Here $C(\cdot)$ and $S(\cdot)$ are the standard Fresnel integrals,[20] and the F functions are defined as in eq 32b. The range of integration for $y_\perp$ and $y_\parallel$, or $y_\pm$, is $-\infty < y_\pm < \infty$; the essential reason for the difference between these ranges for this special case and the restricted ranges for the general case is the presence of y_-^2 in eq 47. Alternatively, both prolate ($S_\parallel > S_\perp$) and oblate ($S_\parallel < S_\perp$) ellipsoids of revolution are encompassed by eq 48, and the corresponding Fourier variables are likewise unrestricted.

One further integration, over $y_\perp$, can be accomplished in eq 48 for any spectrum since $F(y_\perp)^2$ has simple poles. It will prove useful to reduce the double integral to a sum and single integral for numerical evaluation of this equation in the case of linear chains or otherwise nondegenerate spectra. For a doubly degenerate spectrum eq 48 can be further reduced to a double sum by use of the methods described in the previous section. Since ellipsoids of revolution are not apt to be of interest apart from applications to rubber elasticity, where approximations to spectra are called for, the messy equations generated by the last one or two integrations of eq 48 are not given here.

Conclusion

The general solution to the shape distribution problem has been shown to reside within the theory of multivariate statistics. In practice much more needs to be done to reduce the three-dimensional equation to tractable form before numerical work is undertaken to evaluate it. The asymptotic distributions for linear chains in a space of any dimension has been given.

The distribution for two-dimensional rings has been rederived, whereas that for three-dimensional ellipsoids of revolution is new. The latter is much more easily evaluated than is the full three-dimensional distribution.

Acknowledgment. This work was supported by the Department of Energy, contract DE-AT06-81ER10912 and grant DE-FG06-84ER45123.

References and Notes

(1) Šolc, K.; Stockmayer, W. H., *J. Chem. Phys.* **1971**, *54*, 2756.
(2) Šolc, K. *J. Chem. Phys.* **1971**, *55*, 335.
(3) Šolc, K.; Gobush, W. *Macromolecules* **1974**, *7*, 814.
(4) Eichinger, B. E. *Pure Appl. Chem.* **1975**, *43*, 97.
(5) Eichinger, B. E. *Macromolecules* **1977**, *10*, 671.
(6) Gobush, W.; Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1974**, *60*, 12.
(7) Olaj, O. F.; Lantschbauer, W.; Pelinka, K. H. *Macromolecules* **1980**, *13*, 299.
(8) Eichinger, B. E. *Macromolecules* **1980**, *13*, 1.
(9) Muirhead, R. J. "Aspects of Multivariate Statistical Theory"; Wiley: New York, 1982.
(10) Richards, D.; private communication of a paper submitted to *SIAM Rev.*
(11) Eichinger, B. E. *SIAM Rev.* **1984**, *26*, 117.
(12) Satake, I. *Notices Am. Math. Soc.* **1980**, *27*, 442.
(13) James, A. T. *Ann. Math. Stat.* **1964**, *35*, 475.
(14) Gupta, R. D.; Richards, D. *Ann. Inst. Stat. Math.* **1979**, *31*, 207.
(15) Eckart, C. *Phys. Rev.* **1934**, *46*, 383.
(16) Eckart, C. *Phys. Rev.* **1935**, *47*, 552.
(17) Ben-Israel, A.; Greville, T. N. E. "Generalized Inverses: Theory and Applications"; Wiley-Interscience: New York, 1974.
(18) Steenrod, N. "The Topology of Fibre Bundles"; Princeton University Press: Princeton, NJ, 1951.
(19) Gradshteyn, I. S.; Ryzhik, I. M. "Table of Integrals, Series, and Products"; Academic Press: New York, 1965; Entry 6.671.7, p 731.
(20) Abramowitz, M., Stegun, I. A., Eds. "Handbook of Mathematical Functions"; National Bureau of Standards, Applied Mathematics Section 55, U.S. Government Printing Office: Washington, DC, 1967; p 300.

Effect of Pressure on Polymer–Polymer Phase Separation Behavior

David J. Walsh* and Shamsedin Rostami

Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7, England.

