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Extension of the Flory-Huggins theory to study incompatible polymer blends in solution from phase separation data

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A method is presented to evaluate the Koningsveld *g*-functions for quasi-ternary polymer solutions and blends, involving binary and ternary interactions. A robust set of 12 equations derived from the Flory-Huggins lattice theory, dealing with liquid-liquid phase separation conditions, have been solved using as input data the experimental volume fractions of each component in each coexisting phase. These values were found by means of a liquid microextraction procedure followed by size-exclusion chromatography analysis. Several approximations are proposed and discussed in order to select the best option to predict thermodynamic properties of binary polymer blends and blends in solution. The dimethylformamide/poly(vinylidene fluoride)/polystyrene ternary solution was chosen to test the validity of our proposal. In general, the analytical form of the *g*-function is adequately described by a second order polynomial, the inclusion of the ternary interaction parameter also being recommended. From the values of the PVDF/PS interaction function it can be inferred that this blend behaves as slightly incompatible under environmental conditions, in clear agreement with data previously reported. In contrast, the incompatibility is suppressed when a low molar mass component, such as dimethylformamide, is added, reaching the semidilute regime (total polymer volume fraction $\phi_p \approx 0.35$). Values of the Gibbs free-energy of mixing as a function of the blend composition were also evaluated for both ternary solution and dry blend and discussed in terms of their stability. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

A great number of advanced materials for technological applications are based on mixtures of two or three polymers. However, binary and ternary polymer blends constitute very complex systems in solid state as well as in melt or in solution[1-3]. In addition, despite the increasing interest in translation of the formalism for model polymer systems to real ones, most of the theoretical calculations have been carried out with empirical and approximate models. In general, the phase diagrams are the main tool to illustrate and to understand the thermodynamic behaviour of multicomponent polymer systems, in particular upper and lower critical solution temperatures, binodal and spinodal equilibrium curves, multicritical polymer concentration, etc.[4].

Undoubtedly, the Flory-Huggins (FH) lattice theory[5] is the most accessible, and hence often most widely used to predict qualitatively the phase separation phenomena in binary and ternary polymer solutions and blends. This approach has the advantage that almost all polymer-solvent and polymer-polymer interaction parameters, necessary to implement any thermodynamic quantity, are available[6-8] for a great number of polymers and solvents. Other approaches, such as the equation-of-state (EOS) and related approaches and group contribution methods, can also be considered as highly attractive for prediction of the behaviour of multicomponent polymer mixtures. Recently, most sophisticated theories seeking to avoid the shortcomings introduced by the FH treatment, attempt to throw light on the behaviour of these complex systems. In this regard, deserves to be mentioned the lattice cluster theory (LCT) of Freed and coworkers[9-11] and the 'reference interaction side model' (RISM)[12] extended to homopolymer melts (PRISM)[13,14], which both give a good account of the intermolecular correlations. The analogue of the FH interaction parameter, in this last context, is expressed in terms of direct correlation functions. A description in depth of the above treatments can be seen in some classical books and in two reviews recently published[1-5,15,16].

There have been many attempts to improve the original FH formalism in order to predict properly the thermodynamic behaviour of real polymer systems. Among the modifications suggested, the most often reported is that consisting of the introduction of a χ-parameter dependent upon temperature and composition[4,8,17]. Following the Koningsveld recommendation, nowadays most

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reports concerning this field use the g-function instead of the χ-parameter.

In this context, an alternative approach has been pursued in our laboratory. In a previous report[18], an extension of the FH formalism to ternary solvent/polymer/polymer systems, involving binary and ternary interaction parameters composition-dependent has been developed, and reliable predictions of polymer–polymer compatibility have been found. Briefly, our proposal requires accurate phase composition data from liquid–liquid phase separation experiments at constant temperature and pressure. Liquid phase microextraction in conjunction with size-exclusion chromatography (s.e.c.) provides a suitable way to generate proper experimental data. From each microextraction experiment we find the composition of two points of the ternary phase diagram, each one located at the intersection of a given tie-line with each branch of the phase separation curve. Thus, phase separation results have been used to simultaneously obtain the binary and ternary interaction parameters as well as their derivatives as a function of the composition for solvent/polymer/polymer systems and for dry polymer blends which exhibit, at least, a certain degree of incompatibility. Polymer pairs largely recognized as compatible cannot be treated with this methodology since drastic experimental conditions are needed to obtain the two phase region, and under these extreme conditions s.e.c. experiments cannot be carried out.

Recently, Mumby and coworkers[19,20] have used a computational method involving the solution of a nonlinear system of equations for the determination of both temperature- and composition-dependence of the FH interaction parameters. The treatment is restricted to binary systems (polymer/solvent or polymer/polymer mixtures) where the polydispersity effects, previously studied in a quantitative manner[21–24], have also been included in order to predict cloud-point curves. Moreover, progress in the prediction of thermodynamic properties arises from the combination of the FH expressions with molecular simulation and Monte Carlo methods. In this context, attempts to modify FH formalism involving size-effects or chain stiffness have been reported, to calculate phase diagrams of model polyurethanes[25,26].

This paper represents an extension of a previous contribution[18] and develops new strategies to improve the thermodynamic predictions for ternary polymer systems. In order to test our proposal, phase separation experiments have been conducted on a dimethylformamide (DMF)(1)/poly(vinylidene fluoride) (PVDF)(2)/polystyrene (PS)(3) ternary system. A set of 27 original mixtures have been used to calculate the composition of each component in the two coexisting phases in equilibrium.

On the other hand, liquid–liquid phase equilibrium condition for ternary systems has served to obtain three basic equations to adequately describe, in the framework of the FH theory, the equilibrium condition of each component in each phase. By fitting the composition values into these equations, g-functions for polymer–solvent, polymer–polymer and ternary interaction parameters have been evaluated. Results from several options and approximations are developed and discussed not only for the above ternary system but also for the PVDF/PS blend. Finally, the Gibbs free-energy of mixing at constant pressure and temperature has been evaluated as a function of the polymer composition in order to qualitatively understand the correlation between phase stability and compatibility in polymer blends.

EXPERIMENTAL

Chemicals

Poly(vinylidene fluoride) (PVDF) was kindly supplied by Penwalt Corp. (Oxford, UK) and designated as Kynar 721. The polydispersity index and weight-average molar mass (M_w) were 2.70 and 674000, respectively, as determined by s.e.c. using polystyrene calibration standards. Polystyrene (PS) was purchased from Tosoh Corp. (Tokyo, Japan) with $M_w = 15000$ and polydispersity index 1.02, as specified by the supplier. Dimethylformamide (DMF) from Scharlau (Barcelona, Spain) of s.e.c. grade was used as solvent. The densities of the chemicals were 0.9445, 1.78 and 1.05 g ml^{-1} for DMF, PVDF and PS, respectively.

Chromatography

The liquid chromatograph consisted of a Model 590 solvent-delivery system and a U6K universal injector from Waters (Mildford, MA, USA). Detection was carried out with a Model ERC-7522 Erma (Tokyo, Japan) refractive index detector and chromatograms were recorded by using a dual-channel recorder (Yokogawa Electric Works, Tokyo, Japan). The system was equipped with three μ-styragel columns (30 cm length × 0.78 cm i.d.) packed with highly cross-linked styrene-divinylbenzene copolymer of 10^5, 10^4 and 10^3 Å nominal pore-size from Waters and with an effective molar mass range separation from 200 to 4 million. DMF, used as the mobile phase, was previously degassed and clarified by passing it under vacuum through a 0.45 μm regenerated cellulose filter from Micro Filtration Systems (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.

