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On the thermodynamic treatment of poly(vinylidene fluoride)/polystyrene blend under liquid–liquid phase separation conditions

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This paper deals with experimental and theoretical investigations on the compatibility of binary polymer blends in solution. The experimental phase boundary of a crystalline polymer such as poly(vinylidene fluoride) with polystyrene (an amorphous polymer) in dimethylformamide as solvent has been determined by size-exclusion chromatography at 25°C. The composition of the coexisting phases has been used to calculate interaction parameters by means of the Flory–Huggins-type function for the free energy of mixing, including composition dependence of the polymer–polymer interaction parameter and a first correction term denoted as ternary interaction parameter. The calculation of these parameters involves the solution of a system of equations that should be equal to the number of unknown parameters. Diverse approximations have been proposed in order to reduce the number of equations to be solved; they are mainly concerned with the composition dependence of both binary polymer–polymer and ternary interaction parameters and of their derivatives.

(Keywords: poly(vinylidene fluoride); polystyrene; phase separation)

INTRODUCTION

Studies of miscibility and phase separation of polymer blends are of current interest because they provide information needed to develop materials tailored for specific applications[1,2]. Experimentally, it is well known that mixtures of most polymer pairs are incompatible and the phase diagrams obtained are composed of two-phase regions[3–5]. The boundary between two- and single-phase regions in multicomponent polymer systems can be experimentally established either from cloud point[6,7], critical point[8,9], spinodal curve[9] or coexistence curve[10–12] measurements. The understanding of liquid–liquid phase separation of polymer blends in solution requires the appropriate theoretical background to account for some features, such as lower and upper critical solution temperature behaviour, binodal and spinodal curves, and critical composition. Moreover, a limited portion of the phase diagram is occupied by the critical region, a phenomenon that has attracted considerable attention[13,14]. Many attempts have been made to model the thermodynamic phase behaviour of such systems, and these can be classified into three categories: (i) mean-field lattice theories[15]; (ii) equation-of-state theories[16–18]; and (iii) group contribution methods[19–21]. For nearly half a century, the Flory–Huggins theory extended[22] to ternary systems has been the simplest and most useful lattice theory for these systems containing two flexible polymers and a common solvent. This theory involves a polymer–polymer interaction parameter, empirically defined as 'apparent', that is inversely proportional to temperature.

Polymer–polymer interaction parameters can be evaluated from several techniques which, as Prolongo *et al.*[23] pointed out, can be divided into two groups: (i) those from measurements performed on the binary polymer–polymer system or dry blend; and (ii) those from measurements performed on ternary solvent–polymer–polymer systems. In general, deficiencies of lattice models have been widely reported[24–26], and several approaches to reconcile the deficiencies have been suggested. In this regard, Tompa[22], and subsequently Orofino and Flory[27] and others[28], proposed that one should consider the so-called Flory–Huggins interaction parameter, χ_{FH}, as not only temperature-dependent but also polymer composition-dependent. Other expressions for χ_{FH} have also been proposed, some of which are very complicated[29–31]. Moreover the literature[32] shows that the calculated interpolymer interaction parameters for blends and for solutions of polymer mixtures rarely agree[23,33] with those determined experimentally. These discrepancies have been attributed to several factors, such as the peculiarities of the experimental techniques, experiments on polymer blends in the solid state (dry blends) with respect to those made on the same polymer pair in solution, and differences inherent to the samples assayed, i.e. polydispersity, molecular weight, tacticity, crystallinity etc.[34–36]. Despite the considerable efforts made to confer universality to the Flory–Huggins parameter, its

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molecular meaning has remained an enigma. For instance, a number of widely recognized features are displayed by χ_{FH}, such as: negative values denote polymer–polymer miscibility; it is a sensitive function of both polymer concentration and dissimilarity of the polymers; and its absolute values decrease monotonically with the degree of polymerization (N), but remain non-zero in the asymptotic $N \rightarrow \infty$ limit.

In this paper, we report a methodology to evaluate inter-polymer interaction parameters to predict compatibility in polymer blends. Our treatment can be summarized as follows.

(a) We use the Flory–Huggins lattice theory extended to solvent (1)/polymer (2)/polymer (3). The original form of the non-combinatorial term of the free energy of mixing has been modified by taking into account a composition-dependent binary interaction parameter, g_{ij}, as well as a first-order correction term, g_T, which refers to ternary interactions, or interactions other than binary ones.

(b) Thermodynamic equations dealing with phase equilibrium in terms of the chemical potentials of the components are implemented, using a modified Flory–Huggins theory for the free energy of mixing.

(c) The input data needed to solve the above system of equations are the compositions of each component in the two coexisting phases, which have been evaluated from liquid–liquid phase separation experiments at constant temperature by means of the size-exclusion chromatography (s.e.c.) technique. The advantages of s.e.c. for determining the composition of conjugate phases in a solvent–two-polymer system have been widely reported[37–39].

(d) The analytical solution of a system of equations at two levels of accuracy has been carried out using a computer. At the first level, the ternary parameter g_T as well as its related derivatives have been omitted[40] in the original equation of the free energy of mixing. In the second approach, our treatment considers g_T as well as its corresponding derivative expressions.

To test the validity of our proposal, we have chosen a strongly asymmetrical blend of two polymers in a common solvent, such as dimethylformamide (DMF) (1)–poly(vinylidene fluoride) (PVDF) (2)–polystyrene (PS) (3) at 25°C. The meaning of 'asymmetrical', as used here, must be considered in a whole sense because: (i) the polymerization index of both polymers is very different; (ii) PVDF is a polydisperse commercial sample, whereas PS is a standard monodisperse sample; (iii) it is well known that PVDF is a crystalline polymer, in contrast to the amorphous morphology of the atactic PS used here; (iv) a different molecular structure between constituent repeat units of both PVDF and PS is also evident; and (v) the affinity of both polymers to DMF is different, as can be inferred from the comparison of the viscometric polymer–solvent interaction parameter values recently reported[41,42].

EXPERIMENTAL

Chemicals

PVDF was kindly supplied by Penwalt Corp. (Oxford, UK) and its grade designation was Kynar 721. The intrinsic viscosity of PVDF was 90.52 ml g^{-1} in DMF at 25°C. The polydispersity index and weight average molecular weight, M_w, of PVDF were 2.70 and 674000, respectively, as determined by s.e.c. using PS calibration standards. PS was purchased from TSK standard (Tosoh Corp., Minato-ku, Tokyo, Japan) with M_w 5970 and polydispersity index 1.02, as specified by the supplier. DMF of s.e.c. grade from Scharlau (Senmenat, Barcelona, Spain) was used as solvent. The densities of the chemicals were 0.9445, 1.78 and 1.05 for DMF, PVDF and PS, respectively. All chemicals were used without further purification.

H.p.l.c. equipment

The liquid chromatograph consisted of a model 590 solvent-delivery system and a U6K universal injector, both purchased from Waters (Mildford, MA, USA). Detection was carried out with a model ERC-7522 Erma (Tokyo, Japan) refractive index detector. The chromatograms were recorded by using a dual-channel recorder (Yokogawa Electric Works, Tokyo, Japan) which was set at an attenuation of 2 and 8 for measurements involving PVDF and PS, respectively. The system was equipped with three μ-styragel columns of 10^5, 10^4 and 10^3 Å nominal pore size (30 cm length × 0.78 cm i.d.) from Waters (Mildford, MA, USA), with an effective molecular weight range separation of 200 to 4×10^6, which were packed with highly crosslinked styrene–divinylbenzene copolymer. DMF, used as the mobile phase in chromatographic experiments, was previously degassed and clarified by passing it under vacuum through a 0.45 μm Micro Filtration Systems regenerated cellulose filter (Dublin, CA, USA). All chromatographic experiments were conducted at room temperature and the columns were equilibrated overnight prior to starting any experiment. Chromatograms were obtained at a flow rate of 1.0 ml min^{-1} by injection of 90 μl of 0.1% (w/v) solute solutions, prepared using DMF as solvent and with a pressure of 250 psi.

