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Liquid–liquid phase separation in blends of polydisperse linear and branched polyethylenes

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A generalized Flory–Huggins theory is employed to investigate liquid–liquid phase separation in a blend of polydisperse linear and branched polyethylenes (LPE/BPE). A temperature- and concentration-dependent χ parameter is used. The temperature- and composition-dependent coefficients of χ are obtained by fitting to experimental cloud-point data, and having a detailed knowledge of the molecular weight distributions of the two components. The value of χ is found to be small and positive (3.4×10^{-4} ($\varphi_{\mathrm{BPE}} = 0.0$) to 2.6×10^{-4} ($\phi_{\mathrm{BPE}} = 1.0$), $T = 423\,\mathrm{K}$) over the temperature composition range of interest, consistent with an approximately athermal blend with small, non-combinatorial entropic contributions to the free energy of mixing. The magnitude of χ determined here is also in reasonable agreement with values measured previously on related systems. The best-fit cloud-point curve obtained for the LPE/BPE blend is a closed immiscibility loop, which is consistent with the experimental observations. However, no critical point(s) or spinodal(s) are found to exist. It is suggested, based on the limited data available, that a blend comprising two monodisperse LPE/BPE components, with molecular weights corresponding to the weight-average molecular weights of the polydisperse linear and branched polyethylenes, would not undergo liquid–liquid phase separation.

(Keywords: liquid–liquid phase separation; polyethylene blends; Flory–Huggins theory)

INTRODUCTION

There is now a growing body of evidence that liquid–liquid phase separation occurs in blends of linear and branched polyethylenes. In 1988, Barham *et al.*[1] of the University of Bristol, published indirect evidence for the liquid–liquid phase separation in these systems. This evidence was provided by differential scanning calorimetry (d.s.c.) and electron micrography of quenched blend samples. The polymers were commercial materials that were polydisperse. The branched polymer had 10 long branches and 16 short branches per 1000 carbon atoms. Their conclusions were also supported (with reservations) by a parallel study[2]. Independently, Mirabella *et al.*[3] published results suggesting that the extraordinarily high fracture toughness of linear low-density polyethylenes, relative to low-density and high-density polyethylenes, is due to the presence of a second soft phase. It was postulated[3] that this discrete second phase performed a similar function to the rubber-like phase in impact-modified polymers. Subsequent work by the Bristol researchers[4], utilizing a broader range of experimental techniques, has confirmed the occurrence of phase separation in the liquid state. Furthermore, the liquid–liquid phase diagram, which was tentatively thought to be of an upper critical solution temperature (*UCST*) type[1], has been demonstrated[4,5] to be a closed loop, with the lower-temperature portions of the loop being inaccessible owing to crystallization. An investigation of the effect of varying the molecular weight of the linear polyethylene on phase separation has been described[6], but full details of the liquid–liquid portions of these phase diagrams are yet to be published.

Nicholson *et al.*[7] and Balsara *et al.*[8] have performed small-angle neutron scattering (SANS) investigations of blends of polyethylenes having varying degrees of ethyl branching along the chain backbone. However, the effect of the deuterium labelling necessary to perform the SANS experiments upon the measured values of the χ interaction parameter is still unclear. This is particularly the case for polyethylene blends where χ is very small.

Rhee and Crist[9] made cloud-point measurements on blends of linear polyethylene and ethyl-branched polyethylenes. Based on this work they state[9] that 60 ethyl branches per 1000 backbone carbon atoms are required for phase separation from unbranched polyethylene in systems with molecular weights of 118 000. Also, Walsh *et al.*[10] determined equations of state for a number of hydrocarbon polymers, including a series of ethylene–propylene copolymers. These authors state[10] that ethylene–propylene copolymers are predicted to be miscible for less than 15% differences in monomer

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contents at molecular weights of 100 000. These two observations[9,10] might seem to be at odds with the data published by the Bristol group[1,4–6]. However, that would depend on the effect on χ of the length of the branches[10], and of the role of polydispersity in the much more molecularly heterogeneous polymers employed by the Bristol workers[1,3,4]. Indeed, Martínez-Salazar *et al.*[11] have concluded, based on a melting-point depression analysis of high-density polyethylene crystals embedded in molten branched polyethylene, that phase separation may occur with branching contents $\geqslant 2\%$.