Received April 26, 1984

ABSTRACT: An equation based on the equation-of-state theory of Flory and co-workers was used to describe the effect of pressures, up to 900 atm, on the phase separation behavior of various polymer mixtures. The mixtures under consideration were of an ethylene–vinyl acetate copolymer with chlorinated polyethylenes and of a polyether sulfone with poly(ethylene oxide). These had previously been shown to be miscible and to phase separate on heating. The theory was used to simulate the spinodal curves of mixtures at the operating pressures. For mixtures at compositions close to the critical compositions these were compared with the experimental values and were found to be consistent within the experimental uncertainties. Calculations of volume changes on mixing were also carried out by various methods based on experimental and theoretical results and were also self-consistent. For mixtures of polyether sulfone with poly(ethylene oxide) the state properties of the polymers are very diverse. These mixtures show a very large effect of pressure on phase separation temperatures and a very large volume change on mixing.

Introduction

The equation-of-state theory as developed by Flory and his collaborators[1-4] has many advantages over the classical Flory–Huggins theory in describing the properties of polymer mixtures. McMaster[5] examined the contribution of the state parameters to the miscibility of hypothetical mixtures and showed that the theory is capable of predicting both lower critical solution temperature (LCST) and upper critical solution temperature (UCST) behavior. Also, because it abandons a fixed lattice, it is capable of predicting volume changes on mixing and, hence, the effects of pressure on the phase diagram.

Olabisi[6] has applied McMasters' treatment to a real system of polycaprolactone and poly(vinyl chloride). We have also used a modified form of the above theory to simulate the spinodal curves for mixtures of poly(methyl methacrylate) with chlorinated polyethylene,[7] of poly(butyl acrylate) with chlorinated polyethylene,[8] of ethylene–vinyl acetate copolymers with chlorinated polyethylene,[9] and of poly(ethylene oxide) (PEO) with a polyether sulfone

0024-9297/85/2218-0216$01.50/0 © 1985 American Chemical Society

Table I
State Parameters for the Pure Materials

material	$10^{-4}\alpha$, K^{-1}	γ, J cm^{-3} K^{-1}	v_{sp}, cm^3 g^{-1}	$10^{-5}\bar{M}_w$[a]
EVA45	4.5103	0.8045	1.0636	2.56
CPE2	4.4199	0.9544	0.81506	1.82
CPE3	3.6546	0.9592	0.8089	1.2
PES	2.0	1.5	0.7934	0.2
PEO	5.5	1.2	0.9183	0.2

[a] Relative to polystyrene by GPC.

(PES).[10] In each case we calculated a value of the interactional parameter X_{12} from heat of mixing measurements using low molecular mass analogues. The noncombinatorial entropy parameter, Q_{12}, was then used as an adjustable parameter to fit the minimum of the spinodal to the minimum of the experimental cloud point curve. The full spinodal curve was then calculated and compared to the measured cloud point curve. Generally, a favorable (negative) X_{12} had to be balanced by an unfavorable (negative) Q_{12} in order to be consistent with the experimental data.

The effect of pressure on phase separation temperataures has been studied by several authors, for example, in polymer solutions[11] and in mixtures of oligomers.[12,13] Recently we have also reported the results of such studies on high molecular weight mixtures of ethylene–vinyl acetate copolymers with chlorinated polyethylene.[14] In each case authors have related their results to the volume change on mixing, ΔV_m, and heat of mixing, ΔH_m, by the expression for the pressure dependence of the critical solution temperature.

$$(dT/dP)_c = -(d\chi/dP)_T/(d\chi/dT)_P \simeq T\Delta V_m/\Delta H_m \quad (1)$$

In our experimental results the effect of pressure on the cloud points was measured, with samples held in a pressure bomb at various pressures, by using light scattering turbidimetry. The apparatus and technique are described elsewhere.[13,14]

In this paper we interpret these results along with others obtained in a similar way for the same system using a modified form of the equation-of-state theory which we have previously used to simulate spinodal curves at atmospheric pressure.[7-10] We also use the same theory to interpret similar results for mixtures of polyether sulfone with poly(ethylene oxide). This system has previously been studied at atmospheric pressure[10] and the results for the effect of pressure on this system are taken from an internal publication of Imperial College.[15] These polymers have very different equation-of-state parameters from those in the previous system above and a very different value of $(dT/dP)_c$. The two systems together thus provide a very good test of the theory.