Phase separation experiments

The two polymers to be blended were accurately weighed (about 0.3 g total) into a calibrated glass tube of 10.00 ± 0.05 ml. In order to dissolve the two polymers, DMF was slowly introduced in the tube, sealed with Teflon seals, gently shaken, 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. At this moment two phases in equilibrium appeared, the less concentrated phase on top, and the more concentrated phase on the bottom of the tube. Normally, it took several hours to complete the macroscopic phase separation. After two days equilibration time, we first read the volume of each phase, then 250 μl of the top phase were withdrawn by using a microsyringe and weighed accurately. Injection of 90 μl of this solution gives a chromatogram with two peaks corresponding to each polymer. The mass amount of PVDF and PS was obtained by using a calibration curve that relates the height of the peak with the weight of the polymer. 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. Since we extracted a certain volume of the top phase, a non-equilibrium state was reached, 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 until the masses of the three components in the two conjugate phases for five tie-lines were very close in composition. Following this method we obtain 27 groups (labeled 1–27) of five tie-lines (α, β, γ, δ and ϵ) each one.

THEORY

Free-energy of mixing for solvent/polymer/polymer systems

The Flory–Huggins (FH) theory has been adopted to account for the thermodynamic behaviour of a quasi-ternary solvent (1)/polymer (2)/polymer(3) system since it has been recognized as the most useful formalism for polymer solutions. In particular, we consider a mixture of PVDF + PS in a common solvent such as DMF, the PVDF being a polydisperse commercial sample and the PS a monodisperse standard one. The adaptation of the original FH theory to multicomponent polymer systems leads to a large number of terms in the master equation dealing with the free energy of mixing[24]. For this reason, to make quantitative predictions becomes a difficult task.

We consider a chain placed on a lattice of coordination number z (for a cubic lattice $z = 6$). The lattice has N isodiametric sites completely filled, and in a first step no chain ends and voids have been included in our calculations. Let N be the total number of lattice sites, a fraction of these will be filled with N_1 molecules of solvent. In the general case, when both polymers are polydisperse, the number of lattice sites occupied by the polymer 2 will be $N_2 = \sum_{i=1}^{r} N_{2,i}$ and by the polymer 3, $N_3 = \sum_{j=1}^{s} N_{3,j}$, where the first subscript (2,3) refers to one of the potentially polydisperse polymer and the second subscript (i,j) refers to the single molar mass constituents that comprise each of the components. The total system interaction energy for a real solution can be expressed as:

$$N_1 + \sum_{i=1}^{r} x_{2,i}N_{2,i} + \sum_{j=1}^{s} x_{3,j}N_{3,j} \xrightarrow{\Delta G} \text{Quasi-ternary polymer solution} \tag{1}$$

where $x_{2,i}$ and $x_{3,j}$ refer to the polymerization degree and ΔG to the free energy of mixing. It is convenient to write ΔG per lattice site, in order to derive an expression for our ternary solution, as follows:

$$\frac{\Delta G}{N_1 + \sum_{i=1}^{r} x_{2,i}N_{2,i} + \sum_{j=1}^{s} x_{3,j}N_{3,j}} = kT[\phi_1 \ln \phi_1 + \sum_{i=1}^{r} \frac{\phi_{2,i}}{x_{2,i}} \ln \phi_{2,i} + \sum_{j=1}^{s} \frac{\phi_{3,j}}{x_{3,i}} \ln \varphi_{3,j} + \Gamma(T, \phi, M)] \tag{2}$$

where ϕ_1 is the volume fraction of the solvent in the ternary mixture, and $\phi_{2,i}$ and $\phi_{3,j}$ are the volume fractions of species i and j in polymers 2 and 3, respectively. The right-hand side of equation (2) has two main contributions: the first one refers to the combinatorial entropy and the second one, denoted here as $\Gamma(T, \phi, M)$, is a complex function dealing with the enthalpic and the non-combinatorial contribution to the free energy of mixing.

As concerning $\Gamma(T, \phi, M)$ for ternary systems, it has been widely recognized that T and ϕ largely affect the values of Γ-function, whereas the M-dependence is more problematic and at present it has not been well understood. In this regard, it has been reported that the polymer–polymer interaction parameter, χ, does not depend on M for isotopic blends[20,21,27], in clear agreement with the precognized by the FH theory. In contrast, other contributions suggest that χ decreases when M increases in blends of chemically different components[28–30]. In our previous work[18] and here, this dependence has not been considered as a contribution to Γ-function. Nevertheless, it must be recognized that FH theory and some other modifications clearly predict a molar mass dependence of the critical polymer concentration for ternary solutions consisting of polymers of different molecular sizes in a common good solvent[31,32]. Because our treatment is carried out under isothermal conditions and the system is formed by a mixture of two dissimilar well characterized polymer samples in a common solvent, hereafter $\Gamma(\phi)$ will be expressed through[33,34]

$$\Gamma(\phi) = n_1\phi_2 g_{12} + n_1\phi_3 g_{13} + (n_2\bar{x}_2\phi_3 \text{ or } \phi_2 n_3\bar{x}_3)g_{23} + (n_1\phi_2\varphi_3 \text{ or } \phi_1\phi_3 n_2\bar{x}_2 \text{ or } \phi_1\phi_2 n_3\bar{x}_3)g_{\mathrm{T}} \tag{3}$$

where g_{12}, g_{13} and g_{23} are the PVDF–DMF, PS–DMF and PVDF–PS interaction functions, respectively, and g_{T} is a ternary function that takes into account other than binary interactions. n_i ($i = 1, 2, 3$) is the number of moles and the magnitudes $\bar{x}_2$ and $\bar{x}_3$ refer to the average polymerization degree of PVDF and PS closely related to the molar volumes of each component, V_i, according to $V_1/V_2 = 1/\bar{x}_2$ and $V_1/V_3 = 1/\bar{x}_3$, respectively.

Another question to be addressed concerns the lattice size, since not all the entities placed into the lattice display the same volume. For example, in the polymer system chosen here it is evident that the size of the DMF molecules are different from that of the PVDF repeated unit (-CH_2-CF_2-) or of the PS one (C_6H_5-CH-CH_2-). A convenient way to define the size of a lattice site is to assume it to be sufficiently large to hold a solvent molecule or one monomer unit. However, a more accurate treatment can be developed based on the calculation of the molecular surface area and volume using, for instance, the van der Waals radii of the atoms[25]. It is supposed that the chains of both polymers are completely flexible. Nevertheless, the effects of the orientational randomness of segments of a chain molecule and their concentration dependence on the combinatory entropy have been recently discussed[35].

Phase equilibria in quasi-ternary systems

From the theoretical viewpoint, two phases can exist in equilibrium when the chemical potential of each component in both phases is equal. Therefore, the next step requires the calculation of the chemical potentials for the solvent and the two polymers, which can be written, in general, as:

$$\frac{\Delta\mu_i}{RT} = \frac{1}{RT}\left[\left(\frac{\partial \Delta G}{\partial n_i}\right)_c - \frac{\partial \Gamma(\phi)}{\partial n_i}\right]_{T,p,n_{j\neq i}} \tag{4}$$

As can be seen, the chemical potential of each component can be expressed in the framework of the FH theory by two terms, usually named as combinatorial and residual (denoted here by subscript c and by $\Gamma(\phi)$, respectively).

On the other hand, it has been experimentally evidenced[36] that the DMF/PVDF/PS ternary system exhibits a liquid–liquid two phase separation, so that the thermodynamic equilibrium for each component can be expressed as

$$(\Delta\mu_i)' = (\Delta\mu_i)'' \tag{5}$$

Prime and double prime denoting the principal and conjugate phases in equilibrium, respectively. For simplicity, the full expanded version of equation (5) for each component as a function of the volume fractions of each phase, ϕ_i', and ϕ_i'', has been incorporated in the Appendix section. Therefore, in the light of equations (A2), (A3) and (A4), the magnitudes to be evaluated are: $(g_{12})'$, $(g_{13})'$, $(g_{23})'$, $(g_T)'$, $(g_{12})''$, $(g_{13})''$, $(g_{23})''$, $(g_T)''$, as well as their derivatives: $(dg_{12}/d\phi_2)'$, $(dg_{13}/d\phi_3)'$, $(dg_{23}/d\phi_3)'$, $(\partial g_T/\partial\phi_3)'$, $(dg_{12}/d\phi_2)''$, $(dg_{13}/d\phi_3)''$, $(dg_{23}/d\phi_3)''$ and $(\partial g_T/\partial\phi_3)''$.