It is desirable to have a theoretical framework in which to rationalize some of these results. The model systems investigated in some of the above studies may be analysed successfully in terms of simple Flory–Huggins theory for random copolymers[7–9], or using an equation-of-state approach[10]. However, particularly for the more complex cases with branches of various lengths and highly polydisperse components, a more general theoretical approach is required. Plans *et al.*[12] interpreted their data[11] in terms of a Flory–Huggins expression for a ternary system in which holes are regarded as the third component. The concentration of the holes was determined by the extent of branching. While this approach has some appeal, it is still not usable, in its current form, to address the effects of polydispersity.

The effects of polydispersity on cloud-point curves (CPCs) can be profound[13,14]. While there is some experimental evidence[6] that polydispersity of the linear and branched polyethylenes studied by the Bristol group does not have a strong effect on the measured CPCs, this is inconclusive and surprising. Consequently, in order to accurately represent the phase behaviour of a real polymer system, the effects of polydispersity must be incorporated into the model. Extensive experimental and theoretical investigations of the effect of molecular weight distribution on the form of phase diagrams have been conducted previously by Koningsveld and co-workers, and by Solc (see, for example, refs 15–17). Based closely on this earlier work, a method has been described that permits the computation of phase diagrams for quasi-binary polymer systems in which one component may be polydisperse[18], and this has recently been extended to accommodate both components having arbitrary molecular weight distributions[19,31]. This method is employed here to investigate the liquid–liquid phase separation of polydisperse linear and branched polyethylenes.

FREE ENERGY OF MIXING

In a quasi-binary polymer blend, one or both of the components can be polydisperse. In the general case of two polydisperse components, the free energy of mixing is given by the Flory–Huggins type expression:

$$\frac{\Delta G}{RT} = \sum_i n_{1i} \ln \varphi_{1i} + \sum_j n_{2j} \ln \varphi_{2j} + g\varphi_2 \sum_i n_{1i} N_{1i} \quad (1)$$

where n refers to number of moles, φ to volume fraction, and N to relative molar volume of the polymer chains. The first subscript (1 or 2) refers to one of the potentially polydisperse components, and the second subscript (i or j) refers to the single molecular weight (monodisperse) constituents that comprise each of the components. The interaction parameter g is considered to be a function of temperature and composition. The effect of molecular weight on the interaction parameter is typically small[15] and is therefore neglected in equation (1).

It is often desirable to replace g, which cannot be determined directly from experiment, with an interaction parameter χ defined in terms of chemical potentials[20]. The interaction parameters $g(T,\varphi_2)$ and $\chi(T,\varphi_2)$ are related by[15,20]:

$$\chi = g - \varphi_1 g' \quad (2)$$

where $g' = (\partial g/\partial \varphi_2)_T$, and upon integration:

$$\int_{\varphi_2}^{1} \chi(T,\varphi)\,\mathrm{d}\varphi = (1-\varphi_2)g(T,\varphi_2) \quad (3)$$

FUNCTIONAL FORM FOR χ

To obtain quantitative agreement between Flory–Huggins theory and experimental observations for most systems, χ must be considered to be a function of both temperature and composition[19,20–23]. To this end, a form of χ:

$$\chi(T,\varphi_2) = [1 + b_1\varphi_2 + b_2\varphi_2^2][d_0 + d_1/T + d_2 \ln(T)] \quad (4)$$

has been described previously[20], where the coefficients b_i and d_i are adjustable constants. This form of the temperature dependence follows from the assumption that the change in heat capacity upon mixing, Δc_p, is independent of temperature. The quadratic composition dependence was chosen because it has been found to be sufficient to describe most of the experimentally determined χ parameters for solutions[21,22,24]. Finally, it is assumed that the temperature dependence of χ is uniform for all compositions. This expression for χ may be used to represent[20] the five most common types of experimentally[25,26] observed phase diagrams: lower critical solution temperature (*LCST*); *UCST*; combined *LCST*/*UCST*, with the former occurring at higher temperature than the latter; hourglass; and closed loop. Furthermore, this form for χ is sufficient to investigate some more unusual phase phenomena in polymer systems, such as the occurrence of multiple critical concentrations[27], and the coalescence of CPCs[28]. Bae *et al.*[29] have also utilized this approach to describe both vapour–liquid and liquid–liquid equilibria in a number of binary polymer systems.

PHASE EQUILIBRIA IN QUASI-BINARY SYSTEMS

A detailed description of the expressions that define phase equilibria in quasi-binary systems has been given elsewhere[19]. Here, only the expressions directly relevant to this application will be given.