Theory

The chemical potential of component 1 in a polymer mixture is given by[7-10]

$$\Delta\mu_1/RT = \ln\phi_1 + (1 - r_1/r_2)\phi_2 + P_1{*}V_1{*}/RT\{3\tilde{T}_1 \ln(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1) + 1/\tilde{v}_1 - 1/\tilde{v} + \tilde{P}_1(\tilde{v} - \tilde{v}_1)\} + V_1{*}X_{12}\theta_2^2/RT\tilde{v} - V_1{*}Q_{12}\theta_2^2/R \quad (2)$$

where all symbols are defined as shown later. Applying the spinodal condition, $(\partial/\partial\varphi_2)(\Delta\mu_1/RT) = 0$, we obtain[7-9]

$$(\partial/\partial\varphi_2)(\Delta\mu_1/RT) = 0 = -1/\phi_1 + (1 - r_1/r_2) + (P_1{*}V_1{*}/RT_1{*})(-D/(\tilde{v} - \tilde{v}^{2/3})) + P_1{*}V_1{*}D/RT\tilde{v}^2 + PV_1{*}D/RT + V_1{*}X_{12}2\theta_2^2\theta_1/RT\tilde{v}\phi_1\phi_2 - V_1{*}X_{12}D\theta_2^2/RT\tilde{v}^2 - V_1{*}Q_{12}2\theta_2^2\theta_1/R\varphi_1\phi_2 \quad (3)$$

where

$$D = \partial\tilde{v}/\partial\varphi_2 \quad (4)$$

and[7-9]

$$\frac{\partial\tilde{v}}{\partial\varphi_2} = \frac{\dfrac{\partial\tilde{P}}{\partial\varphi_2} - \dfrac{\partial\tilde{T}}{\partial\varphi_2}\left(\dfrac{\tilde{P}}{\tilde{T}} + \dfrac{1}{\tilde{T}\tilde{v}^2}\right)}{\dfrac{2}{\tilde{v}^3} - \dfrac{T(3\tilde{v}^{1/3} - 2)}{3\tilde{v}^{5/3}(\tilde{v}^{1/3} - 1)^2}} \quad (5)$$

with

$$\frac{\partial\tilde{P}}{\partial\varphi_2} = \frac{P}{P{*}^2}\left\{P_1{*} - P_2{*} - \theta_2X_{12}\left(1 - \frac{\theta_1}{\theta_2}\right)\right\} \quad (6)$$

$$\frac{\partial\tilde{T}}{\partial\varphi_2} = \frac{\tilde{T}}{\tilde{P}}\frac{\partial\tilde{P}}{\partial\varphi_2} + \frac{P_2{*}\tilde{T}_2 - P_1{*}\tilde{T}_1}{P{*}} \quad (7)$$

The effect of the term containing $\tilde{P}_1$ in eq 2 and hence that containing P in eq 3 is small and does not describe the main effect of pressure on the phase diagram which is due to its effect on the expansion coefficients and hence on the reduced volume of the mixture $\tilde{v}$. We therefore derive the effect of pressure on the phase diagram directly from the equation of state as follows.

At the temperature where the expansion coefficients, α, and the thermal pressure coefficients, γ, of the component polymers are known and at atmospheric pressure ($P \sim 0$), one can calculate the hard-core pressure $P_i{*}$ and reduced temperature $\tilde{T}_i$ of the components from

$$\tilde{v}_i^{1/3} = 1 + \alpha_iT/(3 + 3\alpha_iT) \quad (8)$$

$$P_i{*} = \gamma_iT\tilde{v}_i^2 \quad (9)$$

$$\tilde{T}_i = (\tilde{v}_i^{1/3} - 1)/\tilde{v}_i^{4/3} \quad (10)$$

and hence $T_i{*}$, the hard-core temperature, from

$$T_i{*} = T/\tilde{T}_i \quad (11)$$

One can then calculate the hard-core pressure $P{*}$ and temperature $T{*}$ of the mixture from

$$P{*} = P_1{*}\phi_1 + P_2{*}\phi_2 - \phi_1\theta_2X_{12} \quad (12)$$

$$T{*} = P{*}/(\phi_1P_1{*}/T_1{*} + \phi_2P_2{*}/T_2{*}) \quad (13)$$

$\tilde{v}$ can then be found iteratively by using the equation of state which, when $P = 0$, is

$$\tilde{v}^{1/3} = 1/(1 - \tilde{T}\tilde{v}) \quad (14)$$

When the pressure is included this becomes

$$\tilde{v}^{1/3} = 1/\{1 - \tilde{T}\tilde{v}/(\tilde{P}\tilde{v}^2 + 1)\} \quad (15)$$

This process can be repeated at any other temperature if $\tilde{T}$ is calculated by using eq 11 and at any chosen pressure. Using eq 2, one thus can calculate the spinodal curve at any given pressure.

