Inverse Gas Chromatographic Study of Polymer Blend Interactions and Their Temperature Dependence

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SYNOPSIS

The temperature dependence of the thermodynamic interactions in blends of polypropylene and a fluorochemical was studied by inverse gas chromatography (IGC). A modified procedure has been proposed to evaluate the effective surface composition in polyblends. This shows that the low surface energy component preferentially concentrates in the surface region of blends. Moreover, the new procedure greatly reduces the probe-to-probe variation of X_{23}, a problem frequently encountered in thermodynamic applications of the IGC method. As a result, IGC may now be used with increased confidence for the determination of interaction thermodynamics in polymer systems over broad temperature ranges. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that the degree of miscibility of components in polymer blends exerts great influence on the processing behaviour of these compositions, as well as on their solid-state properties. A wide gap usually exists between the temperatures used for polymer blend processing and those at which the compound finds application. The temperature dependence of miscibility, or, more precisely, of the thermodynamic interactions among blend components, therefore becomes an important requisite for understanding the behaviour of complex polymer systems.

The method of inverse gas chromatography (IGC) seems to be a suitable candidate for generating the necessary information. IGC has long been considered a useful source for determining thermodynamic interactions between a wide range of polymeric stationary phases and suitable vapour probes,[1-4] with the Flory–Huggins parameters, X_{12}, the usual criterion of measuring the interaction. Furthermore, IGC has held out promise for also measuring the interaction between two nonvolatile

components of a polymer system, but that promise was diminished by frequent observations[5-8] showing that X_{23} varied with the selection of vapour probes. Several workers have attempted to resolve the problem: Most recently, Chee[9] suggested the use of a solubility parameter-related function, which he showed to be independent of vapour probes in an ethylene–vinyl acetate (EVA)/chlorinated polyethylene (PE) blend. In a contemporary publication,[10] we ascribed probe-to-probe variations in X_{23} as being due, in part, to procedures inherent in IGC that hold that the surface and bulk in a multicomponent polymer system is equal. In a proposed modified IGC procedure, this assumption is rejected; instead, the new procedure is based upon the near certainty that surface and bulk compositions differ in a blend of polymers or in other systems involving polymers and other nonvolatile components. Various reasons may be advanced for this. For example, in a two-component blend, regardless of miscibility, it must be the low surface energy component that, at equilibrium, preferentially locates at the surface,[11] creating compositional heterogeneity. The existence of acid/base interactions among the system's materials also may be cited[12] as a source of compositional variations at the surface or within the bulk of the system.

The principle of the modified IGC procedure is summarised in Figure 1. Here, the straight line de-
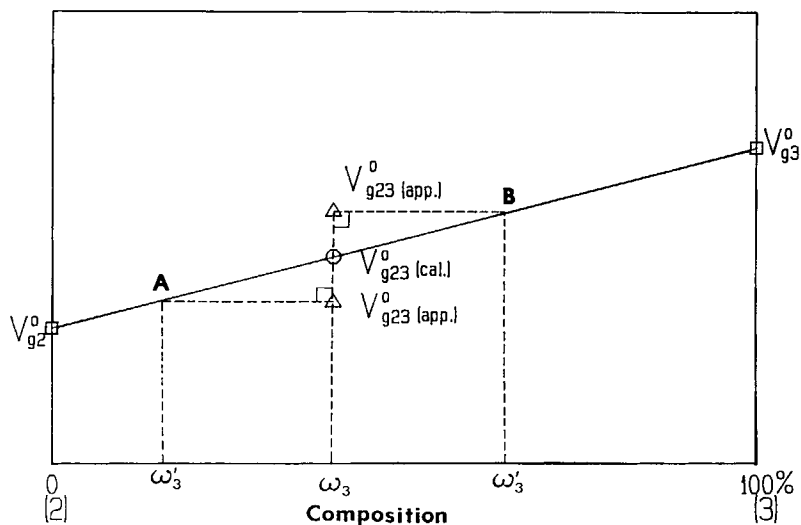
Figure 1 Ideal and experimental relationship in the retention volume-composition diagram of a two-component system.

