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Evaluation of thermodynamic parameters for blends of polyethersulfone and poly(methyl methacrylate) or polystyrene in dimethylformamide

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Liquid–liquid phase separation phenomena have been investigated for a ternary system containing two polymers and a solvent. Namely, dimethylformamide (DMF)/polyethersulfone (PES)/poly(methyl methacrylate) (PMMA) and DMF/PES/Polystyrene (PS). The composition of the three components in the two phases in equilibrium has been determined by size exclusion chromatographic (s.e.c.) analysis. The lattice-based mean-field theory, first developed by Flory and Huggins, has been modified to adequately describe these systems. In this respect, we have assumed that the parameters depend on the polymer concentration, and we have included a ternary parameter. The phase equilibrium compositions have been used as input data to solve a set of equations raised following four different approximations mainly concerned with the composition dependence of the interaction parameters. Values of the Gibbs free energy of mixing as a function of the blend composition were also evaluated and discussed in terms of the blend stability. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The understanding and prediction of the phase behaviour of polymer blends is a challenging theoretical problem of both scientific and commercial importance. Prediction of polymer–polymer miscibility is important, not only for application-oriented studies in polymer materials science but also for basic research in the field of critical phenomena[1–3]. The predictability of phase diagrams for ternary systems composed of two polymers dissolved in a common solvent by means of reliable methods would be of great practical importance for the preparation of membranes[4] or, more generally, for the processing of polymer mixtures[5,6].

In general, the miscibility of a polymer pair is dictated by the change in Gibbs free energy of mixing, ΔG. More precisely, the thermodynamics of a polymeric system are determined by its parameters: the molecular weights of the components and the interaction parameters between the components[7]. The interaction parameters are a measure of the enthalpic interaction between the components; moreover, they contain a nonideality term. Their determination can be performed in a number of ways; among them are static light scattering[8] and osmometry[9] techniques.

In this paper, it is our intention to determine the interaction parameters involved in the phase behaviour of a ternary polymer/polymer/solvent system. We will adopt the Flory–Huggins theory (FH), as most of the studies on miscibility[7,10–12], since by its relative simplicity it gives excellent insight into the underlying properties that cause the phase behaviour. This lattice-based mean-field theory assumes incompressibility, no volume change on mixing, and random local contacts between unlike species. Also, it is considered that the essential characteristics of the phase phenomena of these systems are not the result of polar effects or hydrogen bonding that the FH approach cannot adequately describe. The authors are, however, completely aware that the FH theory is not adequate in the sense that it cannot describe many important effects. For a better quantitative study, other, more sophisticated, theories must be adopted[13–17].

The interaction parameter is often interpreted as an empirical quantity that can be used to bridge the gap between the simple FH[7,11,12] theory and the diverse range of phase behaviour observed experimentally for polymer systems. It is now generally accepted that in order to obtain quantitative agreement between FH theory and experimental observations for most systems the interaction parameter must be considered to be a function of both temperature and composition[18–21]. Also a ternary interaction parameter has been included to take into account contributions other than the binary ones.

The present work was undertaken as a continuation of previous work[22,23], to deepen the knowledge of the thermodynamics of ternary polymer systems. Studied here are the ternary systems dimethylformamide (DMF)/polyethersulfone (PES)/poly(methyl methacrylate) (PMMA) and DMF/PES/polystyrene (PS) in terms of the liquid–liquid phase equilibrium compositions. These ternary polymer systems separate in two phases in equilibrium at constant temperature (25°C) under certain composition conditions. From size exclusion chromatographic (s.e.c.) analysis the composition of the two phases can be known allowing to determine the binary and ternary interactions

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parameters using the FH theory for four different approximations.

EXPERIMENTAL

Chemicals

PES Victrex 3600P is a high engineering plastic, kindly supplied by ICI (Wilton, UK). The polydispersity index and weight average molar mass, M_w, were 2.60 and 38 000, respectively, as determined by s.e.c. using PS calibration standards. The PS standard was purchased from Tosoh Corp. (Tokyo, Japan) with $M_w = 18\,100$ and polydispersity index 1.01, as specified by the supplier. PMMA was purchased from Polymer Laboratories (Shropshire, UK) with $M_w = 750\,000$ and polydispersity index 1.05, as specified by the supplier. DMF from Scharlau (Barcelona, Spain) of s.e.c. grade was used as solvent. The densities of the chemicals were 1.32, 1.05, 1.20 and 0.9445 g ml^{-1} for PES, PS, PMMA and DMF, 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 ID) packed with highly crosslinked styrene–divinylbenzene copolymer of 10^5, 10^4 and 10^3 Å nominal pore-size from Waters. DMF, used as the mobile phase, was previously degassed and clarified by passing it under vacuum through a 0.45 mm 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 ml 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, and 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 2 days equilibration time, we first read the volume of each phase, secondly 250 ml of the top phase were withdrawn by using a microsyringe and accurately weighed. Injection of 90 ml of this solution gave a chromatogram with two peaks corresponding to each polymer. The mass amount of PES, PS and PMMA was obtained by using a calibration curve that relates the height of the peak with the weight of the

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)/PES(2)/PMMA(3)

Run	Tie-line	ϕ_1'	ϕ_2'	ϕ_3'	ϕ_1''	ϕ_2''	ϕ_3''
1	α	0.93792	0.05915	0.00293	0.93844	0.01800	0.04356
	β	0.94456	0.01376	0.04168	0.94624	0.01660	0.03716
	γ	0.93078	0.06853	0.00069	0.94035	0.01755	0.04210
	δ	0.94627	0.05273	0.00100	0.93474	0.01935	0.04591
	ϵ	0.94299	0.05596	0.00105	0.93583	0.01837	0.04580
2	α	0.94039	0.05405	0.00556	0.93034	0.01626	0.05340
	β	0.93342	0.06552	0.00106	0.94046	0.01622	0.04332
	γ	0.93817	0.06055	0.00128	0.93514	0.01532	0.04954
	δ	0.92448	0.07087	0.00465	0.94911	0.01305	0.03784
	ϵ	0.93593	0.06272	0.00135	0.93791	0.01471	0.04738
	ζ	0.93726	0.06001	0.00273	0.93603	0.01608	0.04789
3	α	0.94174	0.05038	0.00788	0.93748	0.01851	0.04401
	β	0.94084	0.04966	0.00950	0.93980	0.01769	0.04251
	γ	0.94469	0.04914	0.00617	0.93073	0.02502	0.04425
	δ	0.94246	0.04859	0.00895	0.93401	0.01810	0.04789
	ϵ	0.94311	0.04872	0.00817	0.93255	0.02078	0.04667
	ζ	0.94326	0.05051	0.00623	0.93475	0.02275	0.04250
4	α	0.94135	0.05696	0.00169	0.93587	0.01818	0.04595
	β	0.94320	0.05476	0.00204	0.93173	0.01725	0.051029
	γ	0.94319	0.05620	0.00061	0.93303	0.01908	0.04789
	δ	0.94222	0.05673	0.00105	0.93518	0.02057	0.04425
	ϵ	0.94281	0.05584	0.00135	0.93301	0.01753	0.04966
	ζ	0.94470	0.05361	0.00169	0.92908	0.02219	0.04873
5	α	0.91713	0.02247	0.06040	0.94026	0.05622	0.00352
	β	0.95570	0.03464	0.00966	0.92908	0.02982	0.04110
	γ	0.95261	0.01815	0.02924	0.94328	0.04042	0.01630
	δ	0.94036	0.02935	0.03029	0.93905	0.04113	0.01982
	ϵ	0.94373	0.04011	0.01616	0.93431	0.03306	0.03263