Spinodal

The spinodal curve defines the boundary between unstable and metastable mixtures, and is given explicitly by:

$$\frac{1}{N_{1w}(1-\varphi_2)} - [2\chi(T,\varphi_2) + \varphi_2\chi'(T,\varphi_2)] + \frac{1}{\varphi_2 N_{2w}} = 0 \quad (5)$$

where N_{1w} and N_{2w} are the weight-average relative molar volumes of the two components.

Critical point

The critical point is the point on the CPC and spinodal curve where the two phases become identical and form one phase. Explicitly, it is given by:

$$\frac{N_{2z}}{(N_{2w}\varphi_2)^2} - \frac{N_{1z}}{(N_{1w}\varphi_1)^2} + [3\chi'(T,\varphi_2) + \varphi_2\chi''(T,\varphi_2)] = 0 \tag{6}$$

Here, N_{1w} and N_{1z}, and N_{2w} and N_{2z} are the weight-average and *z*-average relative molar volumes of components 1 and 2, respectively.

Cloud-point curve

The CPC describes the precipitation temperature as a function of solute concentration. It is defined by the two expressions[19]:

$$\sigma_2 - \sigma_1 = \varphi_2'\chi(\varphi_2') - \varphi_2''\chi(\varphi_2'') + \int_{\varphi_2''}^{\varphi_2'} \chi \,\mathrm{d}\varphi \tag{7}$$

and

$$\begin{aligned}\sigma_1(\varphi_1' + \varphi_1'') + \sigma_2(\varphi_2' + \varphi_2'') &= 2\left[\left(\frac{\varphi_1''}{N_{1n}''} + \frac{\varphi_2''}{N_{2n}''}\right) - \left(\frac{\varphi_1'}{N_{1n}'} + \frac{\varphi_2'}{N_{2n}'}\right)\right] \\ &\quad - (\varphi_2'' - \varphi_2')(\chi\varphi_2' + \chi\varphi_2'') - (\varphi_2'' + \varphi_2')\int_{\varphi_2''}^{\varphi_2'} \chi \,\mathrm{d}\varphi\end{aligned} \tag{8}$$

where σ_1 and σ_2 are two separation factors that define the partitioning of each polymer component between the two phases, N_{1n} and N_{2n} are the number-average relative molar volumes of the two components, and the primed and double-primed symbols denote quantities in the principal and conjugate phases, respectively.

Once the normalized weight distributions, w_{1j}' and w_{2j}', of the polymer constituents at the cloud point are given, φ_2'' becomes a function of φ_2' and σ_2 because of the relations:

$$\begin{aligned}\varphi_2'' = \sum_j \varphi_{2j}'' &= \varphi_2' \sum_j \frac{\varphi_{2j}'}{\varphi_2'} \exp \sigma_2 N_{2j} \\ &= \varphi_2' \sum_j w_{2j}' \exp \sigma_2 N_{2j}\end{aligned} \tag{9}$$

and σ_1 becomes a function of σ_2 and φ_2', since:

$$\begin{aligned}(1 - \varphi_2') \sum_i w_{1i}' \exp \sigma_1 N_{1j} + \varphi_2' \sum_j w_{2j}' \exp \sigma_2 N_{2j} \\ = \sum_i \varphi_{1i}'' + \sum_j \varphi_{2j}'' = \varphi_1'' + \varphi_2'' = 1\end{aligned} \tag{10}$$

Equations (7) and (8) can therefore be treated as two equations in three variables:

$$F_1(\sigma_2, \varphi_2, T) = 0 \tag{7$'$}$$

$$F_2(\sigma_2, \varphi_2, T) = 0 \tag{8$'$}$$

From these equations we can derive a two-dimensional parametric curve with σ_2 as the parameter in the region in which the matrix

$$\begin{bmatrix} \dfrac{\partial F_1}{\partial \varphi_2} & \dfrac{\partial F_1}{\partial T} \\ \dfrac{\partial F_2}{\partial \varphi_2} & \dfrac{\partial F_2}{\partial T} \end{bmatrix}$$

is non singular.

Shadow curve

In a quasi-binary system, an additional curve is needed to provide information about the total concentration of component 2 in the incipient phase. This is known as the shadow curve, and is defined by the locus of the incipient phases coexisting with the principal phase that just became clouded. Once the volume fractions on the cloud-point curve are known, the volume fractions on the shadow curve can be calculated using equation (9).