termined by experimental retention volumes of two pure components, V_{g2}^0 and V_{g3}^0, predicts the retention volumes for any mixture of components 2 and 3 provided the surface and bulk compositions are identical. In practise, the retention volume for probes contacting a mixed stationary phase generally falls off the straight line. As shown in the figure, for a bulk composition ω_3 the experimental retention
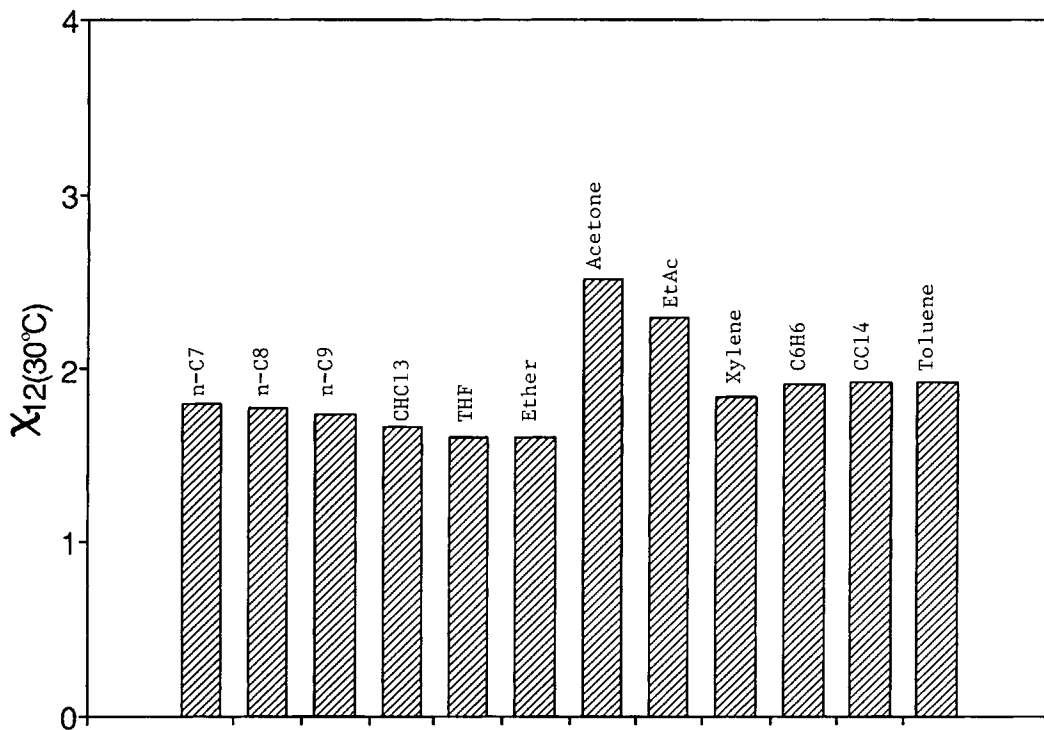

Figure 2 Histogram of solute–PP interaction parameter, χ_{12}, at 30°C.

volume $V^0_{g23(app.)}$ permits the definition of the effective surface composition, ω'_3, given by the construction linking the theoretical line with the experimental datum. The effective (or real) interaction parameter, $X_{23(eff.)}$, can then be calculated from $V^0_{g23(app.)}$ and ω'_3. With this convention, we found[10] that the probe dependence of X_{23} for a polypropylene–fluorochemical (PP/FC) blend was reduced substantially.

The present article extends the information in Ref. 9 to a broader temperature range. Given the wide temperature range separating processing and use temperatures for PP, a systematic study of temperature dependence in polymer/solute and polymer/additive miscibilities is relevant. The results presented here extend the earlier data (limited to 80°C) to as high as 160°C, corresponding to the onset of the melting range for PP. The validity of the new procedure is thereby retested.

EXPERIMENTAL

The host polymer was a PP resin supplied by The Shell Company with $M_w = 1.2 \times 10^5$ and $M_n = 1.67 \times 10^4$. The FC was an oligomer with a formula weight of 852; both of these materials were used in our previously reported work.[10] Blends containing 0.1, 1, 10, and 20 wt % FC were prepared by mixing with a Brabender Plasticorder apparatus operating at 180°C and 50 rpm.