polymer. Once we knew the mass of each component in the 250 ml top phase, the respective quantities in the bottom phase could 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 we had the masses of the three components in the two conjugate phases for five or six tie-lines very close in composition. Following this method we obtained five groups (labelled 1–5), each of five or six tie-lines (α, β, γ, δ, ϵ and ζ).

RESULTS AND DISCUSSION

In order to study the miscibility of a ternary system solvent(1)/polymer(2)/ polymer(3), we have prepared different PES(2)/(PMMA)(3) and PES(2)/(PS)(3) mixtures by adding DMF(1) as a common solvent until phase separation occurs. According to the procedure described in Section 2, the volume fractions of each component (i = 1,2,3) in the two phases in equilibrium ϕ_i' and ϕ_i'' (a given tie-line) have been determined. Thus, *Tables 1* and *2* compile the equilibrium compositions obtained by s.e.c. analysis of different tie-lines (denoted by α, β, γ, δ, ϵ and ζ) for five different runs for DMF(1)/PES(2)/PMMA(3) and DMF(1)/PES(2)/PS(3) systems, respectively, at 25°C. For both systems, the two phases reach equilibrium in the solvent rich region, with a slight increase in miscibility gap for the system DMF/PES/PS. The values of the composition for two coexisting phases of diverse tie-lines (*Tables 1* and *2*) have been used as input data to calculate the different parameters involved in the theoretical description of the miscibility. For this reason, we use the Gibbs free energy of mixing two polymers in the presence of a solvent, ΔG, as a function of concentration-dependent interaction parameters. In the framework of the mean-field approximation[7] ΔG of a ternary system solvent(1)/polymer(2) /polymer(3) originated by mixing n_1, n_2 and n_3 moles of the corresponding components that occupy $n_1 + n_2\bar{x}_2 + n_3\bar{x}_3$ moles of lattice sites, $\bar{x}_i$ ($i = 2,3$) being the average polymerization degree, reads for a ternary system[22–26]:

$$\begin{aligned}\frac{\Delta G}{RT} &= (n_1 + n_2\bar{x}_2 + n_3\bar{x}_3)(\phi_1 \ln\phi_1 + \frac{1}{\bar{x}_2}\phi_2 \ln\phi_2 \\ &\quad + \frac{1}{\bar{x}_3}\phi_3 \ln\phi_3 + \phi_1\phi_2 g_{12} + \phi_1\phi_3 g_{13} + \phi_2\phi_3 g_{23} \\ &\quad + \phi_1\phi_2\phi_3 g_{\mathrm{T}}) = n_1 \ln\phi_1 + n_2 \ln\phi_2 + n_3 \ln\phi_3 \\ &\quad + n_1\phi_2 g_{12} + n_1\phi_3 g_{13} + (n_2\bar{x}_2\phi_3 \text{ or } \phi_2 n_3\bar{x}_3) g_{23} \\ &\quad + (n_1\phi_2\phi_3 \text{ or } \phi_1 n_2\bar{x}_2\phi_3 \text{ or } \phi_1\phi_2 n_3\bar{x}_3) g_{\mathrm{T}} \qquad (1)\end{aligned}$$

where ϕ_i ($i = 1,2,3$) is the volume fraction of component i; g_{ij} ($i = 1,2$; $j = 2,3$; $i \neq j$) is the thermodynamic interaction parameter between a molecule of component 1 and a chain segment of polymers 2 and 3 or between two monomer units, and g_{T} is the so-called ternary interaction parameter with still unclear physical meaning and that includes interactions that are ternary in nature[27]. According to equation (1), g_{23} is the interaction parameter between two segments of polymer 2 and 3 with mean polymerization degrees $\bar{x}_2$ and $\bar{x}_3$; thus g_{23} refers to the interaction between polydisperse species 2 and 3 with mean average volume fraction

$$\phi_2 = \sum_{i=1}^{m_2} \phi_{2,x_i} \text{ and } \phi_3 = \sum_{j=1}^{m_3} \phi_{3,x_j}$$

Table 2 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)/PES(2)/PS(3)

Run	Tie-line	ϕ_1'	ϕ_2'	ϕ_3'	ϕ_1''	ϕ_2''	ϕ_3''
1	α	0.75617	0.03298	0.21085	0.90271	0.08198	0.01531
	β	0.74700	0.02551	0.22749	0.90026	0.08301	0.01673
	γ	0.75691	0.02444	0.21865	0.89866	0.08459	0.01675
	δ	0.73748	0.04106	0.22146	0.90879	0.07695	0.01426
	ϵ	0.74813	0.03288	0.21899	0.90351	0.08102	0.01547
2	α	0.73872	0.05911	0.20217	0.90085	0.06972	0.02943
	β	0.71543	0.07358	0.21099	0.90281	0.06843	0.02876
	γ	0.64713	0.09371	0.25916	0.90488	0.06699	0.02813
	δ	0.67684	0.06433	0.25883	0.91775	0.05804	0.02421
	ϵ	0.76330	0.02709	0.20961	0.89677	0.07391	0.02932
3	α	0.81927	0.04421	0.13562	0.89755	0.06884	0.03361
	β	0.82037	0.04410	0.13553	0.89693	0.06925	0.03382
	γ	0.82338	0.03882	0.13780	0.90343	0.06521	0.03136
	δ	0.82206	0.03901	0.13893	0.90409	0.06455	0.03136
	ϵ	0.83132	0.03200	0.13668	0.89423	0.07146	0.03431
4	α	0.65276	0.08028	0.26696	0.90794	0.06570	0.02636
	β	0.70374	0.05999	0.23627	0.90557	0.06774	0.02669
	γ	0.70109	0.05452	0.24439	0.90590	0.06836	0.02574
	δ	0.63935	0.07444	0.28621	0.90909	0.06617	0.02474
	ϵ	0.63954	0.07896	0.28150	0.90953	0.06569	0.02478
5	α	0.83920	0.02030	0.14050	0.90009	0.06825	0.03166
	β	0.78794	0.04990	0.16216	0.92301	0.05231	0.02468
	γ	0.81588	0.02787	0.15625	0.90872	0.06374	0.02754
	δ	0.81594	0.02886	0.15520	0.90885	0.06325	0.02790
	ϵ	0.80797	0.04146	0.15057	0.90243	0.06812	0.02945