Phase separation experiments

The two polymers to be blended were accurately weighed (about 0.2 g total) into a graduated glass tube of 10.00 ± 0.05 ml. In order to dissolve the two polymers, DMF was slowly introduced into the tube, sealed with Teflon seals, shaken gently, heated up to 45–50°C to promote solution of the polymers, and left to reach equilibrium at 25°C. DMF was added until solution of the polymers was accomplished, and at this moment two phases in equilibrium appeared: the less concentrated phase on top and the more concentrated phase at the bottom of the tube. Normally, it took several hours to complete the macroscopic phase separation. After 2 days equilibration time, the volume of each phase was read, then 250 μl of the top phase was withdrawn by using a μ-syringe and accurately weighed. Injection of 90 μl of this solution gives a chromatogram with two peaks eluted at well separated volumes that correspond to each of the polymers (by comparing with a previous standard experiment with only one of the polymers). The mass of PVDF and PS was obtained by using a calibration curve (discussed below) that relates the height of the peak with the weight of the polymer. *Figure 1* shows an example of one of these chromatograms with two peaks at elution

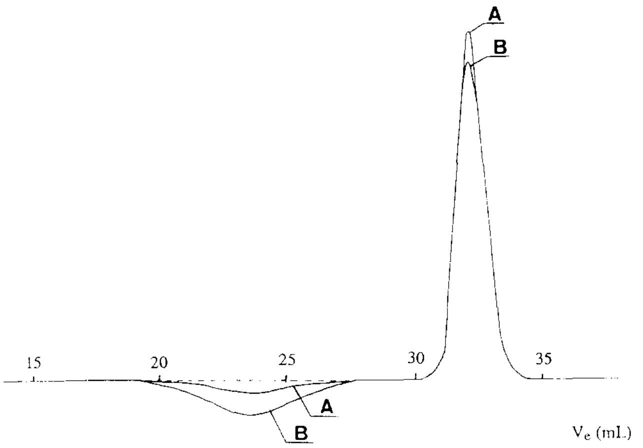

Figure 1 S.e.c. elution profiles of PVDF (first peak) and PS (second peak) in DMF at 25°C for α' points from runs A and B

volumes of 23.60 ml for PVDF and 32.80 ml for PS. Once we know the mass of each component in the 250 μl top phase, the respective quantities in the bottom phase can be obtained by mass balance, taking into account volume corrections. Because we extracted a certain volume of the top phase, a non-equilibrium state was reached, and the tube was shaken again and left to reach a new equilibrium with two phases of concentrations very close to the previous ones. The same procedure was repeated so as to determine the equilibrium masses of the three components in the two conjugate phases of four tie-lines close in composition. Following this method, we obtained three groups (A, B, C) of four tie-lines (α, β, γ, δ).

In order to test the reproducibility of the method, we repeated the same experiment twice, checked the calibration curves by preparing binary samples of precisely known compositions, analysed their compositions after equilibration times of 2 days and 7 days, and obtained the same results.

Calibration

In order to determine the mass of each polymer, we first made a calibration curve by injecting 90 μl of a PVDF or PS solution into DMF at different concentrations to cover a mass range from about 0.1 to 2.0 mg. Different masses cause the polymer eluted peak to reach different heights (the higher for the more concentrated) and allow the height of the peak to be plotted against the mass of the polymer. Such plots are depicted, for PVDF and PS, in *Figures 2a* and *b*, respectively. The calibration graphs, which fit a straight line, are described by the equation:

$$\text{(height of the peak)} = A \times \text{(mass of polymer)} + B$$

where, for PVDF, $A = -1.013$, $B = 36.432$ and the correlation coefficient $r = 0.9985$, and for PS, $A = -6.142$, $B = 101.54$ and $r = 0.9990$. So, to analyse the top phase it suffices to inject a small amount of this phase, and by determining the height of the peaks the corresponding mass is found.

THEORY

Gibbs free energy for solvent–polymer–polymer systems

The system modelled here behaves as a quasi-ternary mixture in which component 1 refers to DMF as solvent, component 2 to PVDF containing a distribution of chain lengths, and component 3 is a monodisperse polymer, PS. For this kind of ternary system, the free energy of mixing, ΔG, can be expressed by the Flory–Huggins equation[8,15] as:

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \Gamma(T, \phi, N) \quad (1)$$

where n_i is the number of moles of component i ($i = 1, 2, 3$), ϕ_i is its volume fraction, and $\Gamma(T, \phi, N)$ accounts for the non-combinatorial entropy of mixing as well as possible enthalpic effects expressed by the implicit Γ function dependent on temperature, volume fraction and molar mass. Flory–Huggins theory originally assumed the last term of equation (1) to be exclusively temperature-dependent. However, it is known experimentally that this term includes the Flory–Huggins interaction parameter χ_{FH}, nowadays also recognized to be composition-dependent. For an isomolecular polymer mixture at a given temperature, the last term of equation (1), according to the formalism developed by Koningsveld and co-workers[8,28], can be expressed as:

$$\Gamma(\phi) = n_1 \phi_2 g_{12} + n_1 \phi_3 g_{13} + n_2 \phi_3 g_{23} \quad (2)$$

where g_{ij} is the binary interaction parameter which is composition-dependent, in contrast to χ_{ij}, which seems to vary in inverse proportion to temperature. In both multicomponent liquid mixtures and polymer solutions, a common practice has been to assume that the excess free energy is a simple additive function of the binary constituents g_{ij}. One factor largely ignored in empirical and theoretical treatments has been the possible existence of ternary interactions. However, it has been reported that in some cases ternary interactions[43–48] should be included. In this regard, equation (2) can be improved by including an additional term denoted by g_T (or g_{123}),

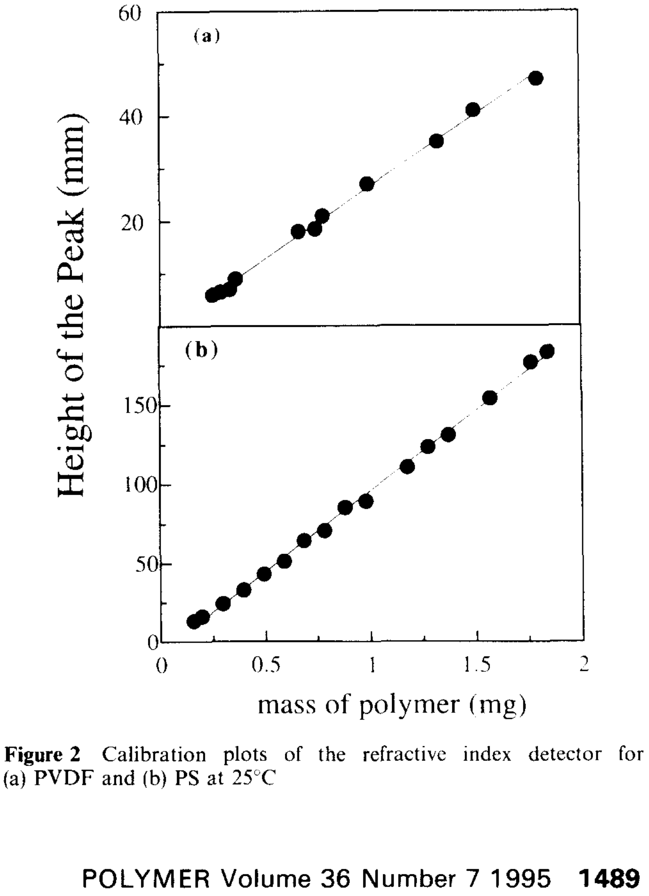

Figure 2 Calibration plots of the refractive index detector for (a) PVDF and (b) PS at 25°C

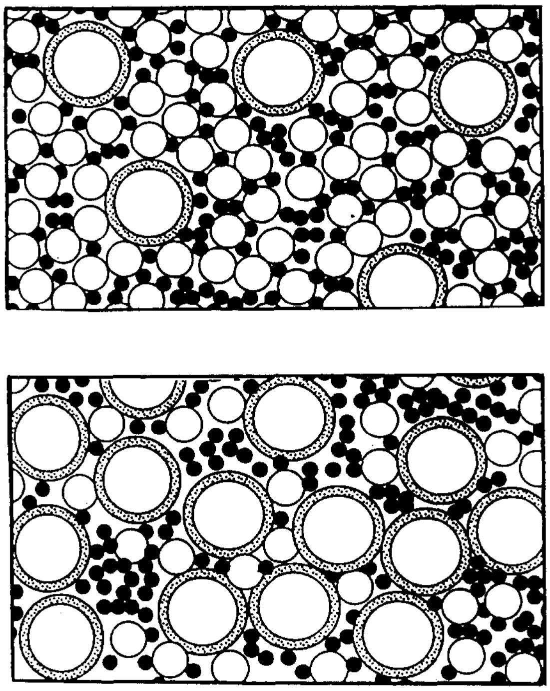

Figure 3 Pictorial representation of the PS-rich (top) and PVDF-rich (bottom) phases in two coexisting phases. The large and small open circles represent PVDF and PS, respectively, and the filled circles denote DMF molecules as common solvent. For simplicity, both polymer samples are assumed to be monodisperse

which in the present work refers to other than two-body interactions:

$$\Gamma(\phi)=n_1\phi_2 g_{12}+n_1\phi_3 g_{13}+n_2\phi_3 g_{23}+n_1\phi_2\phi_3 g_\mathrm{T} \quad (3)$$

We believe that an improved equation can be obtained for the free energy of mixing of ternary polymer systems by coupling equation (3), instead of equation (2), with equation (1). Owing to the fact that we want to use equation (1) for liquid–liquid phase separation in solvent–polymer–polymer systems and, according to statements by other authors[49–52], to establish a complete description of these polymer solutions in the semidilute concentration range[53], ternary interactions should be included. This parameter is also considered to be composition-dependent, by analogy with the g_{ij} parameters. Quantitative evaluation of both g_{ij} and g_T parameters for polymer–mixed solvent systems have been reported recently[54].