Chromatographic columns were prepared for pure components and for the blends specified above. Chromosorb W (AW-DMCS treated, 60/80 mesh with a specific surface area of 1.2 m^2/g) was the support for the stationary phases, deposited from xylene solutions. Following conventional drying and ashing procedures,[5,13] the stationary phases were packed in previously degreased, washed, and dried steel columns. To separate efficiently the probe and reference (air) peaks, 60-cm columns were used at lower temperatures (30–80°C), while 120-cm columns were preferred for work in the 100–160°C range. This ensured that net retention times did not fall below 2 s and that reproducibility in repeat injections of mobile phases remained better than 3%. Chromatographic data were obtained with a Perkin-Elmer Sigma 2 unit equipped with a thermal conductivity detector. Pure helium was the carrier gas. As suggested by Galin and Rupprecht,[13] gas flow rates were maintained at 10 mL/min and stationary phase concentration at 7–8 wt %, these specifications
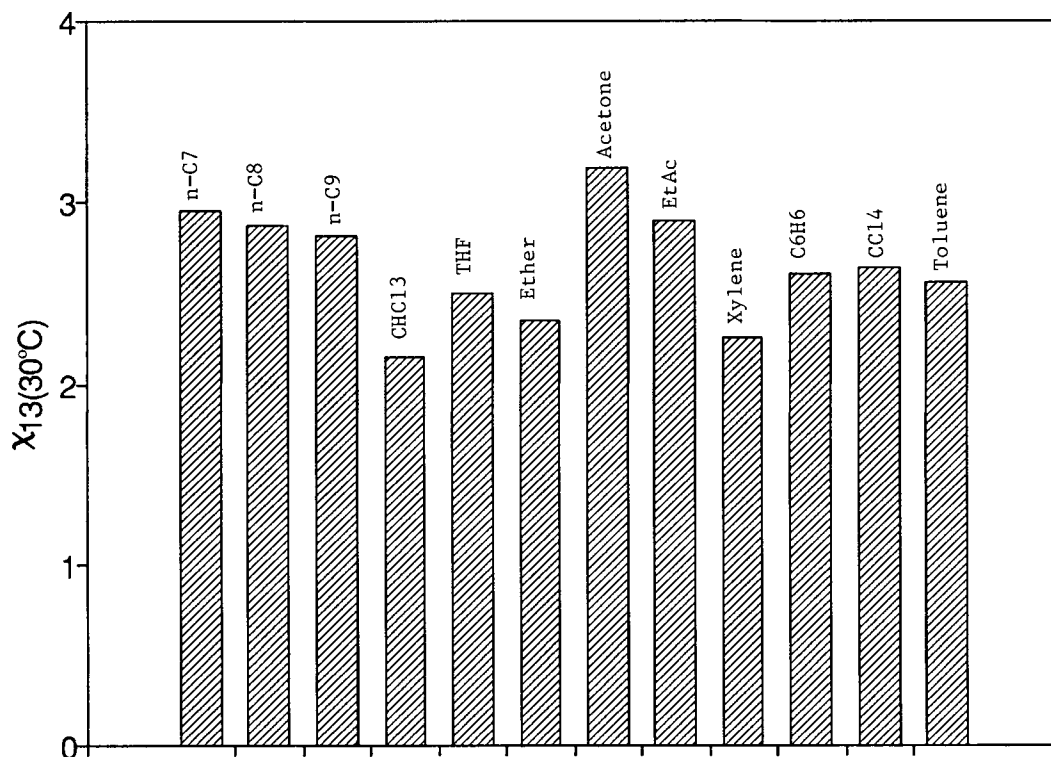

Figure 3 Histogram of solute–FC interaction parameter, X_{13}, at 30°C.

being preferred for high data reproducibility. Substrates were conditioned under a flow of helium at 110°C for several hours and then probed with a total of 12 vapours, always at very high dilution. The vapours are identified in the following sections.

RESULTS AND DISCUSSION

The histograms of Figures 2 and 3 present values of X_{12} and X_{13} at a reference temperature of 30°C, re-