where ϕ_{2,x_i} and ϕ_{3,x_j} are the volume fraction of the chains of polymer 2 with degree of polymerization x_i and of polymer 3 with degree of polymerization x_j. The symbols m_2 and m_3 refer to the number of chains of polymers 2 and 3 with different degree of polymerization. Note that g_{ij} and g_T are considered to be concentration-dependent parameters in contrast to the original FH theory that assumed them to be exclusively temperature dependent and to most of the reported literature[19,21,25,28,29] on the field due to the inherent mathematical complexity in solving the equilibrium equations. Moreover, it is assumed that the binary g_{ij} interaction parameters are truly binary[29], i.e. that they are only dependent on the components i and j. The interaction parameters are thus dependent on the following variables:

g_{12} is dependent on $\phi_2/(\phi_1+\phi_2)$
g_{13} is dependent on $\phi_3/(\phi_1+\phi_3)$
g_{23} is dependent on $\phi_3/(\phi_2+\phi_3)$
g_T is dependent on $(\phi_2+\phi_3)/(\phi_1+\phi_2+\phi_3)=\phi_2+\phi_3$

In order to calculate the different interaction parameters involved in equation (1) one should start, from the theoretical viewpoint, from the Gibbs' two-phase equilibrium condition[30] that under constant temperature and pressure is expressed by:

$$\Delta\mu_i(\phi_1,\phi_2,\phi_3)'=\Delta\mu_i(\phi_1,\phi_2,\phi_3)'' \tag{2}$$

where $i=1,2,3$ refers to the different components of the ternary mixture, and the prime and double prime refer to the two coexisting phases. Here, the expressions for the chemical potentials of the solvent, $\Delta\mu_1$, and of the two polymers, with mean polymerization degree $\bar{x}_2$ and $\bar{x}_3$, $\Delta\mu_{2,\bar{x}_2}$ and $\Delta\mu_{3,\bar{x}_3}$, in the framework of the FH theory can be expressed as:

$$\begin{aligned}\frac{\Delta\mu_1}{RT}&=\frac{1}{RT}\left(\frac{\partial\Delta G}{\partial n_1}\right)_{n_2,n_3,p,\mathrm{T}}\\&=\ln\phi_1+\left(1-\frac{V_1}{V_2}\right)\phi_2+\left(1-\frac{V_1}{V_3}\right)\phi_3\\&\quad+\left[g_{12}-\frac{\phi_1\phi_2}{\phi_2+\phi_3}\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}\right]\phi_2(1-\phi_1)\\&\quad+\left[g_{13}-\frac{\phi_1\phi_3}{\phi_2+\phi_3}\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right]\phi_3(1-\phi_1)\\&\quad-\left[g_{23}+\phi_3\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right]\phi_2\phi_3\\&\quad+\left[g_\mathrm{T}-\frac{\phi_1\phi_3}{1-2\phi_1}\left(\frac{\partial g_\mathrm{T}}{\partial\phi_3}\right)\right]\phi_2\phi_3(1-2\phi_1)\end{aligned} \tag{3}$$

$$\begin{aligned}\frac{\Delta\mu_{2,\bar{x}_2}}{RT}&=\frac{1}{RT}\left(\frac{\partial\Delta G}{\partial n_2}\right)_{n_1,n_3,p,\mathrm{T}}\\&=\ln\phi_2+\left(1-\frac{V_2}{V_1}\right)\phi_1+\left(1-\frac{V_2}{V_3}\right)\phi_3\\&\quad+\left[g_{12}+\phi_2\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}\right]\phi_1(1-\phi_2)\frac{V_2}{V_1}\\&\quad-\left[g_{13}+\phi_3\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right]\phi_1\phi_3\frac{V_2}{V_1}\\&\quad+\left[g_{23}-\frac{\phi_2\phi_3}{\phi_1+\phi_3}\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right]\phi_3(1-\phi_2)\frac{V_2}{V_1}\\&\quad+\left[g_\mathrm{T}-\frac{\phi_2\phi_3}{1-2\phi_2}\left(\frac{\partial g_\mathrm{T}}{\partial\phi_3}\right)\right]\phi_1\phi_3(1-2\phi_2)\frac{V_2}{V_1}\end{aligned} \tag{4}$$

$$\begin{aligned}\frac{\Delta\mu_{3,\bar{x}_3}}{RT}&=\frac{1}{RT}\left(\frac{\partial\Delta G}{\partial n_3}\right)_{n_1,n_2,p,\mathrm{T}}\\&=\ln\phi_3+\left(1-\frac{V_3}{V_1}\right)\phi_1+\left(1-\frac{V_3}{V_2}\right)\phi_2\\&\quad-\left[g_{12}+\phi_2\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}\right]\phi_1\phi_2\frac{V_3}{V_1}\\&\quad+\left[g_{13}+\phi_3\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right]\phi_1(1-\phi_3)\frac{V_3}{V_1}\\&\quad+\left[g_{23}+\phi_3\frac{\mathrm{d}g_{23}}{\mathrm{d}\phi_3}\right]\phi_2(1-\phi_3)\frac{V_3}{V_1}\\&\quad+\left[g_\mathrm{T}+\frac{\phi_1\phi_3+\phi_2\phi_3}{1-2\phi_3}\left(\frac{\partial g_\mathrm{T}}{\partial\phi_3}\right)\right]\phi_1\phi_2(1-2\phi_3)\frac{V_3}{V_1}\end{aligned} \tag{5}$$