These 16 unknowns have been generated considering exclusively the polymer–polymer and polymer–solvent composition dependence of the residual contribution to the free energy of mixing. If one wishes to perform a more realistic treatment, i.e. optimization of the lattice size, polydispersity effects, chain stiffness etc., the total number of unknowns will increase, which would imply implementation of a more sophisticated expression for the ΔG function. It is convenient to outline that we are exclusively concerned with the evaluation of g_{12}, g_{13}, g_{23} and g_T as a function of the composition for ternary solvent/polymer/polymer systems in order to rationalize the complex phase behaviour of polymer blends in terms of interactions.

Moreover, rather than presenting the mathematical details of the calculations, we shall only discuss the physical meaning of the interaction parameters as well as the related assumptions made to reach the final results. In this regard, it is convenient to clarify the assumptions handled here, which can be classed into three categories:

a) Assumptions inherent to the FH theory[5,16] such as: i) the neglection of any correlation effects in the occupancy of the lattice sites; ii) the actual number of effective neighbour contacts are still significantly overestimated; and iii) the lattice sites can be occupied independently from each other what is no longer true for self-avoiding and mutually avoiding chains.
b) A second set of assumptions concerns the polymer microstructure and molecular patterns required to model a real polymer chain. The following can fall within this section: free-volume and size effects, flexibility or chain stiffness, tacticity, crystallinity and polydispersity involving molar mass and molar mass distribution.
c) Specific assumptions related to the methodology reported here. It is evident that in order to obtain specific results on multicomponent polymer solutions it is necessary to evaluate complex thermodynamic equations introducing several closure approximations, which in a further step could be suppressed. These kind of assumptions do have a transient nature.

As stated previously, we have arbitrarily chosen the DMF(1)/PVDF(2)/PS(3) ternary system to test the level of fulfillment of our proposal. However, PVDF is a polydisperse commercial sample and has been represented by its average polymerization degree, $\bar{x}_2$. Rigorously, only when the molar volumes of the monomer units, -(CH$_2$-CF$_2$)- and -(C$_6$H$_5$-CH-CH$_2$)- and that of the DMF are of the same order, $\bar{x}_2$ can be regarded as a true polymerization degree[37]. Obviously, the size of these entities are far off this condition as a consequence of the strong asymmetric character of the involved polymer mixture. The above argument can be considered as an example of the assumptions included in (b) where size and polydispersity effects have been disregarded.

Other assumptions assumed throughout the paper refer to the inclusion or not of the so-called ternary interaction parameter, g_T, as well as the composition dependence of g_{ij}, g_T and their derivatives. These questions are examples of the simplifications falling within (c) and we submit the reader to the next section where these approaches have been detailed in depth, in the so-called options A, B and C.

RESULTS AND DISCUSSION

Different PVDF/PS mixtures have been prepared adding DMF as common solvent until phase separation occurs. Following the procedure detailed in Experimental, it is possible to evaluate the composition of both ϕ_1' and ϕ_1'' phases denoted by the tie-line α in *Table 1*. Successive extractions and injections for s.e.c. analysis of the suitable amounts from the top phase, and further reequilibration of the system allow to obtain the composition of the remaining tie-lines. As a numerical example of the procedure, *Table 1* compiles the composition of the α, β, γ, δ and ϵ tie-lines from run 8. The same methodology has been followed for the remaining polymer mixtures. For the sake of simplicity, *Table 2* shows the average composition values for the principal $\langle\phi_i'\rangle$ and conjugate phases $\langle\phi_i''\rangle$ obtained with the 5 tie-lines and for 27 runs analysed by s.e.c. for the DMF/PVDF/PS system.

For calculation purposes, we have used as input data the α–ϵ tie-line compositions of the 27 runs compiled in *Table 2*. The expanded equations dealing with the equilibrium conditions of liquid–liquid phase separation experiments have been written in the Appendix. The computational method used here is based on these equations, being ϕ_i' and ϕ_i'' the input data and the g_{ij}

Table 1 Values of the composition for the principal (ϕ_i') and conjugate (ϕ_i'') phases in equilibrium as determined by s.e.c. at 25°C for DMF(1)/PVDF(2)/PS(3) system

Tie-line	ϕ_1'	ϕ_2'	ϕ_3'	ϕ_1''	ϕ_2''	ϕ_3''
α	0.90215	0.00198	0.09587	0.94375	0.02902	0.02723
β	0.90318	0.00161	0.09521	0.94232	0.03051	0.02717
γ	0.89113	0.00053	0.10834	0.94803	0.02932	0.02265
δ	0.90100	0.00199	0.09701	0.94818	0.02825	0.02357
ϵ	0.89613	0.00494	0.09893	0.96535	0.01967	0.01498

Table 2 Mean composition values obtained from five tie-lines (α–ϵ in each case) for diverse DMF(1)/PVDF(2)/PS(3) mixtures

Run	$\langle\phi_1'\rangle$	$\langle\phi_2'\rangle$	$\langle\phi_3'\rangle$	$\langle\phi_1''\rangle$	$\langle\phi_2''\rangle$	$\langle\phi_3''\rangle$
1	0.97050	0.00372	0.02578	0.85241	0.07942	0.06817
2	0.96332	0.00778	0.02891	0.69515	0.28977	0.01508
3	0.94337	0.01898	0.03765	0.95540	0.03760	0.00700
4	0.92965	0.03004	0.04030	0.93571	0.04262	0.02167
5	0.93565	0.01691	0.04744	0.94002	0.03192	0.02807
6	0.91585	0.01674	0.06741	0.95605	0.03448	0.00947
7	0.87457	0.05529	0.07014	0.96239	0.02762	0.00999
8	0.90925	0.00557	0.08517	0.94568	0.03622	0.01810
9	0.89814	0.00583	0.09603	0.95276	0.02167	0.02557
10	0.89872	0.00221	0.09907	0.94953	0.02602	0.02445
11	0.89217	0.00845	0.09938	0.95447	0.02538	0.02015
12	0.89829	0.00150	0.10021	0.95617	0.02920	0.01463
13	0.89608	0.00365	0.10027	0.95040	0.02817	0.02143
14	0.87921	0.01016	0.11063	0.96059	0.02139	0.01802
15	0.84942	0.01790	0.13268	0.94338	0.05158	0.00504
16	0.86398	0.00067	0.13535	0.94872	0.03351	0.01778
17	0.83239	0.02897	0.13864	0.96701	0.02517	0.00782
18	0.83755	0.02004	0.14241	0.95514	0.03656	0.00830
19	0.78016	0.07557	0.14427	0.95463	0.04021	0.00516
20	0.79642	0.05783	0.14575	0.95393	0.03971	0.00636
21	0.84175	0.00674	0.15151	0.91757	0.07137	0.01105
22	0.82702	0.01451	0.15846	0.94729	0.04182	0.01090
23	0.70220	0.13107	0.16673	0.96072	0.02843	0.01085
24	0.79998	0.02743	0.17259	0.95811	0.02846	0.01344
25	0.80592	0.00074	0.19333	0.88998	0.10678	0.00342
26	0.74462	0.03646	0.21893	0.94805	0.04688	0.00603
27	0.64428	0.12419	0.23153	0.96014	0.03478	0.00508

parameters as well as their respective derivatives, the unknowns to be evaluated. Obviously, one can attempt to solve a set of 16 equations to directly obtain the 16 unknowns detailed above. However, some rational approximations can be made in order to reduce the calculations. Next, we proceed to relate the different options selected to obtain the numerical values of the unknowns at different polymer compositions. Notice that we emphasize on the concentration dependence of the parameters g_{ij} and g_T that are closely related with the concept of compatibility in polymer blends. In addition, all the raw data used in our calculations come from a given run, as can be seen in the example given in *Table 1* which is constituted by five adjacent tie-lines. It is also evident that the shifts in concentration for each component among tie-lines of the same run can be neglected because the amount of matter removed from the top phase for each microextraction for s.e.c. analysis is very small.