spectively, for PP and FC stationary phases. As shown in Figure 2, the interaction parameter for PP remains roughly constant for most of the vapours used. Exceptions are slightly stronger interactions (lower X) with chloroform, tetrahydrofuran (THF), and diethyl ether (weak solvents for the polyolefin), and greater rejection (higher X) for the polar vapours of acetone and ethyl acetate. The X_{13} values (Fig. 3) tend to be higher, suggesting that the FC is less compatible with many of the selected vapours. Acetone and ethyl acetate again are most strongly re-
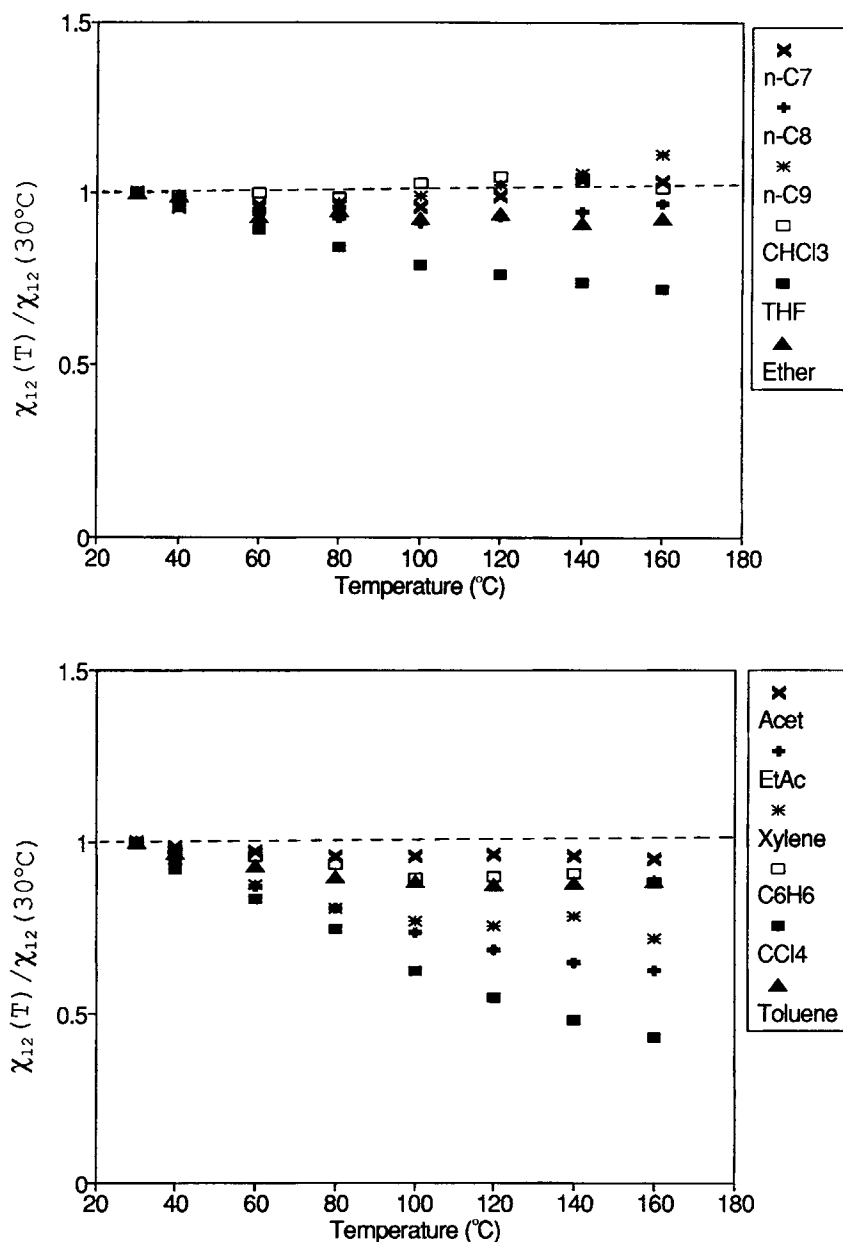

Figure 4 Dependence of X_{12} (T)/X_{12} (30°C) upon temperature.

jected. Comparing Figures 2 and 3 suggests that in two-component PP/FC systems the vapours will tend to partition preferentially to PP segments occupying surface regions accessible to the vapours.

The temperature dependence of χ_{12} and of χ_{13} normalised to the 30°C reference values is shown in the sections of Figs. 4 and 5. The interactions between stationary phases and vapours tend generally to increase with increasing temperatures. For PP, the known solvent chloroform is particularly tem-