Therefore, from the equilibrium condition (equation (2)) developed by substituting equations (3)–(5) for the coexisting phases we obtain three equations to be solved with the following unknowns: $(g_{12})'$, $(g_{13})'$, $(g_{23})'$, $(g_T)'$, $(g_{12})''$, $(g_{13})''$ $(g_{23})''$, $(g_T)''$, as well as their derivatives: $(\mathrm{d}g_{12}/\mathrm{d}\phi_2)'$, $(\mathrm{d}g_{13}/\mathrm{d}\phi_3)'$, $(\mathrm{d}g_{23}/\mathrm{d}\phi_3)'$, $(\partial g_T/\partial\phi_3)'$, $(\mathrm{d}g_{12}/\mathrm{d}\phi_2)''$, $(\mathrm{d}g_{13}/\mathrm{d}\phi_3)''$, $(\mathrm{d}g_{23}/\mathrm{d}\phi_3)''$ and $(\partial g_T/\partial\phi_3)''$. For calculation purposes, we have used as input data the α–ζ tie-line compositions defined by the coordinates $(\phi_1',\phi_2',\phi_3')$ and $(\phi_1'',\phi_2'',\phi_3'')$ of the different runs compiled in *Tables 1* and 2 on the basis of a ternary diagram. So, for each tie-line we could write down a set of three equations. However, as we have 16 unknowns, a set of 16 equations should have to be solved. To simplify the calculation process some rational approximations can be carried out to reduce the mathematical procedure. In this way, we next proceed to explain the different approximations made in this paper that are summarized in four options (A–D) that we consider as representatives of all the complex mathematical calculations.

Options A and D

In order to obtain the maximum number of parameters, and according to previous papers[22,23,29], we only assume that either g_{12} or g_{13} parameters change linearly with polymer composition. Remember that both g_{12} and g_{13} are defined as binary parameters[31] and essentially depend on $\phi_2/(\phi_1+\phi_2)$ or $\phi_3/(\phi_1+\phi_3)$, respectively. In this way, it has been assumed that $\mathrm{d}g_{12}/\mathrm{d}\phi_2$ in what we call option A, and $\mathrm{d}g_{13}/\mathrm{d}\phi_3$ for option B are constant at any polymer concentration; that is, they do not change for the two conjugate phases of a given tie-line neither among the different tie-lines of a given run. Thus, for Option A:

$$\left(\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}\right)'=\left(\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}\right)''=\frac{\mathrm{d}g_{12}}{\mathrm{d}\phi_2}$$

and for Option B:

$$\left(\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right)'=\left(\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}\right)''=\frac{\mathrm{d}g_{13}}{\mathrm{d}\phi_3}.$$

Here for each option we have eliminated one unknown, so 15 unknowns have to be determined and we need to solve a set of 15 linear equations. As three linear equations come out by introducing the two compositions in equilibrium of a given tie-line in the phase equilibrium equations (equations (2)–(5)), we need five tie-lines for every system of 15 equations to be raised. For DMF/PES/PMMA (*Table 1*) we have obtained by s.e.c. analysis two runs (1 and 5) of five tie-lines and three runs (2, 3, 4) of six tie-lines; consequently, we obtain two sets plus 6 × 3 sets of the 15 unknowns, respectively. On the other hand, for the DMF/PES/PS system only five sets of the 15 unknowns can be computed since each run has only five tie-lines.

In this way, each volume fraction of a given tie-line is substituted into the equilibrium condition (equations (2)–(5), being the total unknowns to be evaluated: (i) for Option A: $(g_{12})'$, $(g_{13})'$, $(g_{23})'$, $(g_T)'$, $(g_{12})''$, $(g_{13})''$, $(g_{23})''$, $(g_T)''$, as well as their derivatives: $(dg_{12}/d\phi_2)$, $(dg_{13}/d\phi_3)'$, $(dg_{23}/d\phi_3)'$, $(\partial g_T/\partial \phi_3)'$, $(dg_{13}/d\phi_3)''$, $(dg_{23}/d\phi_3)''$ and $(\partial g_T/\partial \phi_3)''$; and (ii) for Option B: $(g_{12})'$, $(g_{13})'$, $(g_{23})'$, $(g_T)'$, $(g_{12})''$, $(g_{13})''$ $(g_{23})''$, $(g_T)''$, as well as their derivatives: $(dg_{12}/d\phi_2)'$, $(dg_{13}/d\phi_3)$, $(dg_{23}/d\phi_3)'$, $(\partial g_T/\partial \phi_3)'$, $(dg_{12}/d\phi_2)''$, $(dg_{23}/d\phi_3)''$ and $(\partial g_T/\partial \phi_3)''$.

Option C

The next approximation assumes that the concentration dependence of the binary interaction parameters solvent–polymer can be neglected within a narrow concentration range such as the one considered into a set of adjacent tie-lines[22,23,29], i.e. $dg_{1i}/d\phi_i \rightarrow 0$ ($i = 2, 3$), and according to the nomenclature proposed by Flory $g_{12} = \chi_{12}$ and $g_{13} = \chi_{13}$. This approximation has been usually taken into account to theoretically describe the phase diagram for most of the binary as well as the ternary polymer systems. In contrast, the g_{23} and g_T parameters retain the same concentration dependence as explicited in the preceding options. At this point we need to solve a set of 12 equations to obtain the actual 12 unknowns, namely: $(\chi_{12})'$, $(\chi_{13})'$, $(g_{23})'$, $(g_T)'$, $(\chi_{12})''$, $(\chi_{13})''$, $(g_{23})''$, $(g_T)''$, $(dg_{23}/d\phi_3)'$, $(dg_{23}/d\phi_3)''$, $(\partial g_T/\partial \phi_3)'$ and $(\partial g_T/\partial \phi_3)''$.

In this option we need the composition of at least four tie-lines to solve a set of 12 equations. So, we get five and 15 sets of the 12 unknowns when five and six tie-lines per run are available to be combined in groups of four.

Option D

Finally we try to reduce the mathematical calculation at its minimum. For this reason we assume that: (i) the binary solvent–polymer parameters are independent of the polymer composition in all the composition range where phase separation takes place. In the preceding option this assumption has been restricted to the concentration range of each branch of the coexistence curve obtained from phase separation experiments; (ii) we omit the ternary parameter in the Gibbs free energy of mixing: $g_T = 0$. Most of the work carried out in the literature with the FH equation to interpret the ternary polymer systems follows these approximations due to the mathematical complexity of the other options[32,33]. These simplifications yield the following six unknowns: χ_{12}, χ_{13}, $(g_{23})'$, $(g_{23})''$, $(dg_{23}/d\phi_3)'$ and $(dg_{23}/d\phi_3)''$, and it suffices with two tie-lines to solve the six equations raised for this option. A set of five tie-lines per run allow to obtain (by combining them by pairs) 10 sets of the six unknowns, whereas with six tie-lines available 15 sets of the six unknowns are directly computed.

According to the different options explained above combined with the data compiled in *Tables 1* and *2*, the number of parameters that can be obtained for the system DMF/PES/PMMA is much greater than for the system DMF/PES/PS, although the miscibility gap of the latter is wider.