Option A

Let us consider a linear concentration dependence of the g_{12} and g_{13} interaction parameters upon a narrow composition range, as the one delimited in *Table 1* for the ϕ_i' and ϕ_i'' values. In this way, each volume fraction of a given tie-line is substituted into equations (A2), (A3) and (A4) (see Appendix), being the total set of unknowns to be evaluated: $(g_{12})'$, $(g_{13})'$, $(g_{23})'$, $(g_{\mathrm{T}})'$, $(g_{12})''$, $(g_{13})''$, $(g_{23})''$, $(g_{\mathrm{T}})''$, $(dg_{23}/d\phi_3)'$, $(\partial g_{\mathrm{T}}/\partial\phi_3)'$, $(dg_{23}/d\phi_3)''$ and $(\partial g_{\mathrm{T}}/\partial\phi_3)''$. It has been assumed that $(dg_{12}/d\phi_2)' = (dg_{12}/d\phi_2)''$ and $(dg_{13}/d\phi_3)' = (dg_{13}/d\phi_3)''$, being these derivatives easily evaluated from the equations:

$$(g_{12})'' = (g_{12})' + (\phi_2'' - \phi_2')\frac{dg_{12}}{d\phi_2}$$

$$(g_{13})'' = (g_{13})' + (\phi_3'' - \phi_3')\frac{dg_{13}}{d\phi_3} \qquad (6)$$

For this purpose we need a set of 12 linear equations to obtain the above 12 unknowns fitting the ϕ' and ϕ'' values from at least four tie-lines. Because five different tie-lines per run are available, as shown in *Table 1*, we can obtain different combinations of four tie-lines, such as: $\alpha\beta\gamma\delta$; $\alpha\beta\gamma\epsilon$; $\alpha\beta\delta\epsilon$; $\alpha\gamma\delta\epsilon$ and $\beta\gamma\delta\epsilon$, which allows us to generate five sets of numerical values for the aforementioned 12 unknowns. By extension of this procedure to the remaining 26 runs compiled in *Table 2*, we will obtain 5×27 ϕ-values for each unknown.

Option B

In this option we assume that the concentration dependence of the polymer–solvent interaction parameters can be reasonably omitted within a narrow concentration range[18,38], such as the one considered into a set of adjacent tie-lines. Therefore $dg_{12}/d\phi_2$ and $dg_{13}/d\phi_3$ will tend to zero. In contrast, the g_{23} and g_{T} parameters retain the same concentration-dependence as explicited in the preceding option. This simplification yields the following unknowns: $(\chi_{12})'$; $(\chi_{13})'$, $(g_{23})'$, $(g_T)'$, $(\chi_{12})''$, $(\chi_{13})''$, $(g_{23})''$, $(g_T)''$, $(dg_{23}/d\phi_3)'$, $(dg_{23}/d\phi_3)''$ $(\partial g_T/\partial\phi_3)'$ and $(\partial g_T/\partial\phi_3)''$. Notice that we have introduced the notation χ_{12} and χ_{13} instead of g_{12} and g_{13} since $g \rightarrow \chi$ when $dg/d\phi \rightarrow 0$ (assumed in this option only for the polymer–solvent interaction parameters).

As will be seen in the next section, we present two kinds of data labelled in all cases as options B_1 and B_2 in the respective plots. In both cases we have used the approach stated above. Points for option B_1 have been selected according to the usual statistical criterion, whereas points for option B_2 correspond to the same compositions that those depicted in option A.

Option C

We include here a crude approach affecting both polymer–solvent and ternary interaction parameters, hence we have fully suppressed their concentration dependence and well as the g_T parameter. Notice that in this option we consider the polymer–solvent interaction parameters as non-dependent of polymer concentration in all the composition range where phase separation takes place, in contrast with the preceding option when the same assumption has been restricted to the concentration range of each branch of the coexistence curve obtained from liquid–liquid phase separation experiments. See for example Figure 4 in the preceding paper[18], where the PVDF-rich and PVDF-poor branches of the coexistence curve were displayed. This approach holds the following 6 unknowns: χ_{12}, χ_{13}, $(g_{23})'$, $(g_{23})''$, $(dg_{23}/d\phi_3)'$ and $(dg_{23}/d\phi_3)''$. Recalling that the composition of five tie-lines per run are available, and that we need to perform in this option a set of 6 equations to evaluate the above 6 unknowns, one can make 10 different combinations of pairs of tie-lines per run, such as: $\alpha\beta$; $\alpha\gamma$; $\alpha\delta$; $\alpha\epsilon$; etc.

Data analysis

Owing to the high number of values generated within a given option (for example, 270 sets of χ_{ij}, g_{23}, and $dg_{23}/d\phi_3$ values in the C-option), a selection of these data has been analysed. In this way, data falling outside of the range of three times the standard deviation were discriminated to the end fit. The results and discussion will be presented in the following order: first, the polymer–solvent interaction parameters χ_{ij} and g_{ij}; second, the g_{23} parameter will be shown and discussed, and finally the g_T parameter will be considered as well as the free energy of mixing in terms of blend compatibility.

Figure 1 shows the composition-dependence of the polymer–solvent interaction parameters, g_{12} and χ_{12}, against the reduced volume fraction $\phi_2/(\phi_1 + \phi_2)$ for the DMF(1)/PVDF(2)/PS(3) system and all the calculation options explained before. Similarly, *Figure 2* displays the values of the g_{13} or χ_{13} parameters *versus* $\phi_3/(\phi_1 + \phi_3)$ for the same system and the four options (A, B_1, B_2 and C from top to bottom as in *Figure 1*).

As can be seen, in *Figures 1* and *2* a good quantitative fit has been achieved, in general, except for option C where a gross scatter of data is observed. In this last case, as expected, the agreement is quite poor, as a consequence of the crude approximation introduced which neglects the dependence of the interaction parameters on polymer concentration in all the composition range where phase separation takes place.

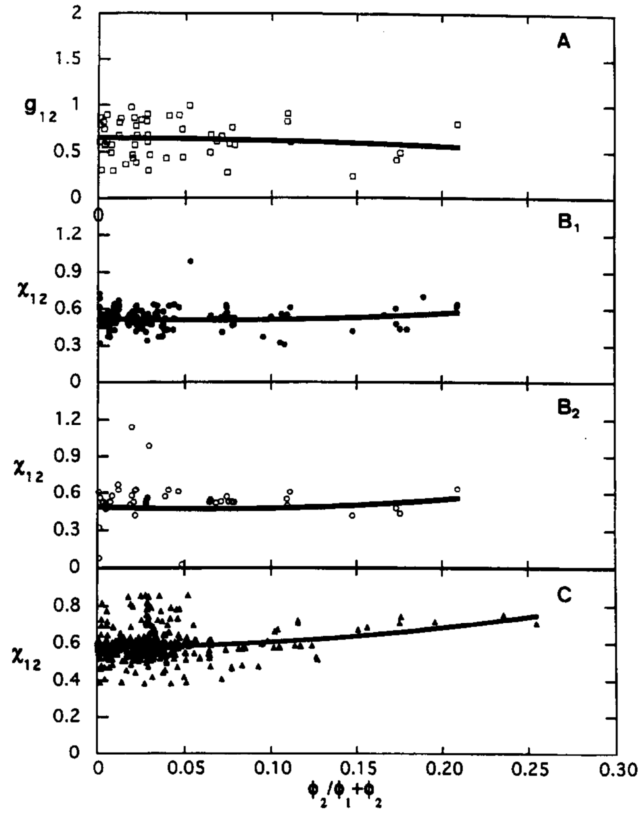

Figure 1 Plot of the interaction parameters g_{12} and χ_{12} against the ternary polymer system composition, $\phi_2/(\phi_1 + \phi_2)$ for DMF/PVDF/PS system. The four plots refer, from top to bottom, to options A, B_1, B_2 and C. Solid lines were obtained by a second-order polynomial fit