perature sensitive while rather surprisingly the surface miscibility of the linear alkanes changes very little. The alkanes, however, become increasingly miscible with FC as the temperature rises into the > 100°C range, while interactions with ether and chloroform remain relatively unchanged. These observations point to complex variations in probe partitioning when mixed stationary phases are involved. For example, χ_{12} and χ_{13} for chloroform are roughly equivalent at the reference temperature (Figs. 2 and
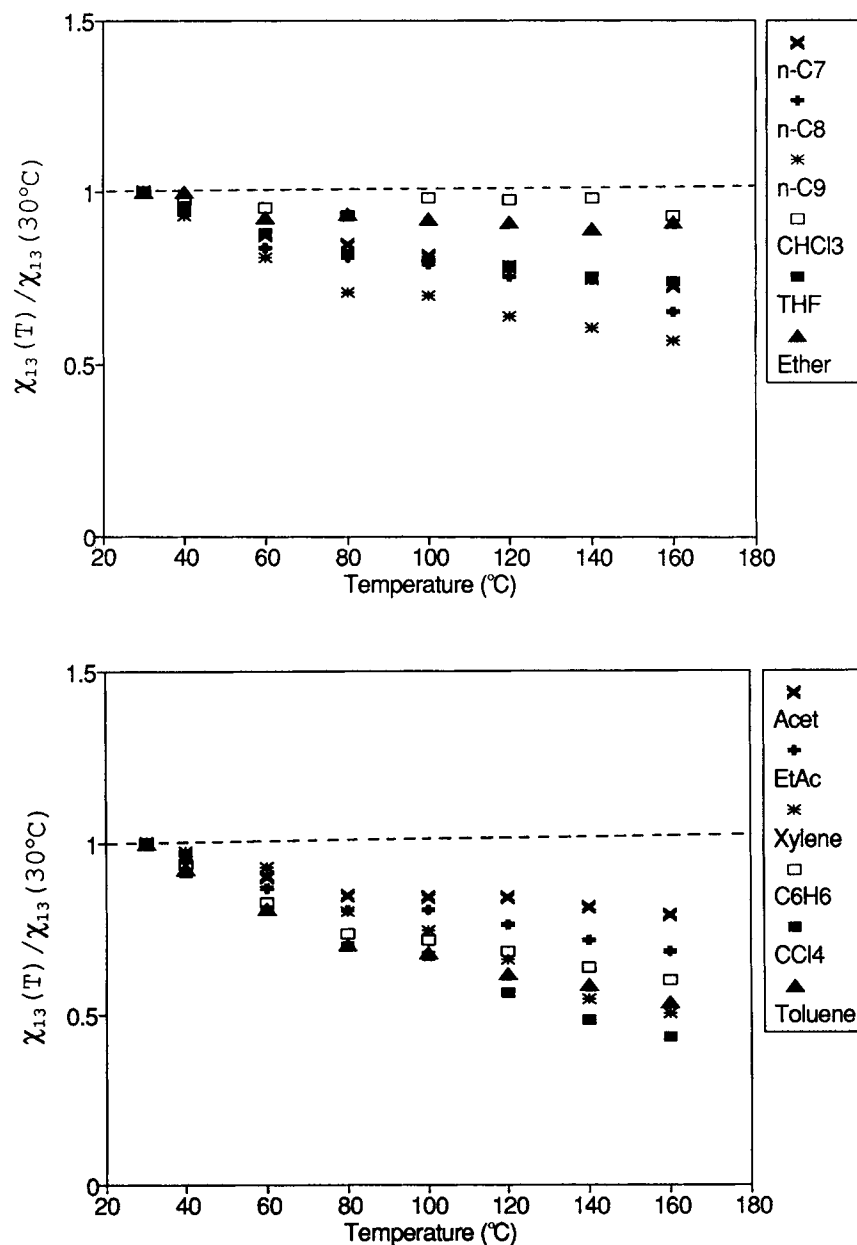

Figure 5   Dependence of χ_{13} $(T)/\chi_{13}$ (30°C) upon temperature.

3) so that more or less random partitioning of this vapour might be expected. At higher temperature, however, chloroform should partition increasingly toward the PP component, consistent with the trends shown in Figures 4 and 5. The reverse is true of the linear alkanes; the trend there should be toward increasing association with FC segments in the near-surface layer as the temperature rises.

The documented temperature variations permit calculations to be made of activation energies for the polymer/vapour interaction process. Arrhenius plots of $\ln \chi$ vs. $1/T$ (K) for all probes were found to be linear, and the resulting activation energies, E, were entered in Table I. E values are invariably negative or zero and their absolute values are greater for FC than for PP as the stationary phase. Expectedly, therefore, the tabled values confirm the tendencies shown qualitatively in preceding figures.

The overall interaction parameter for vapour/mixed stationary phases, $\chi_{1(23)}$, is shown as a function of blend composition in the sections of Figure 6. Data are shown at the reference temperature 30°C. It is evident again that χ_{13} values are greater than the corresponding χ_{12}, with the overall $\chi_{1(23)}$ values lying between the two extremes. As elaborated in our previous publication on this subject,[10] various options are now open for the evaluation of χ_{23}. If the usual assumption is made that surface and bulk

compositions are identical, then from a knowledge of the V_g^0 for individual components and application of the principles illustrated in Figure 1 it is possible to obtain $\chi_{23(cal.)}$ over the entire composition range. This is illustrated in Table II for interactions at 160°C. The values range from -0.03 to 0.67 with substantial probe-to-probe variations much in evidence. The generally positive values of χ_{23} indicate that PP and FC are at best sparingly miscible at 160°C. Figure 7 illustrates the temperature dependence of $\chi_{23(cal.)}$ for the blend over the entire composition range, with xylene as the probe vapour. Clearly, the degree of miscibility increases with increasing temperature and the variation is much more sensitive at higher concentrations of FC.