To corroborate the above statement, *Figure 3* shows a representation of the two coexisting phases under liquid–liquid phase separation conditions for DMF (1)/PVDF (2)/PS (3) at 25°C. By assuming a random coil conformation for both polymers, PVDF is represented by large and PS by small open circles, whose radii are proportional to the coil sizes and molar masses of the polymers. The mean distance between homologous coils accounts for the concentration regime in each phase. The composition in the three-component phases lies on the binodal in a three-component phase diagram. This means that any addition of the minority polymer to the respective phase will induce phase separation. In this regard, it is well known that segregative phase separation occurs when the polymer coils just come into contact with each other. From this point of view, the fact that the PS- and PVDF-rich phases correspond to points on the binodal is an indication that overlap polymer concentration is achieved for the majority component. On these grounds, the physical picture of *Figure 3* (top) displays the PS-rich phase, where the mean distances between PS coils (small circles) tend to $2R$ (R = radius of the equivalent sphere), meaning that a semidilute PS regime seems reasonable. In contrast, if we consider this semidilute polymer concentration as a continuum, the distance between PVDF coils (large circles) becomes larger than $2R$, meaning that a dilute PVDF solution is achieved. Note that excluded-volume effects have not been considered here for the sake of simplicity. The same arguments can be used to explain the bottom part of *Figure 3*, where a semidilute PVDF concentration is shown.

Chemical potential of the components in ternary systems

The insertion of $\Gamma(\phi)$ from equation (3) into equation (1) yields a complete expression for the free energy of mixing for ternary polymer systems:

$$\frac{\Delta G}{RT}=n_1\ln\phi_1+n_2\ln\phi_2+n_3\ln\phi_3+n_1\phi_2 g_{12}+n_1\phi_3 g_{13}+n_2\phi_3 g_{23}+n_1\phi_2\phi_3 g_\mathrm{T} \quad (4)$$

The chemical potential $\Delta\mu_i$ for the component i in the ternary system is defined as $\Delta\mu_i=(\partial\Delta G/\partial n_i)_{T,P,n_j}$, and specifically for the solvent (1) can be obtained from equation (4) as:

$$\frac{\Delta\mu_1}{RT}=\frac{1}{RT}\left(\frac{\partial\Delta G}{\partial n_1}\right)_{T,p,n_2,n_3}=\left(\frac{\Delta\mu_1}{RT}\right)_\mathrm{comb}+\left(\frac{\Delta\mu_1}{RT}\right)_\mathrm{res} \quad (5)$$

Here the subscripts comb and res mean combinatorial and residual chemical potential of component 1, the solvent.

$$\left(\frac{\Delta\mu_1}{RT}\right)_\mathrm{comb}=\ln\phi_1+1-\phi_1-\frac{\mathrm{V}_1}{\mathrm{V}_2}\phi_2-\frac{\mathrm{V}_1}{\mathrm{V}_3}\phi_3 \quad (6)$$

where V_i (i = 1, 2, 3) refers to the molar volume of component i.

$$\begin{aligned}\left(\frac{\Delta\mu_1}{RT}\right)_\mathrm{res}=&\left[g_{12}-\frac{\phi_2\phi_1}{\phi_2+\phi_3}\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}\right](\phi_2^2+\phi_2\phi_3)\\&+\left[g_{13}-\frac{\phi_3\phi_1}{\phi_3+\phi_2}\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right](\phi_3^2+\phi_3\phi_2)\\&-\left[g_{23}+\phi_3\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right]\frac{V_1}{V_2}\phi_2\phi_3\\&+\left[g_\mathrm{T}-\frac{\phi_1\phi_3}{1-2\phi_1}\left(\frac{\partial g_\mathrm{T}}{\partial\phi_3}\right)\right](\phi_2\phi_3-2\phi_1\phi_2\phi_3)\end{aligned} \quad (7)$$

By regarding equations (6) and (7), the combinatorial contribution to the chemical potential can be obtained from the volume fraction and molar volumes of every component, obtained as reported in the Experimental section. A more complex functionality is reached for the residual contribution to the chemical potential. So, this residual function is also dependent on the parameters g_{12}, g_{13}, g_{23}, g_T, $\mathrm{d}g_{12}/\mathrm{d}\phi_2$, $\mathrm{d}g_{13}/\mathrm{d}\phi_3$, $\mathrm{d}g_{23}/\mathrm{d}\phi_3$ and $(\partial g_\mathrm{T}/\partial\phi_3)$. It is evident that g_T and $(\partial g_\mathrm{T}/\partial\phi_3)$ cannot be experimentally determined, and the evaluation of $\mathrm{d}g_{12}/\mathrm{d}\phi_2$, $\mathrm{d}g_{13}/\mathrm{d}\phi_3$ and $\mathrm{d}g_{23}/\mathrm{d}\phi_3$ demands intensive experimental work. As a means of circumventing this difficulty, some assumptions, along with rational simplifications, can be introduced at several levels of accuracy. At this point, it should be noted that we are interested in the evaluation of the above eight parameters, with special emphasis on g_{23}, because the extent of polymer–polymer compatibility, if any, can be interpreted in the light of this interaction parameter. Since g_{23} refers to the energy of contact between both polymers in the absence of solvent, equation (5) can be transformed at $\phi_1 \to 0$ into:

$$\frac{\Delta\mu_1}{RT} = [n_2 \ln \phi_2 + n_3 \ln \phi_3] + g_{12}\phi_2 + g_{13}\phi_3 - \left[\left(g_{23} + \phi_3 \frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right)\frac{V_1}{V_2} - g_{\mathrm{T}}\right]\phi_2\phi_3 \tag{8}$$

Note that equation (8) refers to the chemical potential of the solvent at very low concentration, under conditions similar to those of inverse gas chromatography (i.g.c.). Frequently, the interaction parameter obtained by i.g.c. has been expressed as:

$$\chi_{1(23)} = g_{12}\phi_2 + g_{13}\phi_3 - (\chi'_{23})_{\mathrm{eff}}\phi_2\phi_3 \tag{9}$$

or

$$\chi_{1(23)} = g_{12}\phi_2 + g_{13}\phi_3 - (\chi'_{23})_{\mathrm{app}}\phi_2\phi_3 \tag{10}$$

The meaning of $(\chi'_{23})_{\mathrm{eff}}$ and $(\chi'_{23})_{\mathrm{app}}$ (subscripts eff and app refer to effective and apparent, respectively) is closely related to $(\chi_{23})_{\mathrm{eff}}$:

$$(\chi'_{23})_{\mathrm{eff}} = \frac{V_1}{V_2}(\chi_{23})_{\mathrm{eff}} \tag{11}$$

and

$$(\chi'_{23})_{\mathrm{app}} = \frac{V_1}{V_2}(\chi_{23})_{\mathrm{eff}} - (\chi_{\mathrm{T}})_{\mathrm{eff}} = (\chi'_{23})_{\mathrm{eff}} - (\chi_{\mathrm{T}})_{\mathrm{eff}} \tag{12}$$

Here $(\chi_{23})_{\mathrm{eff}}$ accounts for the polymer–polymer interaction parameter independent of polymer concentration, as was originally assumed by the Flory–Huggins theory, being correlated with g_{23} as follows:

$$(\chi_{23})_{\mathrm{eff}} = g_{23} + \phi_3 \frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3} \tag{13}$$

For the interchange between g and χ parameters, see equations (A10)–(A18) in the Appendix. Moreover, the other polymer–polymer interaction parameter, B_{23}, considered as the interaction energy density, is often used to predict miscibility in polymer blends and can be experimentally determined by i.g.c.[55], d.s.c.[56] and melting point depression[57]. Notice that the last technique is very suitable when one component of the blend is a crystalline polymer such as PVDF, as used in this work. The relationship between χ'_{23} and B_{23} can be expressed as:

$$B_{23} = \frac{RT}{V_1}(\chi'_{23})_{\mathrm{eff}} \tag{14}$$

or

$$B_{23} = \frac{RT}{V_1}(\chi'_{23})_{\mathrm{app}} \tag{15}$$

Summarizing, $(\chi'_{23})_{\mathrm{eff}}$ or $(\chi'_{23})_{\mathrm{app}}$ can be evaluated by two methods: (a) by using equations (9) and (10) together with the experimental $\chi_{1(23)}$, g_{12} and g_{13} values calculated from i.g.c. experiments; and (b) by insertion of the B_{23} values, obtained from some of the techniques mentioned above[55–57] into equation (14) or (15).