OBTAINING χ FOR A BLEND OF POLYDISPERSE LINEAR AND BRANCHED POLYETHYLENES

Fitting procedure

The temperature- and composition-dependent coefficients of χ(d_n and b_n, respectively, in equation (4)) for the linear and branched polyethylene blend studied most extensively by the Bristol group[1,4,5] were extracted by fitting to the cloud-point data of Hill *et al.*[4]. A robust Nelder–Mead simplex method was utilized in this procedure. Each experimental temperature and volume fraction was substituted into one of the two cloud-point equations ((7) and (8)), which was then solved for the third variable. The function to be minimized was then obtained by substituting each set of three variables (two given and one calculated) into the other equation, taking absolute values and summing.

Molecular weight distributions

In order to perform this fitting procedure to experimental cloud-point data, a detailed knowledge of the molecular weight distribution of the polydisperse components is required. (See equations (9) and (10). In addition, before N_{1n}'' and N_{2n}'' in equation (8) can be calculated, the molecular weight distribution in the incipient phase must be determined from the molecular weight distribution in the principal phase.) The two polymers used in the experimental work[1,4,5] were a linear polyethylene (LPE), Sclair 2907, and a branched polyethylene (BPE), BP PN220. The molecular weight distributions for these two polymers were determined by gel permeation chromatography (g.p.c.) using a refractive index detector and a viscosity detector, and applying the universal calibration method. Plots of weight fraction *versus* the logarithm of the molecular weight for the LPE and BPE are shown in *Figures 1* and *2*, respectively. Calculated values of their average molecular weights are given in *Table 1*.

χ obtained

The composition- and temperature-dependent χ parameter

$$\begin{aligned}\chi(T,\varphi_2) = {} & [1 - 0.253\varphi_2] \\ & \times [0.033189 - 1.974/T - 0.00466\ln(T)]\end{aligned} \tag{11}$$

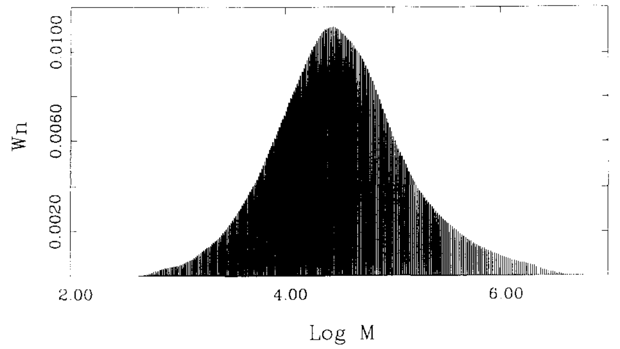

Figure 1 Molecular weight distribution of the LPE as determined by g.p.c. The plot shows the weight fraction, W_n, *versus* the logarithm of the molecular weight, log M

was obtained for the LPE/BPE blend by fitting to the cloud-point data in Table 1 of ref. 4, using the molecular weight distributions shown in *Figures 1* and *2*, and assuming the densities[30] of the two components to be a constant 0.855 g cm^{-3}. The relative molar volumes of the constituents are taken to be relative to the volume of a single–C_2H_4– repeat unit, and the volume of this unit is assumed to be independent of whether it is in a linear or branched chain. Using a quadratic composition-dependent coefficient in the fitting procedure did not substantially increase the quality of the fit. It should be noted that the determined composition dependence of χ is somewhat uncertain because this is particularly sensitive to changes in the high-molecular-weight tails of the molecular weight distributions.

The expression for $\chi(T, \varphi_2)$ given in equation (11) is plotted in *Figure 3*. In this figure, χ can be seen to be small and positive over the temperature range of interest (300–500 K). This is consistent with an approximately athermal system with small non-combinatorial entropic contributions to the free energy of mixing. It is also of interest to note that the original $1/T$ 'enthalpic term' is exothermic, but does not dominate the temperature dependence.

Values of χ reported previously for LPE/BPE blends vary considerably. Of course, χ is sensitive to the frequency of branching and the temperature. However, for a LPE/BPE blend containing a BPE with 26 branches per 1000 backbone carbons, and at a temperature of 423 K, extrapolating the data of Nicholson *et al.*[7] predicts $\chi = 6.8 \times 10^{-5}$. A similar extrapolation of the SANS data of Balsara *et al.*[8] gives $\chi = 4.2 \times 10^{-4}$, and the cloud-point data of Rhee and Crist[9] produce $\chi = 1.1 \times 10^{-4}$. Due to the differences in branch lengths of the polyethylenes investigated here and those used in other studies[7–9], it is inappropriate to compare in a quantitative manner the χ values computed here with those determined previously[7–9]. However, the value of χ determined in this study, which varies from 3.4×10^{-4} to 2.6×10^{-4} over the composition range $\varphi_{BPE} = 0.0$ to 1.0, is in reasonable agreement with the values determined previously[7–9].