Of course, the results in Table II and Figure 7 are based upon premises that cannot be defended in practise. Experimental values of V_{g23}^0 do not lie on the line joining V_{g2}^0 and V_{g3}^0, necessitating an evaluation to be made of the effective surface concentration, ω_3', and finally of $\chi_{23(eff.)}$. This was done for all probes at each of the experimental temperatures, with an illustration of results, again at 160°C, in Table III. This allows for ready comparison with the calculated χ_{23} in Table II. There is qualitative agreement between the two sets of interaction parameters, but in contrast with those in Table II the new set is far more uniform and much less probe dependent. For example, at 0.1% FC in the bulk the results in Table II range from 0.30–0.88 and, as noted already, denote at best limited miscibility of PP and FC. The data in Table III increase from 0.00–0.15; in other words, at this temperature and composition the components are more miscible. At 10 wt % (additive), $\chi_{23(cal.)}$ extends from 0.00–0.63, while $\chi_{23(eff.)}$ has extremes of 0.00 and 0.13. The bracketed values of ω_3' in Table III show how very different surface and bulk compositions seem to be. Invariably, the concentration of FC in the region of the blend surface is higher than called for by stoichiometry. This is a reasonable conclusion to be reached. IGC and contact angle determinations may be used to evaluate the surface energies of the individual blend components.[12,14] The following is the outcome of these evaluations:

Table I Activation Energies for Probes Interacting With PP (χ_{12}) and FC (χ_{13})

	E (kJ/mol)	
	χ_{12}	χ_{13}
n-C7[a]	0	-2.5
n-C8[a]	0	-3.1
n-C9[a]	0	-4.6
CHC13	0	0
THF[b]	-2.8	-2.5
Ether	0	-0.8
Acetone	0	-1.8
EtAc[b]	-4.0	-3.0
Xylene	-2.6	-6.1
C6H6	0	-4.2
CCl4	-7.2	-6.8
Toluene	0	-5.1

[a] n-C7, n-C8, and n-C9 refers to n-hexane, n-heptane, etc.
[b] THF and EtAc refer to tetrahydrofuran and ethyl acetate, respectively.

PP: $\gamma_S^D = 32.6$ mJ/m^2 (IGC),

and 31.5 mJ/m^2 (contact angle)

FC: $\gamma_S^D = 24.8$ mJ/m^2 (IGC),
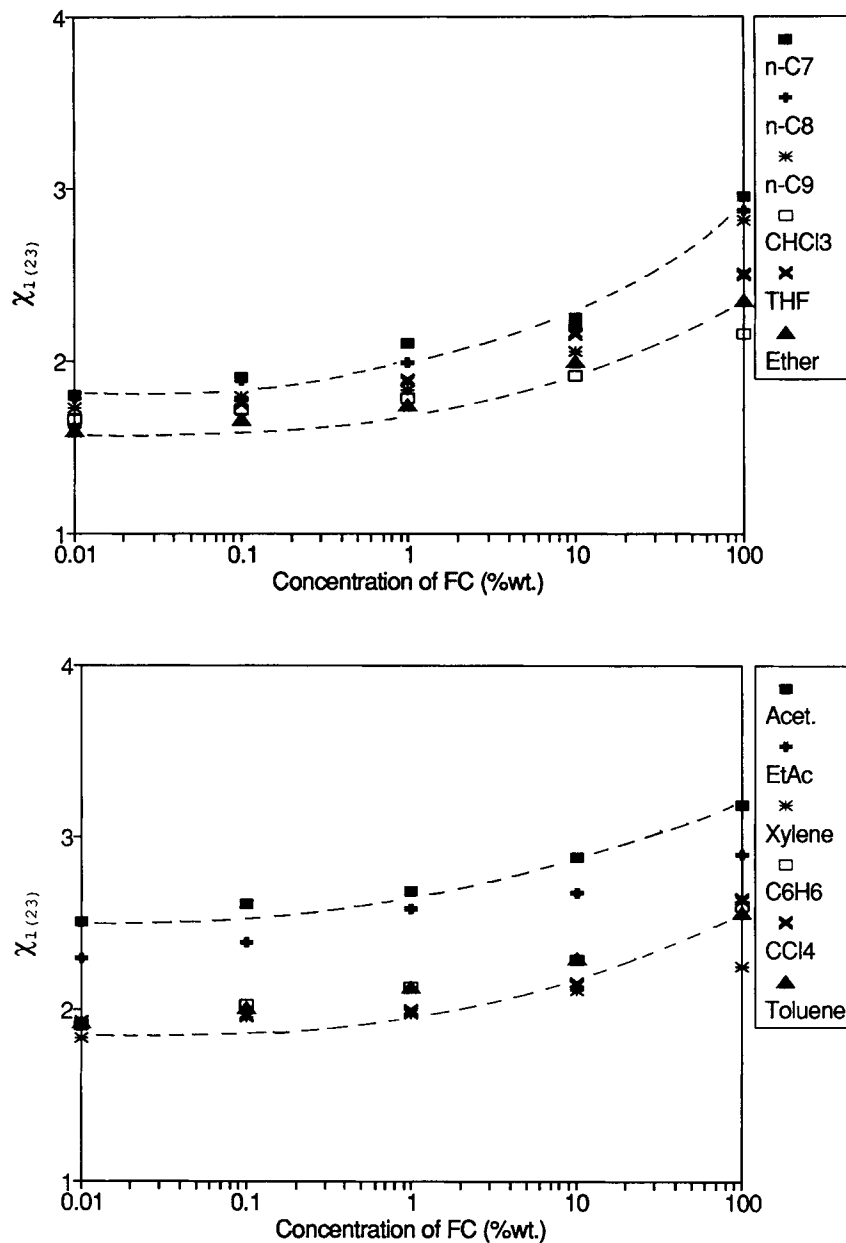
and 22.7 mJ/m^2 (contact angle)

Figure 6 Overall Flory–Huggins interaction parameter $\chi_{1(23)}$ as function of FC concentration.