The same considerations made for these parameters can be extended to the equations dealing with the chemical potentials of components 2 and 3 in the ternary system. For the sake of simplicity, the expressions for $\Delta\mu_2$ and $\Delta\mu_3$ have been placed in the Appendix.

Phase equilibria in ternary systems

Gibbs' two-phase equilibrium conditions[58] under constant temperature and pressure are expressed by the following equations:

$$(\Delta\mu_1)' = (\Delta\mu_1)'' \tag{16}$$

$$(\Delta\mu_2)' = (\Delta\mu_2)'' \tag{17}$$

$$(\Delta\mu_3)' = (\Delta\mu_3)'' \tag{18}$$

Here, the prime and double prime refer to the two coexisting phases. In the framework of the Flory–Huggins lattice theory, the chemical potential of a component contains two contributions (indicated by subscripts comb and res), therefore equations (16), (17) and (18) can be expressed as:

$$[(\Delta\mu_1)' - (\Delta\mu_1)'']_{\mathrm{comb}} + [(\Delta\mu_1)' - (\Delta\mu_1)'']_{\mathrm{res}} = 0 \tag{19}$$

$$[(\Delta\mu_2)' - (\Delta\mu_2)'']_{\mathrm{comb}} + [(\Delta\mu_2)' - (\Delta\mu_2)'']_{\mathrm{res}} = 0 \tag{20}$$

$$[(\Delta\mu_3)' - (\Delta\mu_3)'']_{\mathrm{comb}} + [(\Delta\mu_3)' - (\Delta\mu_3)'']_{\mathrm{res}} = 0 \tag{21}$$

To solve the above system of equations, the chemical potential of each component has to be expressed as a function of other parameters that are experimentally accessible. In this report, we have proposed the use of a modified expression for the free energy of mixing given by equations (1) and (3), but distinct alternative approaches are also valid to obtain other thermodynamic functions. In this context, some useful approximations for polymer solutions have recently been reviewed[59].

The practical use of equations (19), (20) and (21) can be sorted into two categories. The first is the prediction of polymer–polymer compatibility through miscibility windows, mainly by means of the theoretical prediction of the phase diagram. This strategy requires knowledge of the g_{ij} and g_{T} functionalities, as well as other minor parameters such as the molar volumes of the components. At present, small-angle neutron scattering (SANS) of polymer blends has proved to be the most suitable technique for obtaining accurate results[35] on the concentration dependence of the interpolymer interaction parameter, g_{ij}. However, besides the importance of ternary interactions, as recently recognized[49–52], g_{T} values are essentially absent from the literature.

One can also use the equilibrium conditions in the reverse sense to that explained in the preceding paragraph. Thus, if the ϕ_i values are available for each coexisting phase, one can insert these values into the equilibrium equations, and so attempt to numerically solve the adequate set of equations under certain mathematical constraints. The binary and ternary interaction parameters, as well as their derivatives, are the unknowns. Note that the composition of the solvent/polymer/polymer coexisting phases is tantamount to obtaining the loci of the nodal points (or tie-line) on a phase composition ternary diagram. Details on the application of the s.e.c. technique for direct analysis of the composition of the coexisting phases will be shown in the next section.

RESULTS AND DISCUSSION

Experimental data on liquid–liquid phase separation

In order to obtain the composition of two coexisting phases, we have prepared three different concentrations of polymer mixtures, PVDF (2) + PS (3), adding solvent, DMF (1), until phase separation appears. Following the procedure detailed in the Experimental section, and using the previously determined calibration equations, it is possible to obtain the composition of the two coexisting phases expressed as volume fractions ϕ_i. *Table 1* shows the values of the phase composition corresponding to the binodal equilibrium curve. The line connecting binodal points, i.e. α'–α'' gives a tie-line. As seen, four tie-lines, denoted by α, β, γ and δ, have been evaluated from each of the three original polymer mixtures, labelled as A, B and C, respectively.

We focus our attention on the first set of tie-lines, composed of α, β, γ and δ tie-lines. Each line possesses two points, $\alpha'(\phi'_1, \phi'_2, \phi'_3)$ and $\alpha''(\phi''_1, \phi''_2, \phi''_3)$, for which numerical values, obtained from s.e.c., have been compiled in the first row of *Table 1*. Similar considerations can be made for the remaining data compiled in this table. Tie-lines labelled as α denote the composition of the coexisting phases in the original solvent-mixed polymer solution, in contrast with the β, γ and δ tie-lines which denote the composition of the coexisting phases after successive extraction of 250 μl from the top phase, and further re-equilibration of the composition in both phases. Due to the amount of total polymer (5×10^{-2} mg) extracted from the system for s.e.c. analysis, some plausible approximations can be introduced in the calculation of the interaction parameters; details of this will be given elsewhere. This fact does not introduce any significant error into our approach. Data from *Table 1* have enabled us to build the experimental phase diagram depicted in *Figure 4*. For the sake of simplicity, we have drawn three tie-lines for each of the runs, A, B and C, contained in *Table 1*. In the description of phase diagrams, solution compositions are usually expressed on a weight basis and can be easily transformed into volume fractions. As seen in *Figure 4*, these tie-lines are almost parallel to each other, and this is especially true when tie-lines are close to the critical point, as evidenced from inspection of the apparent slopes of the tie-lines labelled in *Table 1* as B and C. This behaviour agrees with the observations sometimes assumed about the parallelism of tie-lines[60,61]. As illustrated in *Figure 4*, the binodal curve placed on the phase composition triangle for the PVDF/PS blend in DMF shows an asymmetric form; the area where the single-phase region becomes a maximum is located on the side of the PVDF-rich blend solution. This phase diagram displays some resemblance to those for binary solutions of polymers in small-molecule solvents, where the asymmetry is justified in terms of the dissimilarity in dimensions of the respective solvent and polymer molecules.

Numerical calculation of interaction parameters

We next proceed to evaluate binary and ternary interaction parameters (g_{ij} and g_T) as well as their respective derivatives. Recalling that a given tie-line, for example $\alpha'\alpha''$, is defined by the coordinates $(\phi'_1, \phi'_2, \phi'_3)$ and $(\phi''_1, \phi''_2, \phi''_3)$ in the basis of a ternary diagram, three equations can be obtained by introducing the above ϕ values into equations (19), (20) and (21). Looking at the system of three equations, the generated unknowns will be: $(g_{12})'$; $(g_{13})'$; $(g_{23})'$; $(g_T)'$; $(\mathrm{d}g_{12}/\mathrm{d}\phi_2)'$; $(\mathrm{d}g_{13}/\mathrm{d}\phi_3)'$; $(\mathrm{d}g_{23}/\mathrm{d}\phi_3)'$; $(\partial g_T/\partial\phi_3)'$; $(g_{12})''$; $(g_{13})''$; $(g_{23})''$; $(g_T)''$; $(\mathrm{d}g_{12}/\mathrm{d}\phi_2)''$; $(\mathrm{d}g_{13}/\mathrm{d}\phi_3)''$; $(\mathrm{d}g_{23}/\mathrm{d}\phi_3)''$; and $(\partial g_T/\partial\phi_3)''$. In the light of these 16 unknowns, one might describe a system of the same number of equations. However, some rational simplifications can be introduced in order to reduce the number of unknowns; the associated errors in all other parameters (see below) are inconsequential. According to Narasimham *et al.*[39], it is reasonable to consider g_{12} and g_{13} as concentration-independent within a narrow concentration range, such as the one considered in the present work for the adjacent tie-lines of a given run. This partial simplification can be expressed as:

$$g_{12} = \chi_{12} = (\chi_{12})_{\mathrm{eff}}$$

and

$$g_{13} = \chi_{13} = (\chi_{13})_{\mathrm{eff}}$$

Table 1 Values of the composition for two coexisting phases of diverse tie-lines (α, β, γ, δ), expressed as volume fraction, ϕ'_i and ϕ''_i, as determined by s.e.c. at 25°C for DMF (1)/PVDF (2)/PS (3) ternary system