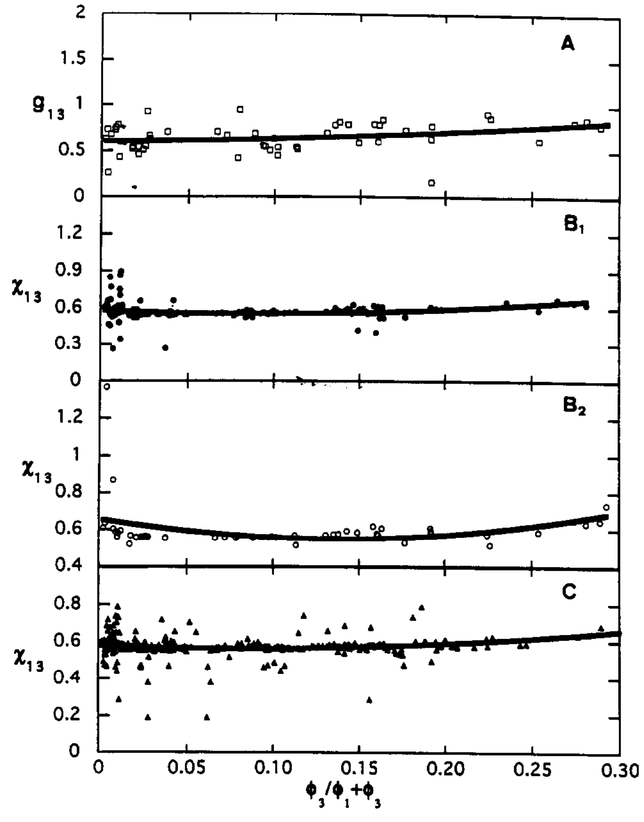

Figure 2 Plot of the interaction parameters g_{13} and χ_{13} against the ternary polymer system composition, $\phi_3/(\phi_1 + \phi_3)$ for DMF/PVDF/PS system. Plots have been built up as in *Figure 1*

In order to test the validity of our proposal we have collected, for comparison, in *Table 3* the values of polymer–solvent interaction parameters extrapolated at infinite dilution (see also column labelled as "a" in *Table 4*) from options A, B_1, B_2 and C together with data previously reported. Note that the evaluation of χ_{1i} $(i = 2, 3)$ from experimental data extrapolated at infinite dilution is a common practice. As might be expected, strong discrepancies between data coming from different options arises since drastic approximations have been introduced in some cases (option C for instance). Despite these uncertainties, a good agreement between the χ_{12} values from options B_1 and B_2 and those previously reported can be observed. Deviations lower than 5% falling within the range of the uncertainty of the molar mass determination corroborate, in this case, the validity of our treatment. However, discrepancies around 7% are observed by comparison of the χ_{13} values. Nevertheless, it must be taken into account the difference in the molar masses of the PS samples used here and in other reports[40–42], which probably is the origin of the large deviation. At present, experimental data of interaction parameters for DMF–PVDF and DMF–PS pairs of the same molar mass as used here have not yet been reported.

Table 3 Comparison between the polymer–solvent interaction parameters at infinite dilution obtained here and those previously reported

Option	χ_{12}	χ_{13}
A	0.652	0.605
B_1	0.522	0.575
B_2	0.458	0.656
C	0.581	0.579
	0.47 ± 0.02[39]	0.49 ± 0.02[40]
	0.50[41]	0.60[41]
	0.617[42]	0.654[42]

Next, *Figure 3* (upper part) shows the composition dependence of polymer–polymer interaction parameter g_{23} as a function of the reduced volume fraction $\phi_3/(\phi_2 + \phi_3)$ which allows us to cover a composition range from 0 (pure PVDF) to 1 (pure PS) for the same options as before. We consider here the PVDF/PS mixture as a dry blend where the order of magnitude and sign of g_{23} is closely related with the concept of blend compatibility at a given composition. In agreement with most data from polymer–polymer interaction parameters, a parabolic form is often reported for the g_{23} composition dependence in real polymer blends.

A second order polynomial fit has also been chosen to account for the composition dependence of g_{23} as illustrated in *Table 4*. Correlation between data extracted from this polynomial fit and the compatibility of the PVDF/PS blends is a difficult task, due in large part to a lack of data experimentally determined under the same conditions as related here. However, in general, this blend is assumed to be weakly incompatible[43–45]. As far as we know, the g_{23} values reported for this blend are very scarce. Two values of 0.013[44] and (0.021 ± 0.002)[45] have been reported denoting slight incompatibility. In addition, from the inspection of *Figure 2* from reference 45 it seems that at PS concentrations above 85%, χ_{23} becomes negative and hence the PVDF/PS blend becomes compatible. It can also be inferred from this figure that for PVDF-rich blends no compatibility is detected. From the results gained here for g_{23}, it is observed that the data coming from A, B_1 and B_2 options are negative and those from option C are positive. As an

Table 4 Coefficients of the polynomial fit $y = a + bx + cx^2$ for the binary and ternary functions as well as the free energy of mixing for DMF(1)/PVDF(2)/PS(3) system at 25°C

Option	Function	Variable	a	b	c	Composition range
A	g_{12}	$\phi_2(\phi_1 + \phi_2)^{-1}$	0.652	−1.194	−1.330	0–0.25
B_1	χ_{12}	"	0.522	−0.441	−3.190	
B_2	χ_{12}	"	0.458	−0.522	4.134	
C	χ_{12}	"	0.581	−0.034	2.739	
A	g_{13}	$\phi_3(\phi_1 + \phi_3)^{-1}$	0.605	−0.045	2.438	0–0.30
B_1	χ_{13}	"	0.575	−0.485	2.769	
B_2	χ_{13}	"	0.656	−1.553	5.657	
C	χ_{13}	"	0.579	−0.386	2.160	
A	g_{23}	$\phi_3(\phi_2 + \phi_3)^{-1}$	−0.621	−0.219	0.713	0–1.00
B_1	g_{23}	"	1.484	−6.379	4.324	
B_2	g_{23}	"	0.736	−5.023	3.460	
C	g_{23}	"	0.178	−0.390	0.260	
A	g_T	$(\phi_2 + \phi_3)$	0.719	−3.167	11.497	0–0.35
B_1	g_T	"	0.777	−2.107	10.814	
B_2	ΔG	$\phi_3(\phi_2 + \phi_3)^{-1}$	−0.021	−1.424	1.202	0–1.00
C	ΔG	"	−0.020	1×10^{-5}	−0.020	
B_2	ΔG_{23}	$\phi_3(\phi_2 + \phi_3)^{-1}$	0.182	−0.005	0.043	0–1.00
C	ΔG_{23}	"	0.019	3×10^{-4}	-2×10^{-4}	
B_2	ΔG_{23}	$\phi_3(\phi_2 + \phi_3)^{-1}$	0.007	−0.005	0.043	0–1.00
C	ΔG_{23}	"	-4×10^{-5}	3×10^{-4}	-2×10^{-4}	

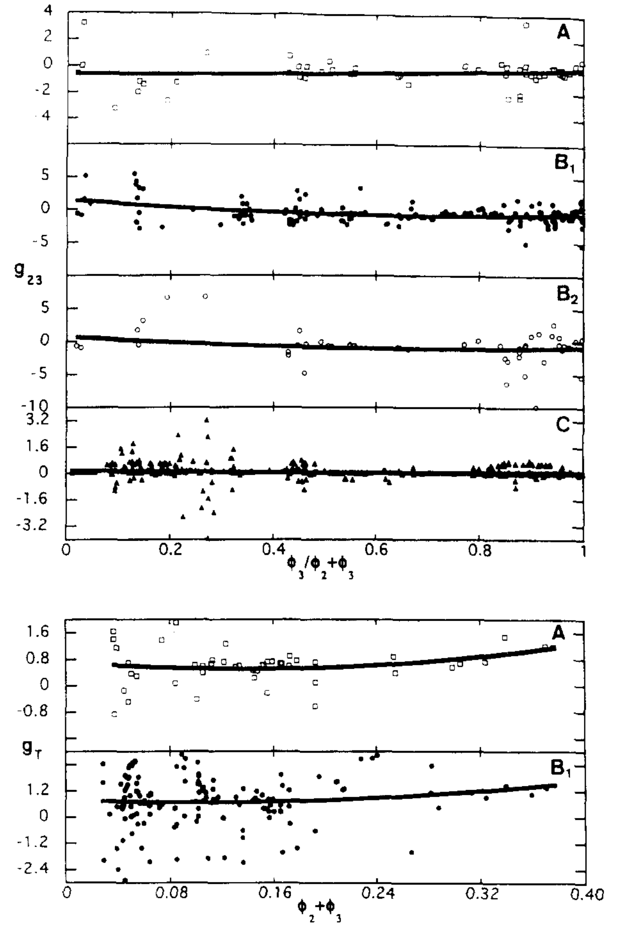

Figure 3 Plot of the polymer polymer interaction parameter g_{23} against the reduced volume fraction, $\phi_3/(\phi_2+\phi_3)$. The four plots refer, from top to bottom, to options, A, B$_1$, B$_2$ and C (upper part). Plot of the g_T parameter as a function of the total polymer concentration, $\phi_2+\phi_3$, according to options A and B$_1$ (lower part). Solid lines were obtained by a second-order polynomial fit