Clearly, there is a thermodynamic requirement for the low surface energy component to dominate the surface composition of blends.[11] This would occur readily during the pretreatment of stationary phases at 110°C (see experimental section). At this temperature, the relatively small FC molecule may be expected to diffuse through the host matrix, the latter considerably above its T_g. The probe-to-probe variation of ω'_3 is significant. This is interpreted as

an artifact of the different χ_{12} and χ_{13} values. The partitioning of vapours between PP and FC sites in the surface region must be expected to change with the ratios of the above χ values. Consequently, each vapour creates a unique set of surface interactions, and this is reliably reflected in the data of Table III.

Given the importance of miscibility considerations over wide temperature ranges, it is instructive to note the contribution to an understanding of the

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Table II Flory–Huggins Interaction Parameter $X_{23(cal.)}$

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	ω_3 (%) Additive										
Probes	0.05	0.1	0.2	0.4	0.6	0.8	1	1.2	1.4	1.6	1.8
n-C7	0.30	0.30	−0.03	−0.03	−0.03	−0.03	−0.03	0.03	0.02	0.04	0.01
n-C8	0.31	0.31	−0.02	−0.02	−0.02	−0.02	−0.02	0.04	0.03	0.07	0.02
n-C9	0.35	0.35	0.03	0.03	0.03	0.03	0.03	0.08	0.07	0.14	0.07
CHCl3	0.30	0.30	−0.03	−0.03	−0.03	−0.03	−0.03	0.03	0.02	0.04	0.01
THF	0.49	0.49	0.17	0.17	0.17	0.17	0.17	0.22	0.21	0.24	0.21
Ether	0.66	0.66	0.34	0.34	0.34	0.34	0.34	0.40	0.39	0.36	0.38
Acetone	0.30	0.30	−0.03	−0.03	−0.03	−0.03	−0.03	0.03	0.02	0.01	0.01
EtAc	0.42	0.42	0.10	0.10	0.10	0.10	0.10	0.15	0.15	0.16	0.14
Xylene	0.31	0.32	−0.01	−0.01	−0.01	−0.01	−0.01	0.04	0.03	0.13	0.03
C6H6	0.35	0.35	0.02	0.02	0.02	0.02	0.02	0.08	0.07	0.11	0.06
CCl4	0.88	0.88	0.56	0.56	0.56	0.56	0.56	0.62	0.61	0.64	0.61
Toluene	0.36	0.36	0.03	0.03	0.03	0.03	0.03	0.09	0.08	0.14	0.07

matter made by the new IGC procedures. The point is illustrated in Figure 8. This is an Arrhenius-type representation for the temperature dependence of $X_{23(cal.)}$ at blend compositions between 1 and 20 wt % FC, where the interaction parameter varies little, and of $X_{23(eff.)}$ at four arbitrarily chosen blend compositions. The two sets of results are quite different.

$X_{23(cal.)}$ follows the Arrhenius concept, establishing a single E value of −13.4 kJ/mol, presumably an activation energy for "miscibilisation" of the system. In the case of $X_{23(eff.)}$, two linear segments are defined, with $E = -25.5$ kJ/mol at temperatures below 80°C and −0.4 mJ/mol at $T > 80$°C. Thus, to approximately 80°C there is a gradual increase in the
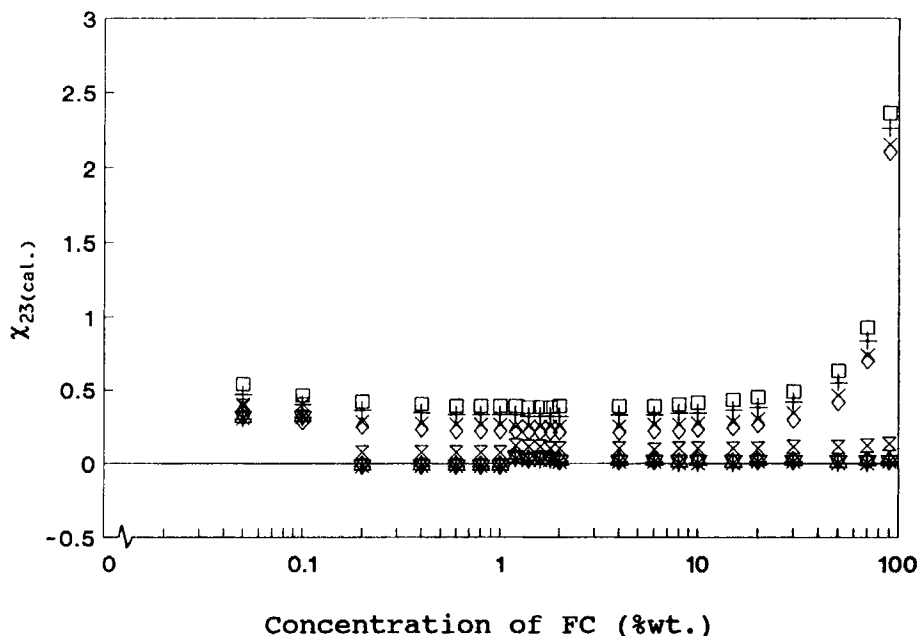