Run	Tie-line	ϕ'_1	ϕ'_2	ϕ'_3	ϕ''_1	ϕ''_2	ϕ''_3
A	α	0.804 38	0.004 01	0.191 61	0.846 33	0.092 74	0.060 93
	β	0.804 98	0.003 29	0.191 73	0.846 08	0.092 58	0.061 34
	γ	0.798 58	0.002 69	0.198 73	0.850 20	0.094 12	0.055 68
	δ	0.823 59	0.001 97	0.174 44	0.838 92	0.094 29	0.066 79
B	α	0.842 66	0.006 24	0.151 10	0.895 00	0.040 76	0.064 24
	β	0.842 25	0.005 18	0.152 57	0.894 89	0.040 88	0.064 23
	γ	0.849 40	0.007 36	0.143 24	0.895 13	0.041 56	0.063 31
	δ	0.861 52	0.012 88	0.125 60	0.893 17	0.040 54	0.066 29
C	α	0.816 50	0.004 71	0.178 79	0.891 95	0.061 09	0.046 96
	β	0.818 27	0.004 25	0.177 48	0.893 53	0.062 82	0.043 65
	γ	0.820 08	0.001 91	0.178 01	0.890 30	0.061 01	0.048 69
	δ	0.824 06	0.007 44	0.168 50	0.893 57	0.063 36	0.043 07

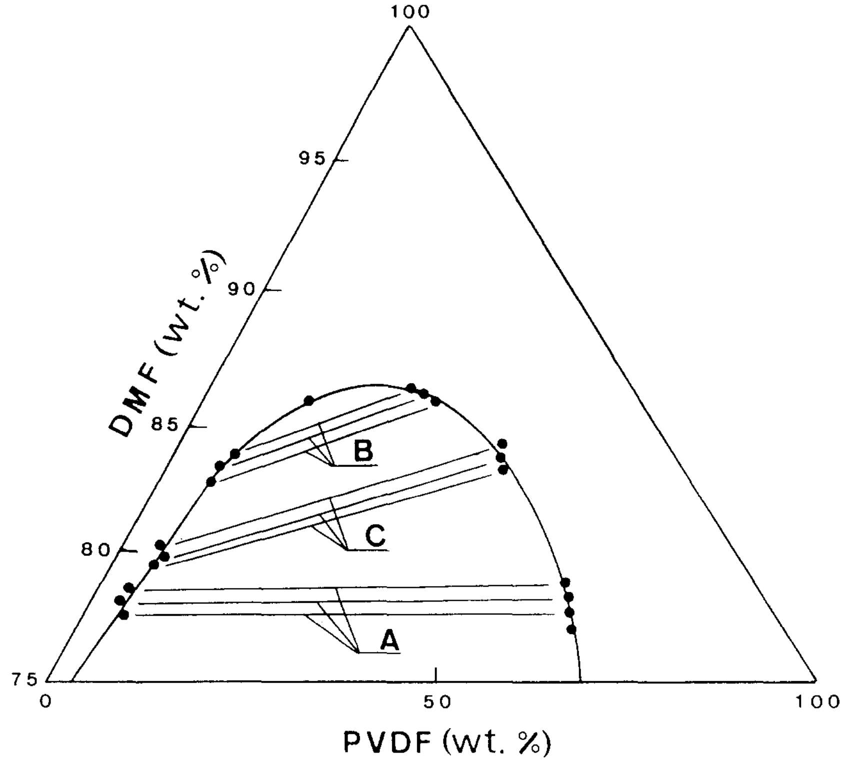

Figure 4 Ternary diagram showing the weight percentage concentrations determined in the PVDF- and PS-rich phases, corresponding to the bottom and top coexisting phases, respectively, at 25°C for runs A, B and C

and consequently

$$dg_{12}/d\phi_2 = dg_{13}/d\phi_3 = 0$$

(see equations (A10), (A11), (A14) and (A15) in the Appendix). An additional simplification can be considered for two adjacent tie-lines. For example, for the combination $A(\alpha\text{–}\gamma)$ one can assume that:

$$(g_{23})'_\alpha = (g_{23})'_\gamma$$

and

$$(g_{23})''_\alpha = (g_{23})''_\gamma$$

and accordingly

$$\left(\frac{dg_{23}}{d\phi_3}\right)'_\alpha = \left(\frac{dg_{23}}{d\phi_3}\right)'_\gamma$$

and

$$\left(\frac{dg_{23}}{d\phi_3}\right)''_\alpha = \left(\frac{dg_{23}}{d\phi_3}\right)''_\gamma$$

Note that to generate an adjacent tie-line, one needs to extract a small volume (250 μl) from the original two coexisting phases, as has been detailed previously. For this reason, g_{23} values can be considered to be equal for the PS-rich phase (denoted by prime) in α and γ tie-lines, and the same for the PVDF-rich phase (denoted by double prime), respectively. However, within a given tie-line the polymer concentration changes strongly from one of the coexisting phases to the other, hence g_{23} values are considered to be different.

At this point, one can introduce a more drastic simplification on the original free energy of mixing by excluding the g_T parameter. This unrealistic assumption is introduced here exclusively for comparative purposes, because ternary interaction cannot be neglected when two-phase systems are used for separation purposes. The concentrations of the polymeric species are quite high, and the solutions fall into the semidilute concentration range[53], as previously stated. Summarizing, with the proposed simplifications the initial 16 unknowns are reduced to six, i.e. g_{12}, g_{13}, $(g_{23})'$, $(g_{23})''$, $(dg_{23}/d\phi_3)'$ and $(dg_{23}/d\phi_3)''$. The insertion of the composition values of two adjacent tie-lines, such as $\alpha'\alpha''$ and $\beta'\beta''$ given in *Table 1*, into equations (19), (20) and (21), taking into account the aforementioned simplifications, gives a system of six equations that can be solved numerically with respect to the above parameters. *Table 2* lists the calculated values of the interaction parameters for three sets of diverse pairs of tie-lines, as shown in *Figure 4*.

An a priori more realistic treatment can be expected when g_T is taken into account. In this case, the new set of unknowns are: g_{12}; g_{13}; $(g_{23})'$; $(g_{23})''$; $(g_T)'$; $(g_T)''$; $(dg_{23}/d\phi_3)'$; $(dg_{23}/d\phi_3)''$; $(\partial g_T/\partial\phi_3)'$; and $(\partial g_T/\partial\phi_3)''$.

Table 2 Values of the binary interaction parameters and their derivatives obtained from the equilibrium conditions of diverse pairs of tie-lines for the DMF (1)/PVDF (2)/PS (3) system at 25°C

Tie-line pairs	g_{12}	g_{13}	$(g_{23})'$	$(g_{23})''$	$(dg_{23}/d\phi_3)'$	$(dg_{23}/d\phi_3)''$
A(α–γ)	0.6910	0.6815	433	839	−10684	−6206
A(α–β)	0.6611	0.6806	422	700	348	−4603
A(γ–δ)	0.6235	0.6776	387	478	15602	−1749
B(α–β)	0.5971	0.6367	304	253	−301	3872
B(β–γ)	0.6454	0.6414	454	515	−2610	1382
B(γ–δ)	0.4062	0.6114	−100	−341	4193	7863
C(α–β)	0.4824	0.6149	292	860	−7370	−93047
C(β–γ)	0.7419	0.6747	721	1225	1475	−9744
C(γ–δ)	0.7078	0.6660	668	1182	−1426	−9709

Obviously, to obtain analytically the numerical values of these 10 parameters one must also solve a system of 10 equations. Otherwise, some simplifications can be introduced when the input data, such as ϕ_i, come from the phase equilibrium experiments. First, for a given tie-line we assume that

$$(\mathrm{d}g_{23}/\mathrm{d}\phi_3)' \approx (\mathrm{d}g_{23}/\mathrm{d}\phi_3)'' = \mathrm{d}g_{23}/\mathrm{d}\phi_3$$

which implies that composition dependence of g_{23} seems to be linear. This a priori crude approximation can be assumed to be valid as long as the difference $(\phi_i'' - \phi_i')$ becomes smaller. This situation seems to be true for symmetrical polymer blends, as has been reported by Bates[62] for homogeneous mixtures of 1,2 and 1,4 isomers of polybutadiene. Note that the blend based on PVDF + PS mixtures is strongly asymmetric; however, we have assumed this approximation to be valid only for the PVDF- or PS-rich mixtures, in accordance with the compositions defined in a given tie-line. In addition, the same approach has been considered for the solvent-mixed polymer ternary interaction parameter:

$$(\partial g_{\mathrm{T}}/\partial\phi_3)' \approx (\partial g_{\mathrm{T}}/\partial\phi_3)'' \approx (\partial g_{\mathrm{T}}/\partial\phi_3)$$

which is also assumed to be valid under the polymer composition range of a given tie-line. Thus, now the parameters to be evaluated are: g_{12}; g_{13}; $(g_{23})'$; $(g_{23})''$; $(g_{\mathrm{T}})'$; $(g_{\mathrm{T}})''$; $(\mathrm{d}g_{23}/\mathrm{d}\phi_3)$; and $(\partial g_{\mathrm{T}}/\partial\phi_3)$.