example, we have calculated g_{23} for a blend rich in PS with a composition $\phi_3 = 0.7$, obtaining for options A, B$_1$ and B$_2$ the following values: -0.425, -0.862 and -1.085 denoting compatibility; and with option C a value of 0.032 that means slight incompatibility, in clear agreement with the previously reported data[44,45] and with the expected behaviour for a PVDF(0.3)/PS(0.7) dry blend. Nevertheless, further experimental and theoretical contributions must be elaborated to clarify the question concerning the DMF behaviour as a possible compatibilizer agent between the PVDF and PS samples.

Lastly, we have also depicted in *Figure 3* (lower part) the values of the g$_T$-parameter as a function of the total polymer concentration, $\phi_2+\phi_3$. This parameter also displays a second order polynomial dependence on composition, in the light of the values of the a, b and c coefficients compiled in *Table 4*. Note that the plotted $(\phi_2+\phi_3)$ values are always lower than 0.4 since mixture compositions higher than this value could produce highly viscous systems and the s.e.c. analysis could lead to large uncertainties in the evaluation of the conjugate phases composition. In general, the inclusion of the g_T parameter in the calculations strongly affects the g_{23} values, in contrast with its negligible influence on the polymer–solvent interaction parameters, g_{12} and g_{13}. Unfortunately, g_T values are absent from almost all contributions on dry blends as well as from blends in solution, being impossible to quantitatively test the accuracy of the g_T data here obtained.

In the light of our findings, we can conclude that the reported methodology, based on the mathematical solution of diverse sets of linear equations (12 equations for options A and B, and 6 equations for option C), allows us to simultaneously obtain the composition-dependence of the g_{12}, g_{13}, g_{23} and g_T interaction parameters. These values can serve not only to predict miscibility or compatibility in polymer blends and for blend in solution, but also to evaluate the non-combinatorial entropy of mixing as well as possible enthalpic effects both captured by the $\Gamma(\phi)$ function in equation (3). Thus, for a given $\phi(\phi_1, \phi_2, \phi_3)$ value one can obtain $\Gamma(\phi)$, inserting the experimental volume fractions and the corresponding interaction parameters into this equation.

Miscibility or compatibility can also be illustrated by calculating the free-energy of mixing as a function of the composition at different temperatures. A schematic drawing of this dependence can be observed in some books (see for instance Figure 2.6 from reference 2) as well as in recent contributions[46], mainly for solvent/polymer and polymer/polymer systems. However, this plot is not a common matter in most of the contributions on thermodynamics of ternary polymer systems. This absence could be attributed to inherent trouble to implement a proper software. Here, we restrict our discussion to the ΔG values obtained from the FH formalism using the experimental ϕ values as well as the g-functions just calculated. It follows that the free energy of mixing, referred to one mole of lattice sites, can be written as:

$$\frac{\Delta G}{RT} = \phi_1 \ln \phi_1 + \frac{V_1}{V_2}\phi_2 \ln \phi_2 + \frac{V_1}{V_3}\phi_3 \ln \phi_3 + \phi_1\phi_2 g_{12} + \phi_1\phi_3 g_{13} + \phi_2\phi_3 g_{23} + \phi_1\phi_2\phi_3 g_T \qquad (7)$$

where we have included the explicit $\Gamma(\phi)$ function from equation (3). For the calculation of ΔG values we have inserted into equation (7) all the experimental ϕ_i' and ϕ_i'' determined by s.e.c. and the associated g_{ij} and g_T computed values according to the A, B$_1$, B$_2$ and C options previously detailed. Obviously, all the obtained data have not been plotted because a gross scatter of points is observed. In order to improve the data correlation we have discriminated points exhibiting large deviations, assuming the same statistical criteria as in *Figures 1, 2* and *3*. The concentration dependence of the ΔG function is adequately described by a second order fit in most cases, and the respective coefficients are also collected in *Table 4*.

The question as to the goodness of fit of the theory cannot, however, be answered since direct comparison of the predictions with experiment is not possible, due to the lack of experimental data for this blend obtained under liquid–liquid phase separation conditions. Nevertheless, some comments on the thermodynamic behaviour of the two coexisting phases, at least from a qualitative viewpoint, need to be emphasized. Thus, *Figure 4* depicts ΔG values against $\phi_3/(\phi_2+\phi_3)$ tantamount to $\phi_3/(1-\phi_1)$ covering all the composition range, for the options previously detailed. Due to the gross scatter of data it seems difficult to analyse the evolution followed by the ΔG values. However, it is clearly observed that plots corresponding to A, B$_1$ and B$_2$ options display a

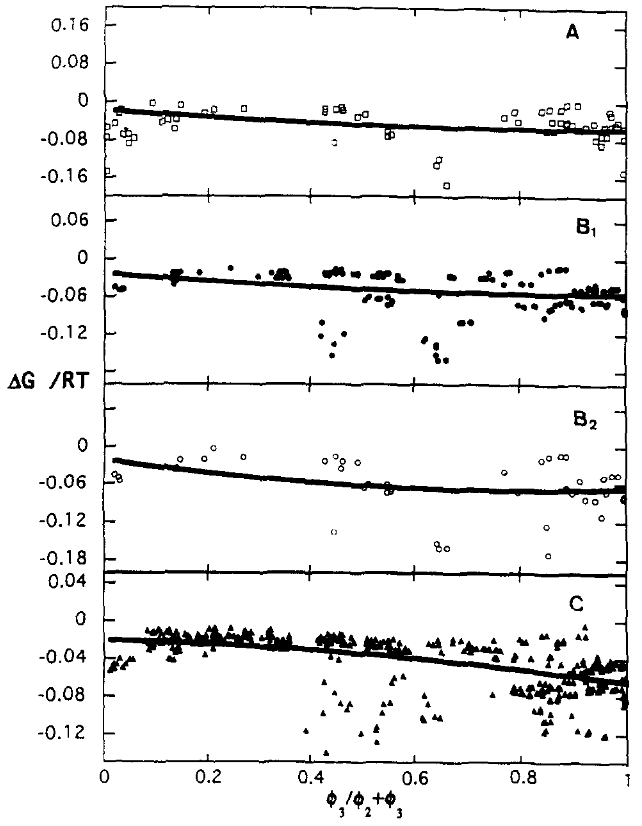

Figure 4 Dependence of the free energy of mixing, $\Delta G/RT$, on the reduced volume fraction, $\phi_3/(\phi_2+\phi_3)$. Plots have been built up as in *Figure 1*

