. E. US Patent 3 227 794, 1966
14 Rostami, S. and Walsh, D. J. *Macromolecules* 1984, **17**, 315
15 Rostami, S. and Walsh, D. J. *Macromolecules* 1985, **18**, 1228
16 Zoller, P., Bolli, P., Pahud, V. and Ackermann, H. *Rev. Sci. Instrum.* 1976, **47**, 948
17 Michels, A., Geldermans, M. and deGroot, S. R. *Physica* 1946, **12**, 105
18 Rivkin, S. L. and Kremnevskaya, E. A. *Prop. Matter Subst.* 1971, 1–17