Data analysis

Since we have now made some approximations in order to reduce the number of unknowns to the number of equations that can be written as a function of the volume fractions of the conjugate phases. Once we obtain the computed unknowns, a selection of these data is first made by neglecting all the data falling outside of the range of three times the standard deviation. Secondly, their physical meaning have to be ascertained to clarify at which extent the approximations carried out in the different options can be meaningful. There are two different concepts that have to be interconnected: the mathematical procedure to solve the equations and the physical significance of the numerical data obtained.

Figure 1 shows the dependence of the binary parameters g_{12} or χ_{12} on the binary mixture composition $\phi_2/(\phi_1 + \phi_2)$ for the different options explained above (A–D from top to bottom) for DMF(1)/PES(2)/PMMA(3) and DMF(1)/PES(2)/PS(3) systems. Remember that these parameters that represent binary solvent–polymer segment interactions depend uniquely on the volume fraction of the polymer(2) in the binary mixture (solvent + polymer)[31,34,35] and so, they are a function of $\phi_2/(\phi_1 + \phi_2)$. As can be observed, there is a good quantitative agreement between the DMF/PES binary interaction parameters, g_{12} or χ_{12}, obtained from both ternary polymer systems for every option assayed. Moreover, this parameter does not show any

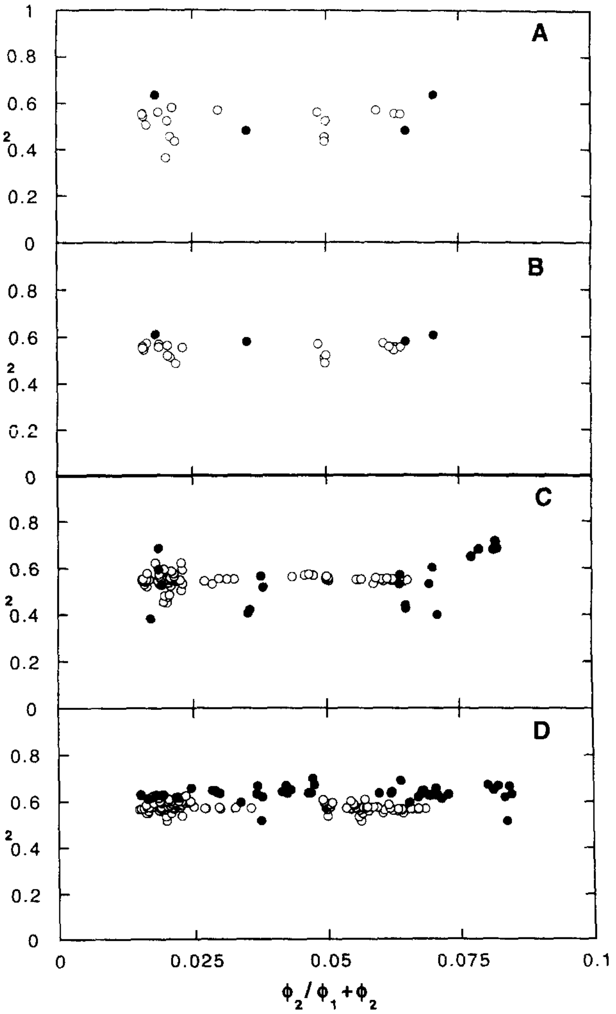

Figure 1 Plot of the interaction parameters g_{12} and χ_{12} against the ternary polymer system composition, $\phi_2/(\phi_1 + \phi_2)$ for DMF/PES/PMMA (○) and DMF/PES/PS (●) systems. The four plots refer, from top to bottom, to options A, B, C and D

significant dependence on the polymer concentration as usually assumed in the literature[29]. Thus the average g_{12} or χ_{12} (for options C and D) values are: 0.524, 0.554 and 0.555 for options A, B and C, respectively, irrespective of the system either DMF/PES/PMMA or DMF/PES/PS. However $\chi_{12} = 0.577$ for DMF/PES/PMMA and a value slightly different of 0.634 for the system DMF/PES/PS is obtained when using option D.

Similar results to those shown in *Figure 1* have been obtained for the binary interaction parameter between DMF–PMMA or DMF–PS, g_{13} (options A and B) or χ_{13} (options C and D). Notice that now the binary parameter characterizes the system assayed. Consequently, the average interaction parameters for DMF/PMMA are 0.485; 0.494; 0.503 and 0.561, and for DMF/PS are 0.604, 0.571, 0.590 and 0.613, for options A, B, C and D, respectively. A practically negligible dependence of this parameter as well as of g_{12} on the polymer concentration is deduced. However, slightly different values for both g_{13} parameters have been estimated in every option.

The values of the derivatives $dg_{12}/d\phi_2$ and $d\phi_{13}/d\phi_3$ can be also numerically obtained with mean values of − 0.052 and − 0.020 for $dg_{12}/d\phi_2$ and − 0.019 and 0.044 for $dg_{13}/d\phi_3$, for options A and B, respectively for DMF/PES/PMMA and − 0.058 and 0.057 for DMF/PES/PS. These dependences are in fact negligible and the approximation $dg_{1i}/d\phi_i = 0$ ($i = 2,3$) is valid.

So, from the inspection of the binary solvent–polymer parameters and their dependence on polymer concentration it can be concluded that: (i) the interaction parameter between DMF and PES, g_{12}, obtained for options A and B or χ_{12} for option C does not depend on the ternary system from which it is deduced; (ii) from the plot of g_{1i} ($i = 2,3$) *versus* $\phi_i/(\phi_1+\phi_i)$ a negligible dependence of the binary parameter on the polymer concentration is observed and corroborated by the very small numerical values of $dg_{1i}/d\phi_i$ obtained from options A and B; (iii) the small values of $dg_{12}/d\phi_2$ and their apparent non-dependence on composition obtained from options A and B support the idea that they can be negligible, as assumed in option C. These statements confirm the validity of the mathematical method used to obtain these parameters.

A test of the mathematical method proposed can be carried out by comparing these interaction parameters with reported ones. So, the g_{12} and g_{13} values are used as a check of the accuracy of the set up. However, values of g_{1i} are difficult to find in the literature since the parameter experimentally obtained is the Flory, χ_{1i}, interaction parameter independent of polymer composition. For the sake of comparison with experimental data the values of χ^0_{13} (χ_{13} at $\phi_3/(\phi_1 + \phi_3) \rightarrow 0$) have been evaluated from the calculated g_{13} parameter according to the following expression[35–37]:

$$\chi^0_{13} = g^0_{13} - \left(\frac{dg_3}{d(\phi_3/(\phi_1 + \phi_3))}\right)_{\phi_3 \rightarrow 0} \qquad (6)$$

where g^0_{13} is the value of g_{13} extrapolated for $\phi_3 \rightarrow 0$. For options C and D the values of χ^0_{13} are directly obtained from the extrapolation at $\phi_3 \rightarrow 0$ of the corresponding plots with values of 0.510 and 0.563 for DMF(1)/PMMA(3) and 0.582 and 0.611 for DMF(1)/PS(3). The χ^0_{13} calculated values (equation (6)) for options A and B are 0.439 and 0.460 for DMF/PMMA and 0.541 and 0.461 for DMF/PS.