The main assumptions in this treatment are that the equation-of-state theory in the simplified form above can be used with constant values of $P{*}$, $T{*}$, and $V{*}$ and that the effect of pressure on X_{12} and Q_{12} can be neglected.

Results and Discussion

The equation-of-state parameters for the pure materials and the binary parameters of mixtures used in this study are given in Tables I and II, respectively. The methods used in determining these parameters and the justification for their values have been given previously.[9,10,14,16,17] These values have been used to simulate the spinodal curves of

Table II
Binary Parameters of Mixtures

mixtures	X_{12}, J cm^{-3}	Q_{12}, J cm^{-3} K^{-1}	S_2/S_1
EVA45/CPE3	-3.2	-0.006 26	1.03
EVA45/CPE2	-2.63	-0.006 76	0.98
PES/PEO	-40	-0.048 2	1.2

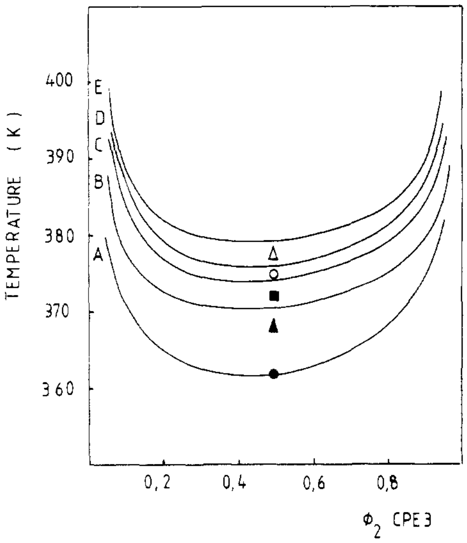

Figure 1. Measured cloud points and simulated spinodal curves for mixtures of ethylene–vinyl acetate copolymer (45% w/w vinyl acetate) with a chlorinated polyethylene (52 wt % chlorine) at 1 (curve A, ●), 300 (curve B, ▲), 450 (curve C, ■), 550 (curve D, ○), and 750 (curve E, △) atm.

various mixtures at different pressures, and these spinodals have been compared to the experimental results available.

Figure 1 shows the results for mixtures of ethylene–vinyl acetate copolymer (45 wt % acetate, EVA45) with chlorinated polyethylene (52 wt % chlorine, CPE3). The experimental results have been previously reported[14] and show a shift in the cloud point of up to 14 °C for elevated pressure up to 750 atm. The simulated spinodals, using data which fit the value of the cloud point at 1 atm, pass remarkably close to these points, being never more than 4 °C away. This compares with an estimated error in the cloud points of ±2 °C. All the experimental results are below the simulated spinodal and this could be explained by uncertainties in the values of the pure-component and binary equation-of-state parameters used in the simulations.

Figure 2 shows the results for mixtures of EVA45 with a chlorinated polyethylene (43 wt % chlorine, CPE2). These experimental results have not been previously reported. They again fit the simulated spinodals with about the same degree of accuracy. These results also cover a range of compositions in the mixture. As one moves further away from the critical point, one is less certain that the spinodal corresponds to the cloud point. The cloud point will lie somewhere within the limits set by the spinodals and the binodal. In this case, over quite a large range of composition the spinodal is relatively flat and thus must be fairly close to the binodal.

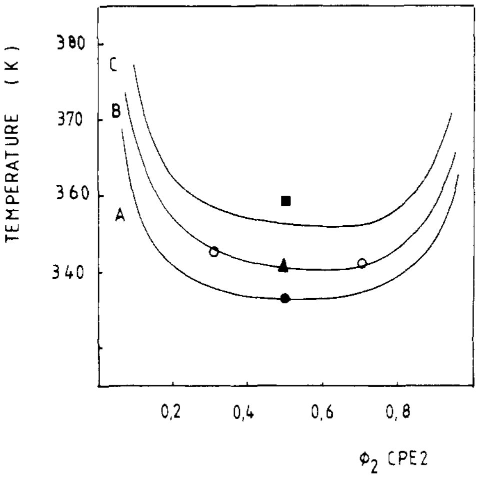

Figure 2. Measured cloud points and simulated spinodal curves for mixtures of ethylene–vinyl acetate copolymer (45% w/w vinyl acetate) with a chlorinated polyethylene (43 wt % chlorine) at 1 (curve A, ●), 300 (curve B, ▲), 858 (curve C, ■), 450 (experiment only, ○) atm.