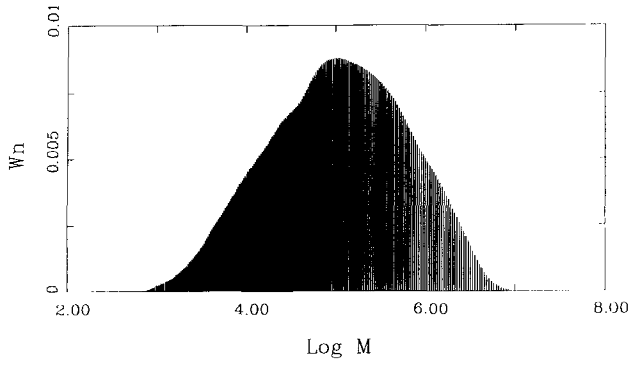

Figure 2 Molecular weight distribution of the BPE as determined by g.p.c. The plot shows the weight fraction, W_n, *versus* the logarithm of the molecular weight, log M

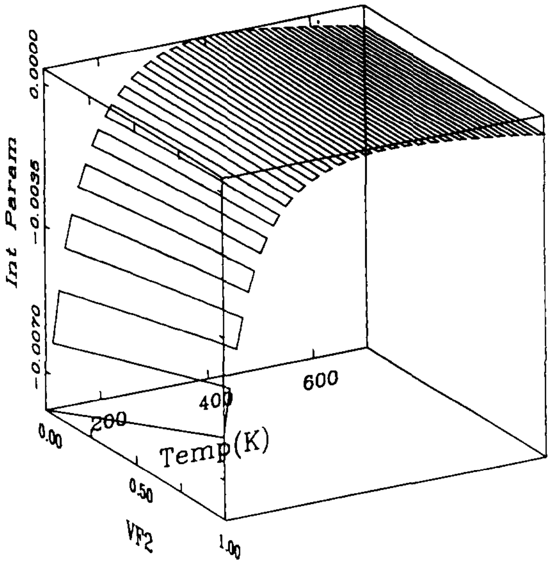

Figure 3 The χ interaction parameter determined (equation (10)) for the LPE/BPE blend, plotted as a function of temperature and the volume fraction of BPE

Predicted cloud-point curve

The experimental cloud-point data of Hill *et al.*[4] are replotted in Figure 4 along with the fitted CPC and the corresponding shadow curve. The latter is the closed loop at lower compositions of the branched polyethylene. Typical tie lines are also shown between the two curves. The calculated CPC can be seen to be in reasonably good agreement with the experimental data[4], and to define a closed immiscibility loop. The shape of the calculated CPC is consistent with the experimental observation[4] of phase separation followed by remixing on cooling an LPE/BPE blend with $\varphi_{BPE} = 0.95$. Note from equation (11) and *Figure 3* that χ decreases with increasing BPE content, but from *Figure 4* it can be seen that phase separation occurs at high BPE contents. This is one indication of the strong effect of polydispersity in determining the positions of the phase boundaries.

Many investigators interpret phase behaviour in polydisperse systems by assuming the components to

Table 1 Average molecular weights of the LPE (Sclair 2907) and BPE (BP PN220)

	LPE	BPE
M_n	12 600	21 100
M_w	97 000	320 000
M_z	825 000	1 710 000

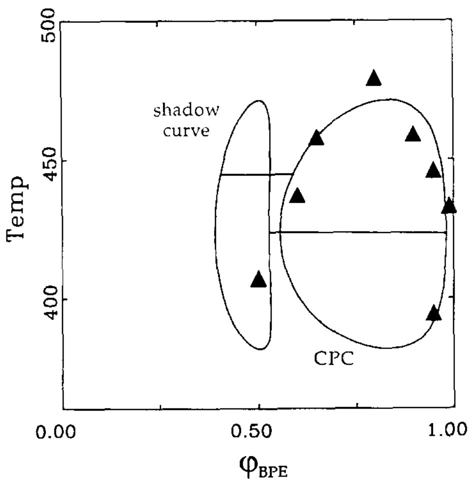

Figure 4 Experimental cloud-point data[4] (▲), fitted cloud-point curve and the corresponding shadow curve. The shadow curve is the closed loop at lower values of φ_{BPE}. Typical tie lines between the two curves are also shown