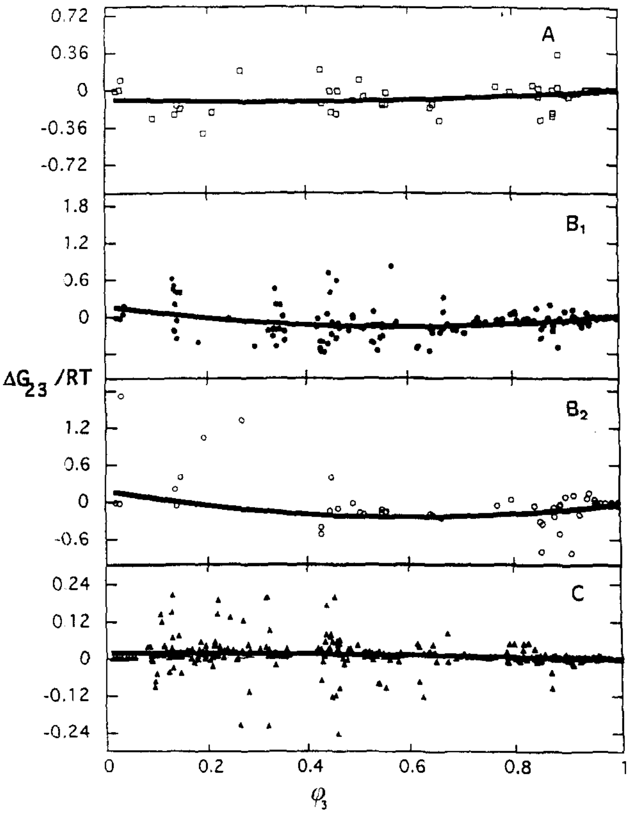

Figure 5 Dependence of the free energy of mixing for PVDF/PS, $\Delta G_{23}/RT$, on the reduced volume fraction, φ_3. Plots have been built up as in *Figure 1*

certain downward curvature towards negative values of ΔG, whereas the C option, excluding the g_T contribution, shows the opposite trend. In the light of this behaviour, the inclusion of the g_T parameter leads to ΔG values more consistent with the stability criteria of the complex ternary system studied here, as it shall be stated later. With the information handled here for the DMF/PVDF/PS ternary system, this contradictory behaviour cannot be fully justified.

On the other hand, it is rather more interesting to discuss the free-energy of mixing in a binary polymer/polymer system as a function of the blend composition. However, it is convenient to remember that the miscibility behaviour in polymer blends can be better illustrated by calculating the free energy of mixing as a function of both composition and temperature. For this end, the FH formalism can be used in two different ways that briefly can be described as follows:

i) Let us consider that the lattice is completely filled by the polymer subunits exclusively and that no chain ends and voids are included in the calculations. The energy of interaction between two unlike monomers is characterized through the interchange energy function g_{23}. The Flory–Huggins expression for the Gibbs free-energy of mixing is then given by:

$$\frac{\Delta G_{23}}{RT} = \frac{\varphi_2}{N_2}\ln\varphi_2 + \frac{\varphi_3}{N_3}\ln\varphi_3 + \varphi_2\varphi_3 g_{23} \qquad (8)$$

where φ_2 and φ_3 are the volume fractions, N_2 and N_3 the relative molar volumes of PVDF and PS, respectively, and g_{23} is the conventional interpolymer interaction function. The new volume fractions are related with those experimentally measured by: $\varphi_2 = \phi_2/(\phi_2+\phi_3)$ and $\varphi_3 = \phi_3/(\phi_2+\phi_3)$, and it is evident that the new boundary condition is $\varphi_2+\varphi_3 = 1$. The ΔG_{23} values obtained through equation (8) have been plotted against the reduced composition φ_3 in *Figure 5*. It is clearly seen that the values for options A, B_1 and B_2 (including g_T) show a similar trend as the g_{23} function depicted in *Figure 3*, whereas option C is slightly different. Therefore, the free energy of mixing in the blend is well characterized through the g_{23} parameter, at least from a qualitative point of view. For simplicity, we present the second order polynomial fit of these data only for options B_2 and C, being the coefficients also compiled in *Table 4*.

ii) Finally, we shall briefly discuss the extension of the FH theory for a virtual ternary system formed by void lattice sites and by the subunits of both polymers. The fraction of void sites is now expressed as ϕ_V, then $\phi_V+\phi_2+\phi_3 = 1$ or $\phi_2+\phi_3 = 1-\phi_V$. Notice that ϕ_V in this case is tantamount to ϕ_1 in the ternary DMF(1)/PVDF(2)/PS(3) polymer system, but considering now ϕ_V as constant (incompressible blend). It would be also useful to consider the blend as compressible and then ϕ_V would behave as strongly dependent on the pressure, which is the starting point of Sanchez–Lacombe lattice-fluid theory[47–49], but this matter falls out of our scope. *Figure 6* shows plots of ΔG_{23} data calculated with equation (8) using the experimental ϕ_2 and ϕ_3 values instead of the reduced volume fractions φ_2 and φ_3, and the corresponding g_{23} data from all options. In this figure, the observed behaviour for ΔG_{23} is similar to that shown in *Figure 5* but with a reduced scatter of points or, in other words,

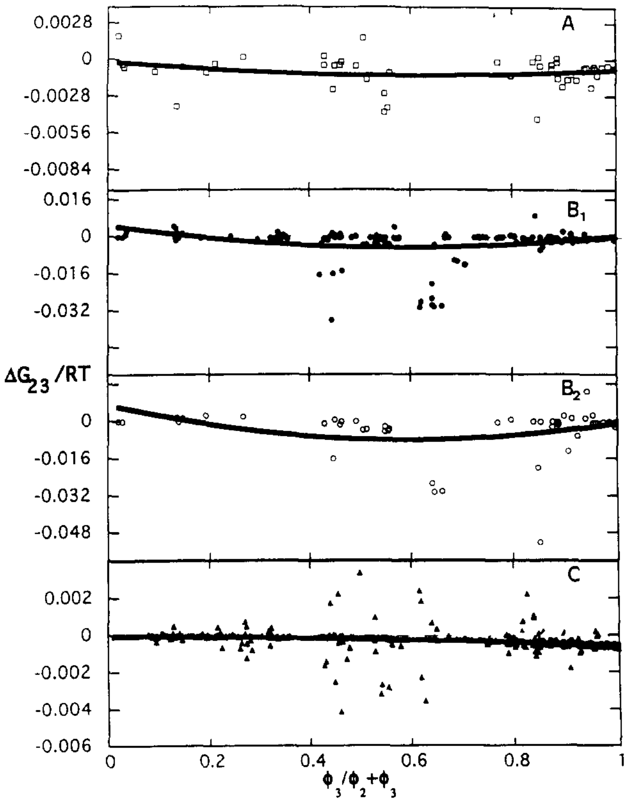

Figure 6 Dependence of the free energy of mixing for PVDF/PS, $\Delta G_{23}/RT$, on the reduced volume fraction, $\phi_3/(\phi_2+\phi_3)$. Plots have been built up as in *Figure 1*

the data are better fitted if the void lattice sites are taken into account.

Summarizing, *Figures 4–6* display most of the data placed around the $\Delta G = 0$ line which are the coefficients of the second order polynomial fit (collected in *Table 4*) and are very small ($\approx 10^{-4}$). This would mean, in principle, that ΔG from *Figure 4* or ΔG_{23} from *Figures 5* and *6* vanishes, which results in the assumption that both entropy (combinatorial and non-combinatorial) and enthalpy of mixing contributions cancel out. Therefore, the polymer mixture under these experimental conditions seem to behave as a metastable and a small perturbation can lead to cloudiness or opacity for the blend solution or in the dry blend, respectively. This conclusion seems to be in agreement with the recently reported behaviour of this blend[43–45] which exhibits a weakly incompatible character.

CONCLUSIONS

Complex behaviour of binary polymer solutions and blends has been studied using an extension of the Flory–Huggins theory. The free-energy function used here mainly includes the composition dependence of the polymer–solvent and polymer–polymer interaction parameters, as well as the ternary interactions by means of the $g_{\rm T}$ parameter, scarcely reported in this kind of study. Experimental ternary phase diagrams for the DMF(1)/PVDF(2)/PS(3) polymer system have been monitored by means of the s.e.c. technique following a procedure previously proposed. A large number of experiments, 27 run × 5 tie-lines each, have been carried out in order to obtain the numerical values for each component in the two phases in equilibrium. From a pragmatic viewpoint, in order to improve the reliability of the calculations of both interaction parameters and Gibbs free-energy of mixing as a function of the polymer composition, we have included several constraints classed within four options. It is clearly evidenced that those including the $g_{\rm T}$ parameter (A, B_1 and B_2 throughout the paper) successfully predict the miscibility and the stability of the coexisting phases. Despite the values of g_{ij}, $g_{\rm T}$, ΔG and ΔG_{23} have large uncertainties, the agreement with the predictions is at least reasonable. Thus, the differences between the χ_{12}, χ_{13} and g_{23} values evaluated here and those obtained from experimental measurements may arise from inherent limitations associated with the techniques together with the meaningful approximation made in each option.