It is evident that we need to perform a system of eight equations to evaluate the above eight unknowns. However, the next two relationships for g_{23} and g_{T}, such as:

$$(g_{23})'' = (g_{23})' + (\phi_3'' - \phi_3')\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}$$

and

$$(g_{\mathrm{T}})'' = (g_{\mathrm{T}})' + (\phi_3'' - \phi_3')\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)$$

reduce the system from eight to six equations. Note that the total number of equations that we need to describe for the computational method is six, regardless of whether g_{T} is included or not. *Table 3* compiles the numerical values for the above binary and ternary parameters, including derivative forms, for different compositions referred to pairs of tie-line combinations (see first column of *Table 3*, where the Greek symbols have the same meaning as in *Table 2*).

Data analysis

Our next concern refers to the numerical analysis of the binary and ternary data contained in *Tables 2* and *3*. Focusing attention on the g_{12} and g_{13} parameters, we see that the computed numerical values are very close for a given set of tie-lines, being practically independent of polymer concentration, a fact that validates the assumption made before. Because these data correspond to a finite concentration of polymer, the extrapolation at infinite dilution holds: $g_{13} = \chi_{13} = (\chi_{13})_{\mathrm{eff}} = 0.60$, and $g_{12} = \chi_{12} = (\chi_{12})_{\mathrm{eff}} = 0.50$. These polymer–solvent interaction parameters obtained from ternary phase diagrams can be compared with those obtained experimentally from binary polymer/solvent systems. In this regard, Lutringer and Weill[42] report $\chi_{12} = 0.47 \pm 0.02$, and Soria *et al.*[41] report $\chi_{13} = 0.49 \pm 0.02$, in fair agreement with our data. However, we feel that more accuracy could be achieved by suppression of any assumptions and by introducing more equations with more unknowns to be solved: work on this is in progress. Unfortunately, the same comparison cannot be established for the g_{23} parameter. As far as we know, no concentration dependence of the PVDF–PS interaction parameter has been reported for the dry blend nor for a solution in DMF. We have selected a representative value of g_{23} as an average value at each side of the binodal. So from *Table 2*, $(\bar{g}_{23})' = 460$ and $(\bar{g}_{23})'' = 756$; as expected, these average parameters are very different for the two coexisting phases. The same conclusion can be extracted from *Table 3*, where ternary interactions have been taken into account, and so the average parameters obtained are $(\bar{g}_{23})' = -1650 \pm 800$ and $(\bar{g}_{23})'' = -3000 \pm 500$. From comparison of both pairs of averaged values, we notice that the latter average value is about twice the former one. Recall that the prime and double prime refer to the PS-rich and PVDF-rich phases at equilibrium, positioned at the top and bottom of the glass tube, respectively, in the experiments of liquid–liquid phase separation conducted here. In the light of these results, no molecular basis for these discrepancies can be inferred from the present treatment. Nevertheless, g_{23} and related interaction parameters are of paramount importance in predicting the phase behaviour in polymer blends. Considerable experimental and theoretical effort[12,23,31,33,35,63–65] has been devoted to obtaining a universal g_{23} expression for a given polymer blend, as well as to evaluating the so-called 'true' polymer–polymer interaction parameter.

Within the possibilities offered by our treatment, we have attempted the suppression of the solvent effects on g_{23} by plotting $(g_{23})'$ and $(g_{23})''$ values from *Tables 2* and *3*, respectively, against the total polymer volume fraction, $\phi_{\mathrm{p}} = \phi_2 + \phi_3$, as can be seen in *Figure 5*. The linear extrapolation of g_{23} at $\phi_{\mathrm{p}} \rightarrow 1$ yields $g_{23} = -1600$ and $g_{23} = 12\,000$; these two uncorrelated values for the polymer–polymer interaction parameter in the absence of solvent can be considered tantamount to the segment–segment interaction parameter for a hypothetical dry blend. According to the first g_{23} data, the PVDF–PS blend should be compatible; however, assuming the second value for g_{23}, a clearly incompatible or unfavourable interaction between both polymers is inferred, in good

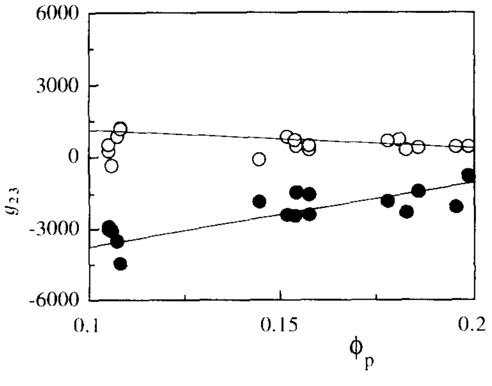

Figure 5 Polymer–polymer interaction parameter, g_{23}, as a function of the total polymer volume fraction, ϕ_{p}, for the PVDF + PS mixtures. Solid lines are the best fit to the calculated values without g_{T} (○) and including g_{T} (●)

agreement with reported data[66]. For this reason, the second g_{23} value seems to be more adequate, due to the fact that this polymer pair is not known to be miscible and supports the importance of including ternary effects. With respect to the values of the first derivatives of g_{23} and g_T parameters, also included in *Tables 2* and *3*, a gross scatter of data is evidenced, along with a change of sign within a set of tie-lines. As can be seen, $dg_{23}/d\phi_3$ represents the slope of g_{23} against ϕ_3. The change of sign in the $dg_{23}/d\phi_3$ values compiled in these tables can be associated with a parabolic ϕ_3 dependence of g_{23} rather than the conventional linear dependence often assumed. In this regard, recent SANS studies on isotopic PS blends[35,67] show that experimental χ_{HD} against ϕ diagrams are convex upwards or convex downwards, with a maximum or a minimum, respectively, at a given composition (see Figure 9 of ref. 36). According to this behaviour, and in the light of the sign of the derivatives compiled in *Tables 2* and *3*, the dependence of g_{23} on ϕ_3 for the blend tested here agrees with the trend exhibited for some isotopic mixtures. Such behaviour cannot be explained by the Flory–Huggins theory. Nevertheless, at least from a qualitative viewpoint, it can be inferred that the often assumed linear g_{23} against ϕ_3 dependence is an oversimplified scheme for highly asymmetric polymer blends, and it should be more appropriate to use a high order (second order) dependence. A last effort has been devoted to test, at least qualitatively, the goodness of the g_{23} data extrapolated at $\phi_p \rightarrow 1$. For this purpose, $(\chi'_{23})_{app}$, often experimentally obtained via i.g.c. measurements, can be evaluated from:

$$(\chi'_{23})_{app} = V_1/V_2(g_{23} + \phi_3 dg_{23}/d\phi_3) - g_T$$

i.e. by coupling equation (13) and equation (12) (*Figure 6*). Thus, by using the values reported in *Table 3* along with the densities of the DMF (1) and PVDF (2) components for V_1 and V_2 evaluation, we find two values of $(\chi'_{23})_{app}$ of 0.25 and −0.08, respectively. Although these values cannot be used as representative of the compatibility or incompatibility of the PVDF–PS mixtures, they are of the same order of magnitude as those reported for other commercial blends analysed by i.g.c.