The experimental values of the interaction parameter at infinite dilution, χ^0_{13}, can be easily obtained from light scattering or viscosity data if different molar masses of a polymer are available. As far as we know there are not reported χ^0_{13} values for the DMF/PMMA system, so we proceed to evaluate it from viscosimetric measurements. For this reason, the intrinsic viscosities in DMF of seven samples of PMMA standards from Polymer Laboratories with molar masses (as evaluated from s.e.c.): 1200000; 650000; 127000; 88000; 67000; 28300 and 9200 and

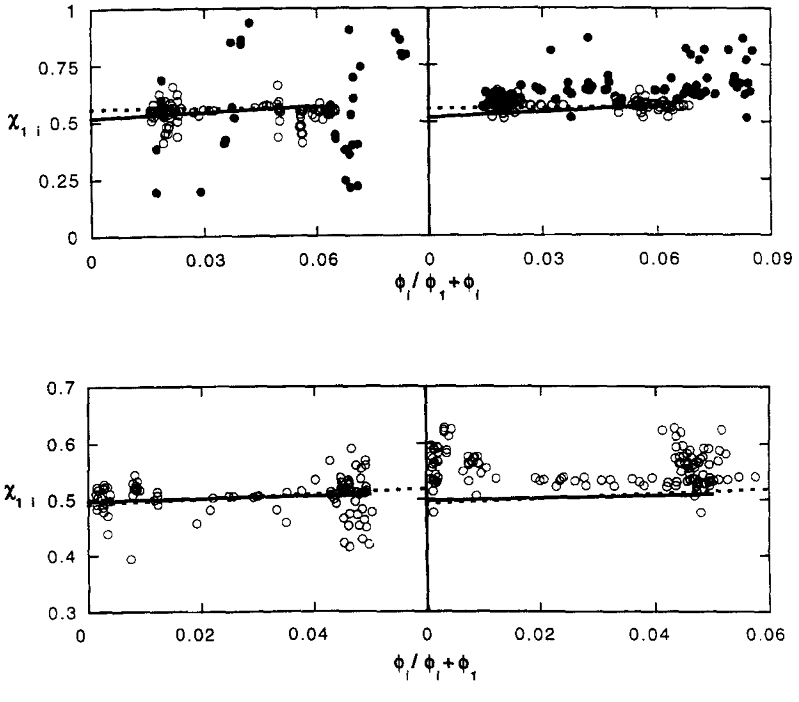

Figure 2 Plot of the interaction parameter χ_{1i} for DMF/PES (top figure) and DMF/PMMA (bottom figure) against the ternary polymer system composition, $\phi_i/(\phi_1 + \phi_i)$ ($i = 2,3$) for DMF/PES/PMMA (○) and DMF/PES/PS (●) systems according to options C (left hand side) and D (right hand side). Solid and dashed lines have been calculated with equation (7) for options A and B, respectively

polydispersity indices $1.04 \leq (M_w/M_n) \leq 1.06$ were measured. From the values obtained the Mark–Houwink–Sakurada equation for PMMA in DMF was $[\eta]/M^{1/2}$ *versus* $M^{1/2}$ (ml g^{-1}). From the slope of the Stockmayer–Fixman plot[38]: $[\eta]M^{1/2}$ *versus* $M^{1/2}$, the viscosimetric interaction parameter B is evaluated, which is related to the χ^0 parameter through

$$B = \frac{2\bar{v}^2}{NV}\left(\frac{1}{2} - \chi^0\right)$$

where $\bar{v}$ is the partial specific volume of the polymer ($\bar{v}$ = 0.805 ml g^{-1} for PMMA), N is Avogadro's number and V the molar volume of the solvent (V_{DMF} = 77.4 ml mol^{-1} at 25°C). So, a value of $\chi^0_{13} = 0.44 \pm 0.02$ for DMF/PMMA system was so obtained, which shows a very good agreement with values from options A and B. Option D deviates the most from the experimental value.

On the other hand, an average value of the interaction parameter χ^0_{13} for DMF-PS independent of polymer concentration at infinite dilution of 0.49 ± 0.02[22,39,40] is reported in the literature in accordance with the values obtained through A, B and C options.

As might be expected, strong discrepancies between data coming from different options arises since drastic approximations have been introduced in some cases (option D for instance). Despite these uncertainties, a good agreement between the χ_{13} theoretical and experimental values can be observed. Deviations can fall within the range of the uncertainty of the molar mass determination, and corroborate the validity of our treatment.

Moreover, we can check the self-consistency among the diverse options by comparing the parameters χ_{1i} (i = 2,3) obtained from options C and D with those calculated from options A and B through the following expression[41]:

$$\chi_{1i} = g_{1i} - \left(1 - \frac{\phi_i}{\phi_j + \phi_i}\right)\left(\frac{dg_{1i}}{d(\phi_i/(\phi_j + \phi_i))}\right) \qquad (7)$$

So, *Figure 2* shows the plot of the binary parameter χ_{1i} against $\phi_i/(\phi_1 + \phi_i)$, being the polymer i PES for the top figure and PMMA for the bottom one, the left-hand side figures refer to χ_{1i} parameters coming from Option C and the left hand side ones to option D. Solid and dashed lines have been calculated with equation (7) for options A and B, respectively, with the experimental g_{1i} and $dg_{1i}/d(\phi_i/(\phi_1 + \phi_i))$ values above obtained. The calculated χ_{1i} parameters for options A and B (solid and dashed lines) practically depict the same values that result to be the mean value of the parameters χ_{1i} calculated from option C with $dg_{1i}/d\phi_i = 0$ (i = 2,3), while the values obtained from option D are overestimated. These data suggest that options A, B and C reproduce much better the interaction parameters, are self-consistent. Option D seems to be at first sight the option with less accuracy due to the inherent approximations. The χ parameter for DMF(1)/PS(3) has also been calculated (results not shown) with a big uncertainty due to the scarce number of primary data, and in general show the same trend.