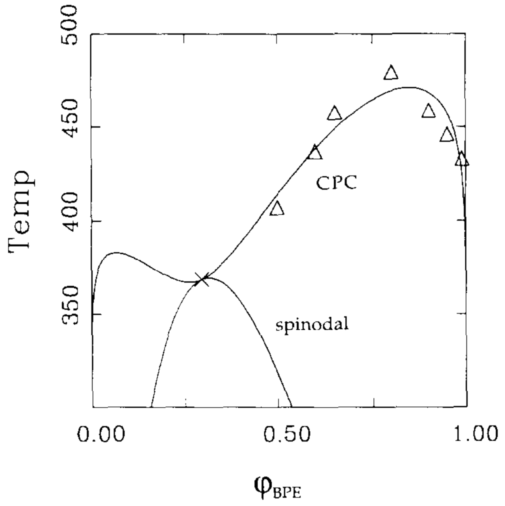

Figure 5 Experimentally determined[4] cloud-point data (△) and CPC fitted to this data by constraining b_2 and d_2 to zero. The spinodal and critical point (×) determined using equation (13) are also shown

be monodisperse. However, if one tries to interpret the experimental data in *Figure 4* without regard to the polydispersity of the components, the position of the maximum in the data, which would be a critical point in a binary blend of monodisperse polymers, is unreasonable. This follows because the BPE is of higher molecular weight than the LPE (see *Table 1*). Thus, one would expect the critical point to occur at $\varphi_{BPE} < 0.5$. At least the location of the maximum in the data with respect to composition is unreasonable in the absence of a massively concentration-dependent χ, or for a system with χ having a quadratic composition dependence leading to multiple critical concentrations[27]. To the authors' knowledge, neither of these situations have been observed experimentally for polymer systems.

The experimental observations are still counterintuitive if one tries to interpret the data in terms of a moderately polydisperse system. For such a system one would still expect a critical point to lie reasonable close to the maximum in the CPC. For a composition-independent χ, equation (6) reduces to

$$\varphi_2^{\text{crit}} = \frac{N_{1w}\sqrt{N_{2z}}}{N_{2w}\sqrt{N_{1z}} + N_{1w}\sqrt{N_{2z}}} \qquad (12)$$

Thus, for the LPE/BPE blend under investigation here, for a composition-independent χ, the critical volume fraction of BPE is predicted to be approximately 0.30. Consequently, either a massively concentration-dependent χ or the existence of multiple critical concentrations would still be required to shift the critical point to the approximate concentration of the maximum in the data shown in *Figure 4* ($\varphi_{BPE} \simeq 0.8$).

However, once one utilizes the details of the molecular weight distributions of the two components in analysing the experimental data, these apparent anomalies are readily understood. For a blend of polymers exhibiting such a high degree of polydispersity, a critical point may well occur at a considerably different composition than any extremum in the CPC. An example of this is shown in *Figure 5*. In this figure, all of the CPC data[4] for the LPE/BPE blend are replotted, except for the lower temperature point at $\varphi_{BPE} = 0.95$. The CPC, which is shown as a solid curve, was fitted to these data while constraining coefficients b_2 and d_2 to zero. Allowing the latter two coefficients to vary does not appreciably enhance the quality of the fit. The χ interaction parameter

$$\chi(T, \varphi_2) = [1 - 0.230\varphi_2][0.0000124 - 0.1384/T] \qquad (13)$$

results from this procedure. The spinodal and critical point (×) determined for the LPE/BPE blend using equation (13) are also shown in *Figure 5*. Note that the critical point does occur at a much lower concentration of BPE ($\varphi_{BPE} = 0.295$) than the maximum in the CPC. However, none of the liquid–liquid boundaries below approximately 405 K are accessible experimentally due to crystallization.