In addition, the PVDF–PS interaction parameter evaluated in absence of DMF is quite close to zero in fair agreement with other experimental data measured by inverse gas chromatography[44] and isothermal crystallization techniques[43,45]. Work is in progress to extend this formalism in order to drastically suppress approximations related to the composition-dependence of the interaction parameters. A more robust set of thermodynamic equations, 15 at least instead of the 12 used here, must be implemented and will be reported in a later contribution. Furthermore, progress on the theory including the effects of polydispersity will improve the predictions in real polymer blends.

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APPENDIX

In the light of equation (1), for a quasi-ternary polymer system the polydispersity effects can be introduced in the free energy of mixing by means of an average degree of polymerization, affecting to the residual part of the function represented by $\Gamma(\phi)$ in equation (3). Because of the ternary polymer system used here is formed by a polydisperse polymer sample, PVDF(2), and by a monodisperse standard polymer, PS(3), equation (3) can be rewritten as:

$$\begin{aligned}\Gamma(\phi) &= n_1\phi_2 g_{12} + n_1\phi_3 g_{13} + (n_2\bar{x}_2\phi_3 \text{ or } \phi_2 n_3 x_3)g_{23} \\ &\quad + (n_1\phi_2\phi_3 \text{ or } \phi_1\phi_3 n_2\bar{x}_2 \text{ or } \phi_1\phi_2 n_3 x_3)g_{\mathrm{T}} \qquad \text{(A1)}\end{aligned}$$

where the average degree of polymerization only remains for the PVDF and it has been removed for the PS sample.

Next, the appropriate thermodynamic equations dealing with the liquid–liquid phase equilibrium can be built for each component by combining equations (4) and (5). Notice that from a practical viewpoint we have inserted into equation (4) the expression for $\Gamma(\phi)$ given by equation (A1). Thus, the final relationships are, for component 1:

$$\begin{aligned}&\ln\left(\frac{\phi_1'}{\phi_1''}\right) + (\phi_2' - \phi_2'')\left(1 - \frac{V_1}{V_2}\right) + (\phi_3' - \phi_3'')\left(1 - \frac{V_1}{V_3}\right) \\ &\quad + \left[(g_{12})' - \frac{\phi_3'\phi_1'}{\phi_3' + \phi_2'}\left(\frac{dg_{13}}{d\phi_3}\right)'\right]\phi_3'(1 - \phi_1') \\ &\quad - \left[(g_{13})'' - \frac{\phi_3''\phi_1''}{\phi_3'' + \phi_2''}\left(\frac{dg_{13}}{d\phi_3}\right)''\right]\phi_3''(1 - \phi_1'') \\ &\quad - \left[(g_{23})' + \phi_3'\left(\frac{dg_{23}}{d\phi_3}\right)'\right]\phi_2'\phi_3' \\ &\quad + \left[(g_{23})'' + \phi_3''\left(\frac{dg_{23}}{d\phi_3}\right)''\right]\phi_2''\phi_3'' \\ &\quad + \left[(g_{\mathrm{T}})' - \frac{\phi_1'\phi_3'}{1 - 2\phi_1'}\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)'\right]\phi_2'\phi_3'(1 - 2\phi_1') \\ &\quad - \left[(g_{\mathrm{T}})'' - \frac{\phi_1''\phi_3''}{1 - 2\phi_1''}\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)''\right]\phi_2'\phi_3'(1 - 2\phi_1') \\ &= 0 \qquad \text{(A2)}\end{aligned}$$

for component 2:

$$\begin{aligned}&\ln\left(\frac{\phi_2'}{\phi_2''}\right) + (\phi_1' - \phi_1'')\left(1 - \frac{V_2}{V_1}\right) + (\phi_3' - \phi_3'')\left(1 - \frac{V_2}{V_3}\right) \\ &\quad + \left[(g_{12})' - \phi_2'\left(\frac{dg_{12}}{d\phi_2}\right)'\right]\frac{V_2}{V_1}\phi_1'(1 - \phi_2') \\ &\quad - \left[(g_{12})'' - \phi_2''\left(\frac{dg_{12}}{d\phi_2}\right)''\right]\frac{V_2}{V_1}\phi_1''(1 - \phi_2'') \\ &\quad - \left[(g_{13})' + \phi_3'\left(\frac{dg_{13}}{d\phi_3}\right)'\right]\frac{V_2}{V_1}\phi_1'\phi_3' \\ &\quad + \left[(g_{13})'' + \phi_3''\left(\frac{dg_{13}}{d\phi_3}\right)''\right]\frac{V_2}{V_1}\phi_1''\phi_3'' \\ &\quad + \left[(g_{23})' - \frac{\phi_2'\phi_3'}{\phi_1' + \phi_3'}\left(\frac{dg_{23}}{d\phi_3}\right)'\right]\frac{V_2}{V_1}\phi_3'(1 - \phi_2') \\ &\quad - \left[(g_{23})'' - \frac{\phi_2''\phi_3''}{\phi_1'' + \phi_3''}\left(\frac{dg_{23}}{d\phi_3}\right)''\right]\frac{V_2}{V_1}\phi_3''(1 - \phi_2'') \\ &\quad + \left[(g_{\mathrm{T}})' - \frac{\phi_2'\phi_3'}{1 - 2\phi_2'}\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)'\right]\frac{V_2}{V_1}\phi_1'\phi_3'(1 - 2\phi_1') \\ &\quad - \left[(g_{\mathrm{T}})'' - \frac{\phi_2''\phi_3''}{1 - 2\phi_2''}\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)''\right]\frac{V_2}{V_1}\phi_1''\phi_3''(1 - 2\phi_2'') \\ &= 0 \qquad \text{(A3)}\end{aligned}$$

and, for component 3:

$$\begin{aligned}&\ln\left(\frac{\phi_3'}{\phi_3''}\right) + (\phi_1' - \phi_1'')\left(1 - \frac{V_3}{V_1}\right) + (\phi_2' - \phi_2'')\left(1 - \frac{V_3}{V_2}\right) \\ &\quad - \left[(g_{12})' + \phi_3'\left(\frac{dg_{12}}{d\phi_2}\right)'\right]\frac{V_3}{V_1}\phi_1'\phi_2'\end{aligned}$$

$$
\begin{aligned}
&+\left[(g_{12})''+\phi_2''\left(\frac{dg_{12}}{d\phi_2}\right)''\right]\frac{V_3}{V_1}\phi_1''\phi_2''\\
&+\left[(g_{13})'+\phi_3'\left(\frac{dg_{13}}{d\phi_3}\right)'\right]\frac{V_3}{V_1}\phi_1'(1-\phi_3')\\
&-\left[(g_{13})''+\phi_3''\left(\frac{dg_{13}}{d\phi_3}\right)''\right]\frac{V_3}{V_1}\phi_1''(1-\phi_3'')\\
&+\left[(g_{23})'+\phi_3'\left(\frac{dg_{23}}{d\phi_3}\right)'\right]\frac{V_3}{V_1}\phi_2'(1-\phi_3')\\
&-\left[(g_{23})''+\phi_3''\left(\frac{dg_{23}}{d\phi_3}\right)''\right]\frac{V_3}{V_1}\phi_2''(1-\phi_3'')\\
&+\left[(g_{\mathrm{T}})'-\frac{\phi_1'\phi_3'+\phi_2'\phi_3'}{1-2\phi_3'}\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)'\right]\frac{V_3}{V_1}\phi_1'\phi_2'(1-2\phi_3')\\
&-\left[(g_{\mathrm{T}})''+\frac{\phi_1''\phi_3''+\phi_2'\phi_3'}{1-2\phi_3''}\left(\frac{\partial g_{\mathrm{T}}}{\partial\phi_3}\right)''\right]\\
&\times\frac{V_3}{V_1}\phi_1''\phi_2''(1-2\phi_3'')=0 \qquad \text{(A4)}
\end{aligned}
$$