Table III
Theoretical Spinodal Points and Experimental Cloud Point Temperatures

comp (w/w)	press., atm	temp, K theory[a]	 expt
	EVA45/CPE3		
50:50	1	363.9[b]	364 ± 2
	300	371.9	368 ± 2
	450	375.3	371 ± 2
	550	377.3	373 ± 2
	750	380.9	378 ± 2
	EVA45/CPE2		
50:50	1	347.0[b]	347 ± 2
	300	351.7	352 ± 2
	858	356.0	360 ± 2
30:70	450	353.7	352 ± 2
70:30	450	353.7	352 ± 2
	PES/PEO		
10:90	1	351.1[b]	351 ± 1
	108	356.3	357 ± 1
	221	361.3	362 ± 1
	348	366.5	367 ± 1

[a] ±0.1 K. [b] Obtained by adjusting Q_{12} to the experimental result.

Figure 3 shows the results for mixtures of polyether sulfone (PES) with poly(ethylene oxide) (PEO). These results have not been previously reported and were obtained by others and form part of an internal report.[15] They were obtained for 90:10 w/w mixtures. This is close to the minimum of the observed cloud point curve which has been reported elsewhere[17] and is included in Figure 3 for comparison. The spinodals fit very close to the experimental results and are within the experimental error, which is ±1 °C for this system due to the sharp cloud points caused by the high mobility in this system. It should be noted that the effect of pressure on the cloud point is twice that observed in the previous system. This arises from the large difference between the expansion coefficients of PEO and PES. The fact that the theory not only fits the experimental results well but successfully predicts the large differences between the systems studied gives one confidence that the main assumptions are justified. The cloud points in the PES/PEO system are sharp and easily reversible on annealing at a lower temperature and thus the cloud point curve probably corresponds closely to the binodal rather than the spinodal. There is therefore little point in comparing any results obtained distant from the minimum of the cloud point curve.

Volume Changes on Mixing. Table III shows the accurately calculated values of the theoretical spinodal points which coincide with the experimental cloud points obtained at different pressures. Using a linear least-squares fit to this data one can obtain values for dT/dP, both based on the theoretical calculation and on the experimental results. These values are given in Table IV. Table IV also gives values of ΔH_m, the heat of mixing of

Table IV
Volume Changes on Mixing at 90 °C As Derived by Various Methods As Described in the Text

	dT/dP, K atm^{-1}			$10^4 \Delta V_m$		
system	theoretical	exptl	ΔH_m, J cm^{-3}	theoretical (eq 1)	exptl (eq 1)	theoretical (eq 16)
EVA45/CPE3 (50:50)	0.22	0.020	-1.3	-7.8	-7.1	-7.2
EVA45/CPE2 (50:50)	0.010	0.014	-0.84	-2.3	-3.2	-4.0
PES/PEO (10:90)	0.044	0.046	-4.0	-48	-50	-48

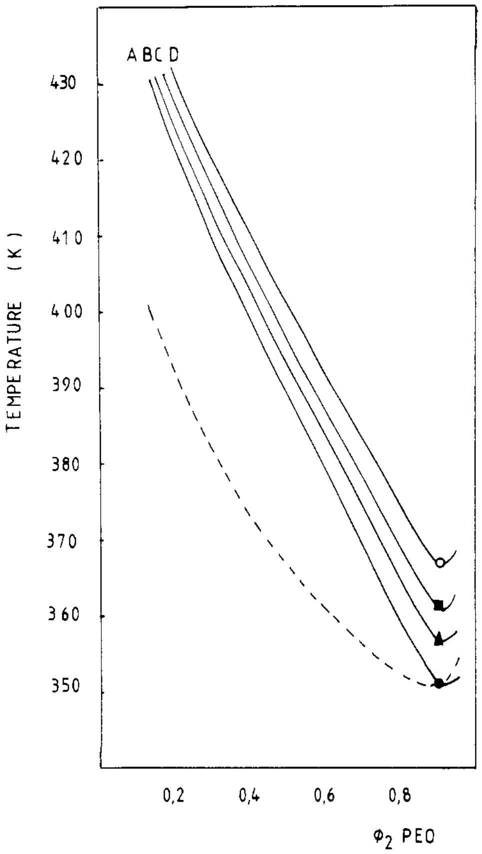

Figure 3. Measured cloud points and simulated spinodal curves for mixtures of polyether sulfone with poly(ethylene oxide) at 1 (curve A, ●), 108 (curve B, ▲); 221 (curve C, ■), and 348 (curve D, ○) atm. The dotted line shows the full experimental cloud point curve for comparison.[17]

low molecular weight analogues at the same composition, as reported previously.[10,16] If one assumes that these compositions are the critical point compositions, then, using eq 1, one can calculate values for the fractional volume change on mixing, ΔV_m. These values, based on both theoretical and experimental values of dT/dP, are also presented.