The following parameters to analyse are the polymer–polymer interaction parameter, g_{23}, the ternary parameter, g_T, and their derivatives $dg_{23}/d\phi_3$ and _$\partial g_T/\partial\phi_3$. In this respect, *Table 3* summarizes the mean values of g_{23}, g_T, $dg_{23}/d\phi_3$ and $\partial g_T/\partial\phi_3$, for the four options and the two ternary systems assayed. Note that it has been assumed that $g_T = 0$ in Option D. Looking carefully on the values obtained, we observe that g_{23} for options A, B and C are negative, whereas a positive value for option D is obtained. Values of this parameter are very scarce in the literature since the parameter usually obtained is the FH interaction parameter, χ_{23}, independent of polymer concentration, and a negative value of this parameter is associated with miscibility between the two polymers. However, the parameter directly included in ΔG is g_{23}, and this is the one with full thermodynamic significance. A negative value of g_{23} will decrease the numerical value of ΔG (equation (1)), and accordingly will favour miscibility between the two polymers. So looking at *Table 3*, options A, B and C give negative values for g_{23} and $dg_{23}/d\phi_3$, whereas for option D a positive value has been obtained for g_{23}. The values of g_T and its derivative are distinct from zero, although they take small numerical numbers. In order to check these results some differential scanning calorimetric (d.s.c.) and viscosimetric experiments have been done, and one T_g at intermediate weight fraction of PES and an increase of the viscosity have been obtained, indicating at first sight that the two polymers, PES/PMMA and PES/PS are miscible with a slight increase in miscibility (from viscosimetric data) for DMF/PES/PS (work in preparation). These experiments are in good accordance with data shown in *Table 3*. From g_{23} values the pair of polymer PES/PMMA seems to be more miscible than PES/PS, which is consistent with the fact that looking at the distribution of charge density the attractive interaction between PES and PMMA should be greater than between PES and PS. Nevertheless, more experimental work is being carried out in order to test the accuracy of the interaction parameters here calculated, and to elucidate the extent of miscibility between the two polymers. So it seems that option D developed with the maximum number of approximations do not reflect properly the miscibility behaviour of a polymer system.

From the calculated g_{23} values we can also obtain the commonly used interaction parameter independent of polymer concentration χ_{23}[41]:

$$\chi_{23} = g_{23} - \left(1 - \frac{\phi_3}{\phi_2 + \phi_3}\right)\left(\frac{dg_{23}}{d(\phi_3/\phi_2 + \phi_3)}\right) \qquad (8)$$

The values for χ_{23} so obtained are plotted in *Figure 3* for the four options A–D and the two systems assayed DMF/PES/PMMA and DMF/PES/PS. The dependence of χ_{23} on $\phi_3/\phi_2 + \phi_3$ is similar to the one obtained for g_{23}. For options A, B and C the parameter takes mainly negative values, whereas for option D smaller and positive values are

Table 3 Mean values of g_{23}, $dg_{23}/d\phi_3$, g_T and $\partial g_T/\partial\phi_3$ parameters as evaluated through diverse options for the two systems

Option	DMF/PES/PMMA				DMF/PES/PS			
	g_{23}	$dg_{23}/d\phi_3$	g_T	$\partial g_T/\partial\phi_3$	g_{23}	$dg_{23}/d\phi_3$	g_T	$\partial g_T/\partial\phi_3$
A	− 1.12	− 3.93	1.24	3.79	− 0.57	− 12.72	0.33	18.72
B	− 0.69	− 11.47	0.76	12.18	− 0.46	− 3.66	0.78	4.01
C	− 0.95	− 9.66	1.08	10.48	− 0.88	− 0.498	1.19	1.749
D	0.06	0.655			0.08	− 0.513		

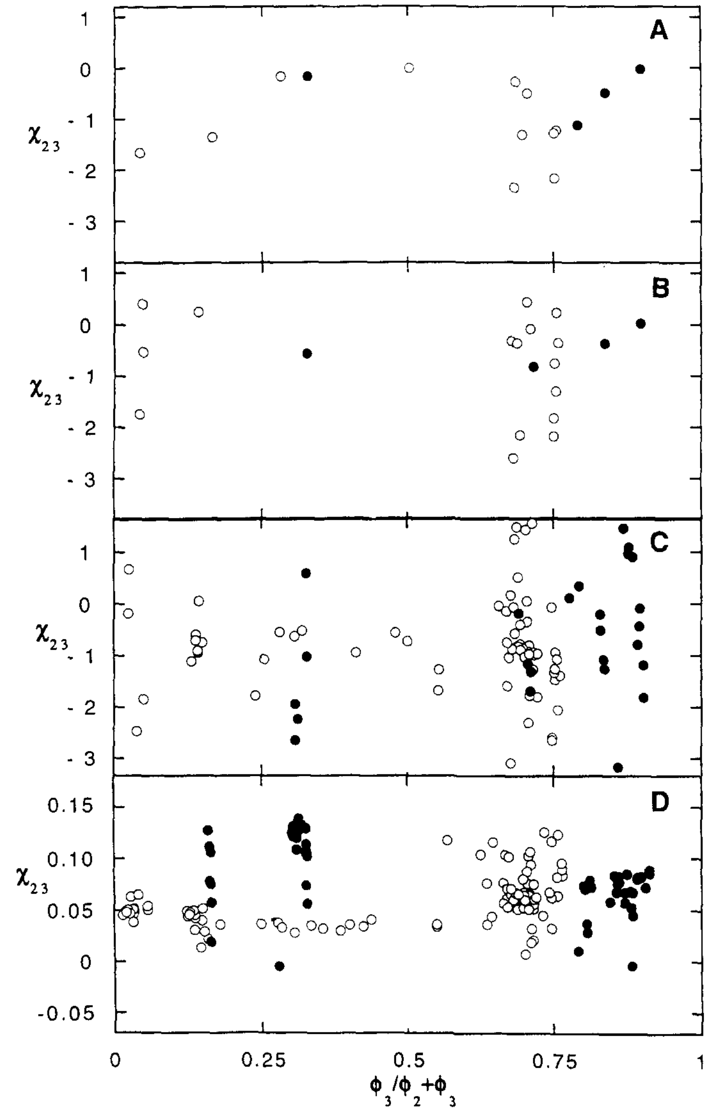

Figure 3 Plot of the polymer–polymer interaction parameter χ_{23} against the reduced volume fraction, $\phi_3/(\phi_2+\phi_3)$. The four plots refer, from top to bottom, to options A, B, C and D

attained. Taking into account most of the work done on this parameter, options A, B and C will indicate that the two polymers, either PES/PMMA or PES/PS, are miscible.