In fact, for the best fit of the CPC to the experimental data which is shown in *Figure 4*, neither critical point(s) nor spinodal(s) is found to exist. This might at first seem somewhat peculiar, but is just a further manifestation of the effects of polydispersity. A spinodal and critical point are present in χ-composition space, but these occur at values of χ that are too high for them to be present in the temperature–composition phase diagram (*Figure 4*). A good deal of caution needs to be exercised in extrapolating too far from this limited amount of experimental data. However, the absence of a spinodal implies that if a blend comprised two monodisperse LPE/BPE components having molecular weights, M, equal to the respective weight-average molecular weights, M_w, in *Table 1*, the blend would be fully compatible in the temperature range of interest. In fact, it can be readily demonstrated by using the $\chi(T, \varphi_2)$ given in equation (11) to predict phase diagrams for related blends, that replacing *either* of the polydisperse polyethylenes with a monodisperse component, with $M = M_w$, produces a fully compatible blend. Of course, a blend comprised of monodisperse components with either of the molecular weights $M \neq M_w$, may still undergo liquid–liquid phase separation. For any pair of φ_2 and T values, and with M for one of the components fixed, the molecular weight (if any) of the other component that is just sufficient to cause spinodal phase separation may be computed readily from equations (5) and (11).

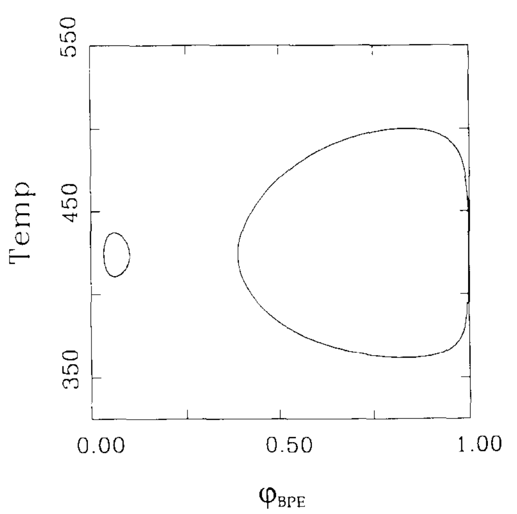

Figure 6 Phase diagram showing two closed-loop CPCs; $d_0 = 0.033225$

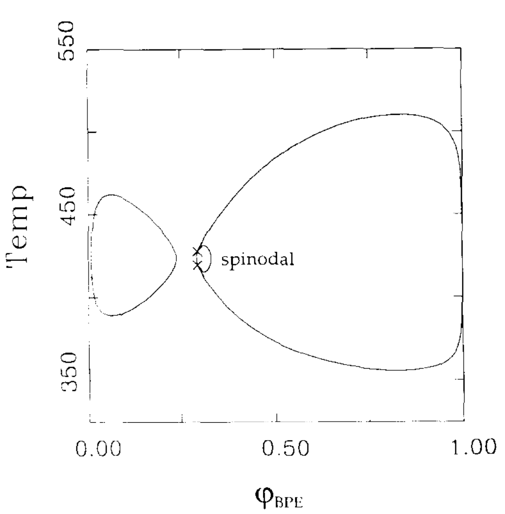

Figure 8 Phase diagram generated with $d_0 = 0.03324$, shortly after the first appearance of critical points (×)

Effect on the phase diagram of increasing χ

The observation of a phase diagram that is comprised of a CPC but no critical point(s) or spinodal(s) is unusual, and, to the authors' knowledge, has not been noted previously. Consequently, it is of interest to examine the effect on the phase diagram of systematically increasing χ by small amounts to probe at what point, if any, critical point(s) and/or spinodal(s) appear. This was done by starting with the expression for χ given in equation (11), and gradually increasing the value of d_0 (initially 0.033189). Some of the phase diagrams that illustrate key points in this process are shown in *Figures 6–10*. We might speculate that an increase in χ for the LPE/BPE blend could result from modifying the branch lengths or increasing the branching frequency in the BPE. However, because changing χ implies modifying the polymer system in a manner that is not yet quantitatively understood, phase diagrams in *Figures 6–10* are discussed in terms of hypothetical systems.

Upon increasing d_0, several interesting phenomena may be observed in the corresponding phase diagrams. Between $d_0 = 0.0332242$ and $d_0 = 0.0332243$, a CPC defining a second closed immiscibility loop appears at low volume fractions of the second component, φ_2. This second closed loop may be seen in the phase diagram in *Figure 6*, which was generated with $d_0 = 0.033225$. As the value of d_0 is increased further, the two loops grow in size. At $d_0 \approx 0.0332395$, a closed-loop spinodal emerges within the larger CPC loop. This is shown in *Figure 7*. (The gap in the CPC in this figure is due to the matrix given in the cloud-point section becoming approximately singular.) Note, however, that there are still no critical points for this system. Critical points first appear at about $d_0 = 0.03324$, and these are shown (×) in the corresponding phase diagram in *Figure 8*. Upon further increasing the value of d_0, the immiscible regions continue to grow in size until the two CPC loops undergo sideways coalescence. Coalesced CPC loops are shown in the phase diagram in *Figure 9* which was generated by setting $d_0 = 0.033241$. Further increasing the value of d_0 causes further expansion of the immiscible region. A later stage of this process is shown in *Figure 10*, where a value of $d_0 = 0.0333$ was used. Note that many of the interesting features of the phase diagrams shown