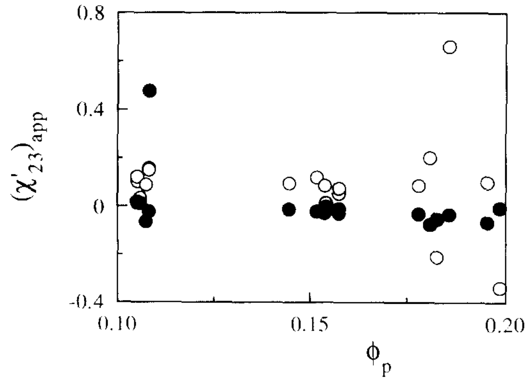

Figure 6 Plot of $(\chi'_{23})_{app}$ from equation (12) as a function of ϕ_p for PVDF + PS mixtures: ○, without g_T; ●, including g_T

CONCLUSIONS

In order to gain more insight into the behaviour of polymer blends, we have developed a thermodynamic formalism accounting for liquid–liquid phase separation for quiescent solvent–polymer–polymer ternary systems. To test its validity, we have selected a strongly asymmetric polymer blend consisting of PVDF and PS mixtures in DMF as common solvent. It has been experimentally evidenced that this ternary system undergoes liquid–liquid phase separation at 25°C and at total polymer concentration lower than 20% by weight, confirming the incompatibility of this polymer pair as observed in the solid state[66]. Quantitative composition analysis of each coexisting phase has been monitored by means of size-exclusion chromatography, allowing us to obtain a set of four adjacent tie-lines from a unique original polymer mixture. Changes in total polymer concentration between adjacent tie-lines and for homologous phases become insignificant. Three polymer mixtures, different in composition, have been used (denoted by runs A, B and C in *Table 1*) to obtain the experimental phase diagram for DMF (1)/PVDF (2)/PS (3) ternary system under the experimental conditions stated above. The shape of the obtained phase diagram (see *Figure 4*) seems to be similar to those corresponding to the incompatible polymer mixtures. The two-phase region, within the binodal curve, is strongly shifted towards the PS-rich phase and the curve exhibits a flattened form near the critical composition. This behaviour is congruent with the asymmetrical feature of the polymer pair assayed here.

Another contribution of this work refers to the theoretical interpretation of the liquid–liquid phase separation in the light of the Flory–Huggins lattice

Table 3 Values of the binary and ternary interaction parameters and their derivatives for diverse pairs of tie-lines for DMF (1)/PVDF (2)/PS (3) system at 25 C

Tie line pairs	g_{12}	g_{13}	$(g_{23})'$	$dg_{23}/d\phi_3$	$(g_T)'$	$\partial g_T/\partial\phi_3$	$(g_{23})''$	$(g_T)''$
A(α–δ)	0.5628	0.6525	−772	11918	0.2659	−3.1005	−2403	0.6903
A(α–γ)	0.5294	0.6357	−2060	2932	0.5862	−0.7627	−2443	0.6857
A(γ–δ)	0.5551	0.6486	−1414	8234	0.4278	−2.1610	−2394	0.6850
B(α–β)	0.5317	0.6340	−1541	15423	0.4549	−3.7955	−2892	0.7875
B(β–γ)	0.5478	0.6371	−1441	18415	0.4400	−4.5454	−2991	0.8224
B(γ–δ)	0.5368	0.6348	−1841	17643	0.5332	−4.3551	−3070	0.8364
C(α–β)	0.5429	0.6395	−2307	9017	0.6494	−2.2003	−3505	0.9416
C(β–γ)	0.4113	0.5458	−11397	−229990	2.8574	55.6555	18863	−4.4652
C(γ–δ)	0.4839	0.6304	−1816	20658	0.5055	−5.0446	−4447	1.1481

theory. In this context, the non-combinatorial contribution to the free energy of mixing for solvent (1)/polymer (2)/ polymer (3) quasi-ternary systems includes not only the conventional binary interaction parameter (concentration dependent) g_{ij}, but also a ternary interaction parameter g_{T} to take into account contributions other than the binary ones. This ΔG function has served to find expressions for the chemical potential of each of the three components. Insertion of the Gibbs condition for phase equilibrium gave rise to a set of six linear equations. The input data to solve the above equations are the molar volumes and the composition of the experimental points lying on the binodal, and the unknowns are the g_{ij} and g_{T} parameters, as well as their derivatives. Some approximations, mainly concerned with the composition dependence of some parameters and the inclusion or omission of g_{T}, have been analysed in depth in order to reduce the initial whole set of unknowns generated with the rigorous thermodynamic approach. The most congruent values for g_{ij} and g_{T} are obtained when both parameters are concentration-dependent on a tie-line and ternary interactions are included. The omission of this last contribution gives aberrant values for most calculated parameters, inconsistent with the experimental data on phase separation. Since the whole set of parameters is not experimentally accessible, we have reported here a numerical method for the calculation not only of the binary and ternary interaction parameters considered as composition-dependent, but also their derivative forms in the immiscible regime.

The validity of our approach is tested at a first level focusing our attention on the binary polymer/solvent g_{12} and g_{13} parameters. Comparison of the calculated and recently reported data shows a fair agreement. Unfortunately, as far as we know, data on g_{23} from PVDF+PS in DMF are absent from the literature, so this comparison cannot be carried out. Because of the great importance of the g_{23} parameter for establishing miscibility criteria for polymer blends, it deserves to be tested, at least from the qualitative viewpoint. Our test of the validity of the g_{23} data has been addressed in two ways. First, g_{23} values at finite concentration have been extrapolated (see *Figure 5*) at $\phi_{\mathrm{p}} \to 1$, which holds a large and positive value ($g_{23} = 12\,000$), consistent with the idea of incompatibility between PVDF and PS previously reported. On the other hand, the $\mathrm{d}g_{23}/\mathrm{d}\phi_3$ values from *Table 3* exhibit large deviations, denoting that the assumption about the linear g_{23} dependence on ϕ_3 is no longer valid for this blend, being more appropriate to a higher order dependence on ϕ_3. Second, we have used the g_{23} values to obtain $(\chi'_{23})_{\mathrm{eff}}$ from equation (12) because these new values can be compared with those obtained experimentally from i.g.c. measurements.

Further studies are underway to investigate the extent of validity of the simplifications introduced in this paper. A more robust system of equations needs to be solved in order to clarify the curvature of the g_{23} dependence on ϕ_3 as well as other assumptions introduced for the sake of simplicity.

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APPENDIX

Equation (7) can be simplified under the assumption that g_{ij} and g_{T} are composition-independent:

$$\frac{\Delta\mu_1}{RT}=\left(\frac{\Delta\mu_1}{RT}\right)_{\mathrm{comb}}+\Big[\chi_{12}(\phi_2^2+\phi_2\phi_3)+\chi_{13}(\phi_3^2+\phi_3\phi_2) -\chi_{23}\left(\frac{V_1}{V_2}\phi_2\phi_3\right)+\chi_{\mathrm{T}}(\phi_2\phi_3-2\phi_1\phi_2\phi_3)\Big] \tag{A1}$$

From comparison with equation (6), the combinatorial part of equation (A1) remains unaltered; however, all the derivatives of the interaction parameters vanish. Notice that this drastic approximation is a poor schema for real polymer blends, because accurate experimental g_{23} data from SANS experiments reveal at least a linear dependence of this parameter on blend composition.

The chemical potential for the polymer (2) can be similarly expressed as:

$$\frac{\Delta\mu_2}{RT}=\frac{1}{RT}\left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,n_3}=\left(\frac{\Delta\mu_2}{RT}\right)_{\mathrm{comb}}+\left(\frac{\Delta\mu_2}{RT}\right)_{\mathrm{res}} \tag{A2}$$

$$\left(\frac{\Delta\mu_2}{RT}\right)_{\mathrm{comb}}=\ln\phi_2+1-\phi_2-\frac{V_2}{V_1}\phi_1-\frac{V_2}{V_3}\phi_3 \tag{A3}$$

$$\begin{aligned}\left(\frac{\Delta\mu_2}{RT}\right)_{\mathrm{res}}&=\left[g_{12}+\phi_2\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}\right]\frac{V_2}{V_1}(\phi_1^2+\phi_1\phi_3)\\&-\left[g_{13}+\phi_3\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right]\frac{V_2}{V_1}\phi_1\phi_3\\&+\left[g_{23}-\frac{\phi_2\phi_3}{\phi_1+\phi_3}\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right](\phi_3^2+\phi_3\phi_1)\\&+\left[g_{\mathrm{T}}-\frac{\phi_2\phi_3}{1-2\phi_2}\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)\right]\frac{V_2}{V_1}(\phi_1\phi_3-2\phi_1\phi_2\phi_3)\end{aligned} \tag{A4}$$

For component 3:

$$\frac{\Delta\mu_3}{RT}=\frac{1}{RT}\left(\frac{\partial G}{\partial n_3}\right)_{T,P,n_2,n_1}=\left(\frac{\Delta\mu_3}{RT}\right)_{\mathrm{comb}}+\left(\frac{\Delta\mu_3}{RT}\right)_{\mathrm{res}} \tag{A5}$$

$$\left(\frac{\Delta\mu_3}{RT}\right)_{\mathrm{comb}}=\ln\phi_3-1-\phi_3-\frac{V_3}{V_1}\phi_1-\frac{V_3}{V_2}\phi_2 \tag{A6}$$

$$\begin{aligned}\left(\frac{\Delta\mu_3}{RT}\right)_{\mathrm{res}}&=-\left[g_{12}+\phi_2\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}\right]\frac{V_3}{V_1}\phi_1\phi_2\\&+\left[g_{13}+\phi_3\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right]\frac{V_3}{V_1}(\phi_1^2+\phi_1\phi_2)\\&+\left[g_{23}+\phi_3\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right]\frac{V_3}{V_2}(\phi_1\phi_2+\phi_2^2)\\&+\left[g_{\mathrm{T}}+\frac{\phi_1\phi_3+\phi_2\phi_3}{1-2\phi_3}\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)\right]\frac{V_3}{V_1}\\&\times(\phi_1\phi_2-2\phi_1\phi_2\phi_3)\end{aligned} \tag{A7}$$