If one calculates $\tilde{v}$ by the method outlined previously, one can also calculate a value of ΔV_m from

$$\Delta V_m = \tilde{v}/(\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2) - 1 \qquad (16)$$

Values derived in this way are also shown in Table IV for comparison. The results are very close considering the approximations made and the possible sources of experimental error. Apart from the errors in dT/dP and an uncertainty in whether this corresponds to the critical condition there is also possible large source of error in ΔH_m arising from the use of low molecular weight analogues which are not identical with the polymers either in chemical composition or in density. One should also point out that in these polymer mixtures the large favorable heats of mixing must be due to specific interactions between the polymers and the equation-of-state theory was not originally designed to cope with such systems. The theory nevertheless appears to describe the behavior of these polymer mixtures very satisfactorily.

Conclusion

Equations based on the equation-of-state theory of Flory and co-workers have been shown to successfully describe the effect of pressure on polymer–polymer phase separation temperatures close to the critical point.

List of Symbols

ΔH_m	enthalpy of mixing
P	pressure
$\tilde{P}_i$	reduced pressure of species i
P_i^*	hard-core pressure of species i
$\tilde{P}$	reduced pressure of mixture
P^*	hard-core pressure of mixture
Q_{12}	interaction entropy parameter
R	gas constant
r_i	chain length of molecule i
S_i	number of contact sites per segment in species i
T	temperature
$\tilde{T}_i$	reduced temperature of species i
T_i^*	hard-core temperature of species i
$\tilde{T}$	reduced temperature of mixture
T^*	hard-core temperature of mixture
V_1^*	molar hard-core volume of component 1
v_{sp}	specific volume of component i
$\tilde{v}_i$	reduced volume of component i
v_i^*	hard-core volume of component i
$\tilde{v}$	reduced volume of mixture
v^*	hard-core volume of mixture
X_{12}	interactional parameter
ϕ_i	segment fraction of species i
θ_i	site fraction of species i
$\Delta\mu_1$	chemical potential of component 1
ΔV_m	volume change on mixing

Registry No. EVA (copolymer), 24937-78-8; PEO (SRU), 25322-68-3.

References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(2) Abe, A.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 2887.
(3) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *65*, 2035.
(4) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3567.
(5) McMaster, L. P. *Macromolecules* **1973**, *6*, 760.
(6) Olabisi, O. *Macromolecules* **1975**, *9*, 316.
(7) Chai, Z.; Ruona, S.; Walsh, D. J.; Higgins, J. S. *Polymer* **1983**, *24*, 263.
(8) Chai, Z.; Walsh, D. J. *Makromol. Chem.* **1983**, *184*, 1549.
(9) Rostami, S.; Walsh, D. J. *Macromolecules* **1984**, *17*, 315.
(10) Walsh, D. J.; Rostami, S.; Singh, V. B. *Makromol. Chem.*, in press.
(11) Saeki, S.; Kuwahara, N.; Konno, S.; Kaneko, M. *Polymer* **1975**, *16*, 445.
(12) Wolf, B. A.; Blaum, G. *J. Polym. Sci., Polym. Symp.* **1977**, *61*, 251.
(13) Tripathi, J. B. P. Ph.D. Thesis, Imperial College, London, England, 1979.
(14) Walsh, D. J.; Higgins, J. S.; Rostami, S. *Macromolecules* **1983**, *16*, 388.
(15) Project Report (with thanks to J. S. Higgins), Department of Chemical Engineering and Chemical Technology, Imperial College, London, England, 1983.
(16) Walsh, D. J.; Higgins, J. S.; Rostami, S.; Weeraperuma, K. *Macromolecules* **1983**, *16*, 391.
(17) Walsh, D. J.; Singh, V. B. *Makromol. Chem.* **1984**, *185*, 1979.