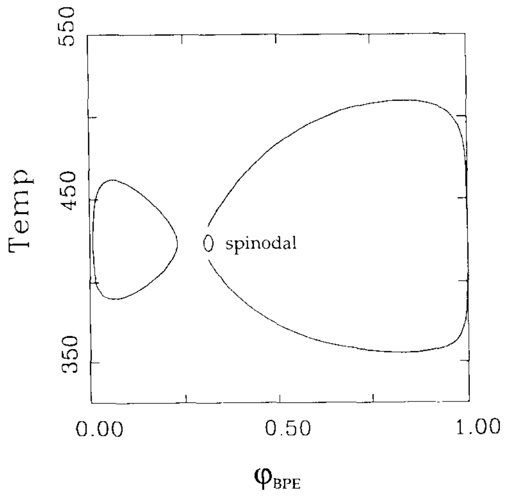

Figure 7 Phase diagram generated with $d_0 = 0.0332395$, showing a closed-loop spinodal emerging within the CPC at higher volume fraction of component 2

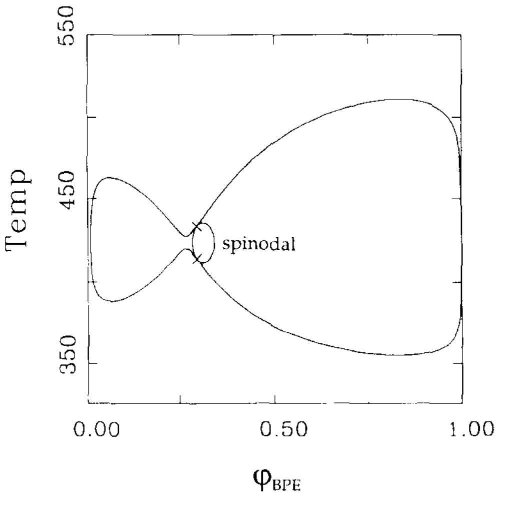

Figure 9 Phase diagram showing CPCs having undergone sideways coalescence; $d_0 = 0.033241$. Critical points are marked as ×

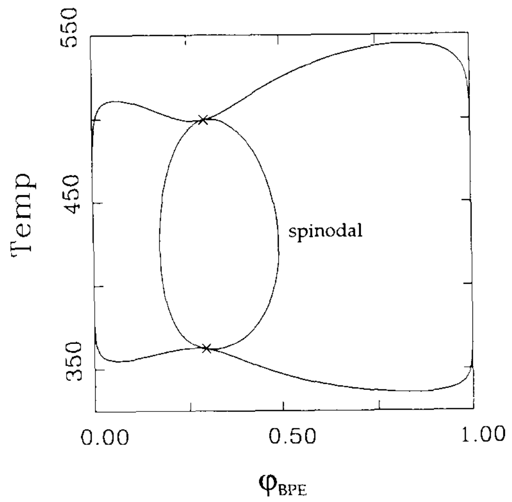

Figure 10 Phase diagram showing the immiscible region having undergone further expansion; $d_0 = 0.0333$. Critical points are marked as ×

in *Figures 6–10* occur above 405 K and thus have the potential to be seen experimentally.

CONCLUSIONS

A generalized Flory–Huggins theory has been used to investigate liquid–liquid phase separation in a blend of polydisperse linear and branched polyethylenes (LPE/BPE). A temperature- and composition-dependent χ was extracted by fitting to experimental cloud-point data, and having a detailed knowledge of the molecular weight distributions of the two components. The magnitude of χ was found to be small and positive in the composition and temperature range investigated, consistent with previous determinations on related systems. The CPC was found to describe a closed immiscibility loop, but no critical point(s) or spinodal(s) were found to exist. It is predicted, based on the limited data available, that polydispersity of both components is necessary for liquid–liquid phase separation to occur in this blend.

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