Although we have attained the same conclusions with both g_{23} and χ_{23}, we think that only g_{23} has physical meaning, since it has been defined as a binary interaction parameter and its variation with $\phi_3/\phi_2+\phi_3$ can be related with the enthalpic and entropic contributions to it, so the polymer concentration can affect the conformation of the polymer chain, and the greater or lesser ease for the segments of both polymers to approach and interact.

In *Table 3* the parameter g_T and its derivative are also included and they depict small numerical values different from zero, similar and with opposite sign to g_{23}. So it seems that this parameter should not be negligible. *Figure 4* shows the plot g_T and g_{23} against $\phi_3/\phi_2+\phi_3$ obtained by linear fitting of the values calculated according to the four options (A–D) and for the two polymer systems DMF/PES/PMMA (part a) and DMF/PES/PS (part b). Surprisingly, g_T and g_{23} parameters show an opposite trend on $\phi_3/\phi_2+\phi_3$ for every option. So, as g_T increases with $\phi_3/\phi_2+\phi_3$, the parameter g_{23} decreases for the PES/PMMA, and the contrary for the PES/PS system, a decrease of g_T that is paralleled by an increase of g_{23}. The ternary parameter partially cancels out g_{23}, and when g_T is not taken into account positive values of g_{23} as in option D are obtained against the negative values of whichever other option with g_T.

On the other hand, the starting point to define the miscibility between two polymers is the free energy of mixing (equation (1)). In this paper we restrict our discussion to the ΔG_{23} values obtained from the FH formalism, using the experimental ϕ values as well as the g-functions above calculated. This is so because 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 by considering 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 energy of mixing, referred to 1 mol of lattice sites in the absence of solvent is then given from equation (1) by:

$$\frac{\Delta G_{23}}{RT} = \frac{V_1}{V_2}\varphi_2 \ln \varphi_2 + \frac{V_1}{V_3}\varphi_3 \ln \varphi_3 + \varphi_2\varphi_3 g_{23} \qquad (9)$$

where $\varphi_2 = \frac{\phi_2}{\phi_2+\phi_3}$ and $\varphi_3 = \frac{\phi_3}{\phi_2+\phi_3}$ are the new volume fractions with $\varphi_2 + \varphi_3 = 1$ the new boundary condition. That means that for a ternary polymer–polymer solution $\phi_1 + \phi_2 + \phi_3 = 1$, so $\phi_2 + \phi_3 = 1 - \phi_1$ and $\frac{\phi_2}{1-\phi_1} + \frac{\phi_3}{1-\phi_1} = 1$. Focusing on equation (9) we note that the combinatorial contribution to ΔG_{23} is nearly negligible, since V_1/V_2 and V_1/V_3 are very small and so is the residual part, and more precisely g_{23} is the parameter that mainly influences the value of ΔG_{23} and so the thermodynamic behaviour between the two polymers.

Figure 5 shows the plot of ΔG_{23} values obtained through equation (9) against the reduced volume composition $\varphi_3 = \frac{\phi_3}{\phi_2+\phi_3}$ for the four options A–D and the two systems assayed in this paper. From the inspection of this figure it is clearly evident that whereas for options A, B and C mainly negative values for ΔG_{23} have been obtained indicating that the two polymers are thermodynamically compatible, interestingly for option D the opposite trend is observed, with positive ΔG_{23} values in all the composition range. Note that in this last option the more drastic approximation with $g_T = 0$ has been taken into account.

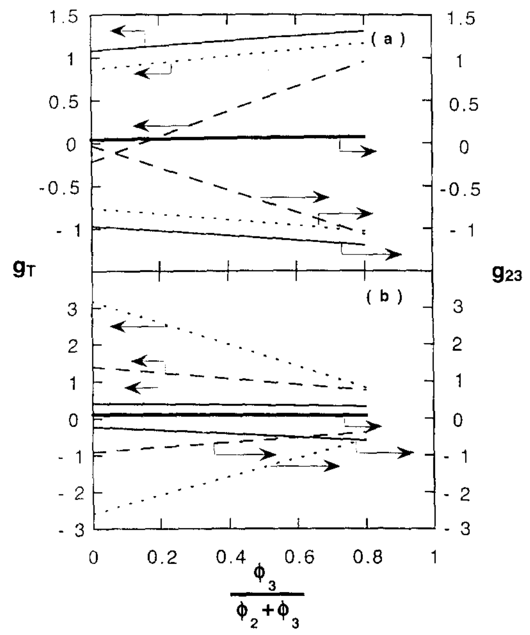

Figure 4 Dependence of the binary, g_{23}, and ternary, g_T, interaction parameters, on the reduced volume fraction, $\phi_3/(\phi_2 + \phi_3)$, for the system DMF/PES/PMMA (a) and DMF/PES/PS (b) according to different options: A (————); B (- - - -); C (···········) and D (————)

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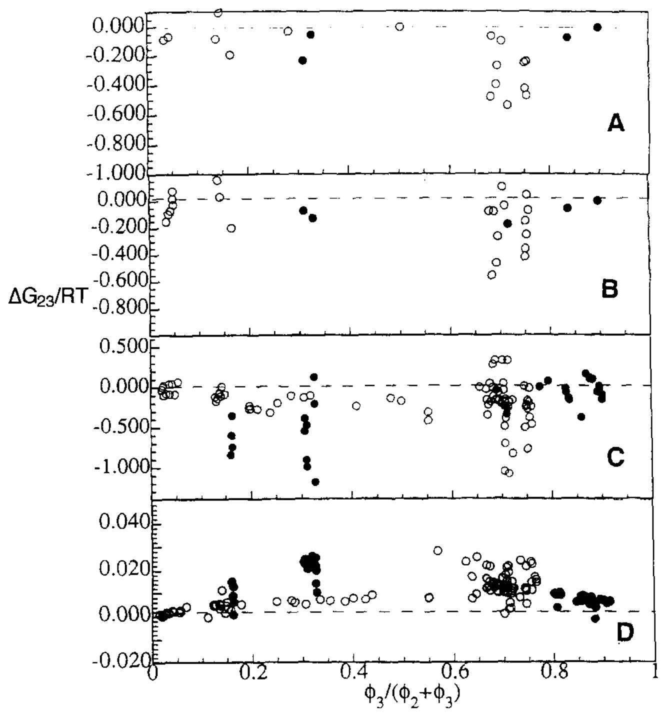

Figure 5 Dependence of the free energy of mixing, $\Delta G_{23}/RT$, on the reduced volume fraction, $\phi_3/(\phi_2 + \phi_3)$ for PES/PMMA (○) and PES/PS (●). The four plots refer, from top to bottom, to options A, B, C and D

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