Equations (A4) and (A7) can be transformed into a simplified version by assuming that binary and ternary interaction parameters are independent of polymer concentration. Thus:

$$\begin{aligned}\left(\frac{\Delta\mu_2}{RT}\right)_{\mathrm{res}}&=\chi_{12}\frac{V_2}{V_1}(\phi_1^2+\phi_1\phi_3)-\chi_{13}\frac{V_2}{V_1}\phi_1\phi_3\\&+\chi_{23}(\phi_3^2+\phi_3\phi_1)+\chi_{\mathrm{T}}\frac{V_2}{V_1}(\phi_1\phi_3-2\phi_1\phi_2\phi_3)\end{aligned} \tag{A8}$$

$$\begin{aligned}\left(\frac{\Delta\mu_3}{RT}\right)_{\mathrm{res}}&=-\chi_{12}\frac{V_3}{V_1}\phi_1\phi_2+\chi_{13}\frac{V_3}{V_1}(\phi_1^2+\phi_1\phi_2)\\&+\chi_{23}(\phi_1\phi_2+\phi_2^2)+\chi_{\mathrm{T}}\frac{V_3}{V_1}(\phi_1\phi_2-2\phi_1\phi_2\phi_3)\end{aligned} \tag{A9}$$

A relationship between χ and g parameters can be easily established from the comparison of the expressions for the residual chemical for each component. Thus, the comparison between equation (7) (g-containing) and equation (A1) (χ-containing) yields:

$$\chi_{12}=g_{12}-\frac{\phi_2\phi_1}{\phi_2+\phi_3}\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2} \tag{A10}$$

$$\chi_{13}=g_{13}-\frac{\phi_3\phi_1}{\phi_3+\phi_2}\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3} \tag{A11}$$

$$\chi_{23}=g_{23}+\phi_3\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3} \tag{A12}$$

$$\chi_{\mathrm{T}}=g_{\mathrm{T}}-\frac{\phi_1\phi_3}{1-2\phi_1}\frac{\partial g_{\mathrm{T}}}{\partial\phi_3} \tag{A13}$$

The comparison between equation (A4) (g-containing) and (A8) (χ-containing) yields:

$$\chi_{12}=g_{12}+\phi_2\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2} \tag{A14}$$

$$\chi_{13}=g_{13}+\phi_3\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3} \tag{A15}$$

$$\chi_{23}=g_{23}-\frac{\phi_2\phi_3}{\phi_1+\phi_3}\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3} \qquad \text{(A16)}$$

$$\chi_T=g_T-\frac{\phi_2\phi_3}{1-2\phi_2}\frac{\partial g_T}{\partial\phi_3} \qquad \text{(A17)}$$

Comparison of equation (A7) (g-containing) with (A9) (χ-containing) gives for χ_{12}, χ_{13} and χ_{23} the expressions attained by equations (A14), (A15) and (A12) respectively, and for χ_T the following:

$$\chi_T=g_T+\frac{\phi_1\phi_3+\phi_2\phi_3}{1-2\phi_3}\frac{\partial g_T}{\partial\phi_3} \qquad \text{(A18)}$$

The actual derivation of the three equations defining the locus of a tie-line on the binodal curve becomes immediate by insertion of the expressions contained in equations (6), (7), (A3), (A4), (A6) and (A7) into equations (19), (20) and (21), respectively. We next show a simplified version of these equations instead of the robust system of equations mentioned above:

$$\begin{aligned}&\ln\left(\frac{\phi_1'}{\phi_1''}\right)+(\phi_2'-\phi_2'')\left(1-\frac{V_1}{V_2}\right)+(\phi_3'-\phi_3'')\left(1-\frac{V_1}{V_3}\right)\\&\quad+\chi_{12}[(\phi_2'^2-\phi_2''^2)+(\phi_2'\phi_3'-\phi_2''\phi_3'')]+\chi_{13}[(\phi_3'^2-\phi_3''^2)\\&\quad+(\phi_2'\phi_3'-\phi_2''\phi_3'')]-\frac{V_1}{V_2}[\phi_2'\phi_3'(\chi_{23})'-\phi_2''\phi_3''(\chi_{23})'']\\&\quad+[(\phi_2'\phi_3'-2\phi_1'\phi_2'\phi_3')(\chi_T)'-(\phi_2''\phi_3''-2\phi_1''\phi_2''\phi_3'')(\chi_T)'']=0\end{aligned} \qquad \text{(A19)}$$

$$\begin{aligned}&\ln\left(\frac{\phi_2'}{\phi_2''}\right)+(\phi_1'-\phi_1'')\left(1-\frac{V_2}{V_1}\right)+(\phi_3'-\phi_3'')\left(1-\frac{V_2}{V_3}\right)\\&\quad+\chi_{12}[(\phi_1'^2-\phi_1''^2)+(\phi_1'\phi_3'-\phi_1''\phi_3'')]\frac{V_2}{V_1}\\&\quad-\chi_{13}(\phi_1'\phi_3'-\phi_1''\phi_3'')\frac{V_2}{V_1}+[(\phi_3'^2+\phi_3'\phi_1')(\chi_{23})'\\&\quad-(\phi_3''^2+\phi_3''\phi_1'')(\chi_{23})'']-\frac{V_2}{V_1}[(\phi_1'^2\phi_3'+\phi_1'\phi_3'^2\\&\quad-\phi_1'\phi_2'\phi_3')(\chi_T)'-(\phi_1''^2\phi_3''+\phi_1''\phi_3''^2-\phi_1''\phi_2''\phi_3'')(\chi_T)'']=0\end{aligned} \qquad \text{(A20)}$$

$$\begin{aligned}&\ln\left(\frac{\phi_3'}{\phi_3''}\right)+(\phi_1'-\phi_1'')\left(1-\frac{V_3}{V_1}\right)+(\phi_2'-\phi_2'')\left(1-\frac{V_3}{V_2}\right)\\&\quad-\chi_{12}[\phi_1'\phi_2'-\phi_1''\phi_2'']\frac{V_3}{V_1}+\chi_{13}[(\phi_1'^2-\phi_1''^2)\\&\quad+(\phi_1'\phi_2'-\phi_1''\phi_2'')]\frac{V_3}{V_1}+\frac{V_3}{V_2}[(\phi_1'\phi_2'+\phi_2'^2)(\chi_{23})'\\&\quad-(\phi_1''\phi_2''+\phi_2''^2)(\chi_{23})'']+\frac{V_3}{V_1}[(\phi_1'^2\phi_2'+\phi_1'\phi_2'^2\\&\quad-\phi_1'\phi_2'\phi_3')(\chi_T)'-(\phi_1''^2\phi_2''+\phi_1''\phi_2''^2-\phi_1''\phi_2''\phi_3'')(\chi_T)'']=0\end{aligned} \qquad \text{(A21)}$$

It is worth noting that equations (A19), (A20) and (A21) are composed of four terms. The first refers to the combinatorial contributions. The second contains the binary polymer–solvent interaction parameters χ_{12} and χ_{13} which in the present work have been considered independent of polymer concentration, so that χ_{12} and χ_{13} are tantamount to g_{12} and g_{13} (see equations (A10) and (A11) or (A14) and (A15)). The third term refers to the polymer–polymer interaction parameter which has been considered as dependent on polymer concentration; for this reason, χ_{23} has been labelled with a prime and double prime to denote its value in each conjugate phase. This polymer concentration dependence of the polymer–polymer interaction parameter can be included into this term by substitution of χ_{23} from equation (A19) and (A21) by g_{23} from equation (A12), and χ_{23} from equation (20) by g_{23} given by equation (A16), using the appropriate ϕ_i' and ϕ_i'' contained in these formulae. The last term contains ternary contributions, meaning not only ternary contacts but also a contribution to the residual chemical potential not included in the binary interaction parameter. Note that χ_T has also been considered as polymer concentration-dependent. In this regard, we have replaced χ_T from equations (A19), (A20) and (A21) by the expressions from equations (A17) and (A18), respectively.