Figure 7 Variation of $\chi_{23(cal.)}$ determined from xylene probe as function of FC concentration. (□), 30°C; (+), 40°C; (x), 60°C; (◊), 80°C; (⊗), 100°C; (∇), 120°C; (∗), 140°C; (△), 160°C.

for Various PP–Additive Blends at 160°C

	ω_3 (%) Additive										
2	4	6	8	10	15	20	30	50	70	90
0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
0.06	0.06	0.06	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.20	0.20	0.21	0.20	0.20	0.21	0.22	0.23	0.25	0.27	0.30
0.38	0.38	0.39	0.38	0.39	0.40	0.42	0.45	0.51	0.58	0.67
0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.13	0.13	0.13	0.13	0.13	0.13	0.14	0.14	0.15	0.16	0.18
0.02	0.02	0.02	0.01	0.02	0.01	0.02	0.02	0.01	0.02	0.02
0.06	0.06	0.06	0.05	0.05	0.05	0.05	0.05	0.04	0.04	0.04
0.60	0.61	0.62	0.62	0.63	0.65	0.68	0.74	0.87	1.04	1.27
0.07	0.07	0.07	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.05

miscibility of the two constituents, but further temperature increments do not greatly improve the degree of miscibility.

CONCLUSION

The IGC technique has been used for the determination of thermodynamic interactions between a polypropylene host and a fluorochemical additive.

Determination of Flory–Huggins χ_{23} values have been carried out at temperatures from ambient to 160°C.

A new procedure for the evaluation of effective surface compositions in polymer blends has been applied in the IGC work. This shows that the minor component preferentially concentrates in the surface region. Moreover, the new procedure greatly reduces the probe-to-probe variation in χ_{23} and increases the confidence of using the IGC technique as a convenient, broadly applicable route to the measurement of interaction states in complex polymer systems.

Conventional and modified IGC procedures lead to somewhat different predictions of miscibility in the system studied and of its temperature variation. Experimental verification of these predictions is to be undertaken.

Table III   Flory–Huggins Interaction Parameter $\chi_{23(eff.)}$ for PP–Additive Blends at 160°C

Probes	0.1% Additive (ω_3')	1% Additive (ω_3')	10% Additive (ω_3')	20% Additive (ω_3')
n-C7	0.01 (13.6)	0.01 (13.6)	0.01 (25.9)	0.01 (38.3)
n-C8	0.00 (26.6)	0.00 (26.6)	0.00 (26.6)	0.00 (44.9)
n-C9	0.13 (11.8)	0.13 (27.1)	0.13 (18.6)	0.12 (45.7)
CHCl3	0.03 (39.4)	0.03 (59.6)	0.02 (79.8)	0.02 (89.9)
THF	0.12 (12.4)	0.13 (27.0)	0.13 (48.9)	0.14 (63.5)
Ether	0.06 (13.0)	0.06 (23.9)	0.06 (34.8)	0.06 (78.2)
Acetone	0.01 (35.5)	0.01 (67.7)	0.01 (83.9)	0.01 (83.9)
EtAc	0.07 (27.3)	0.07 (45.4)	0.07 (63.6)	0.07 (63.6)
Xylene	0.07 (5.9)	0.07 (10.9)	0.07 (9.9)	0.07 (15.8)
C6H6	0.13 (16.7)	0.12 (29.2)	0.11 (62.5)	0.10 (83.3)
CCl4	0.07 (33.5)	0.06 (20.7)	0.06 (28.4)	0.06 (84.9)
Toluene	0.15 (13.0)	0.13 (43.3)	0.12 (81.8)	0.11 (91.9)
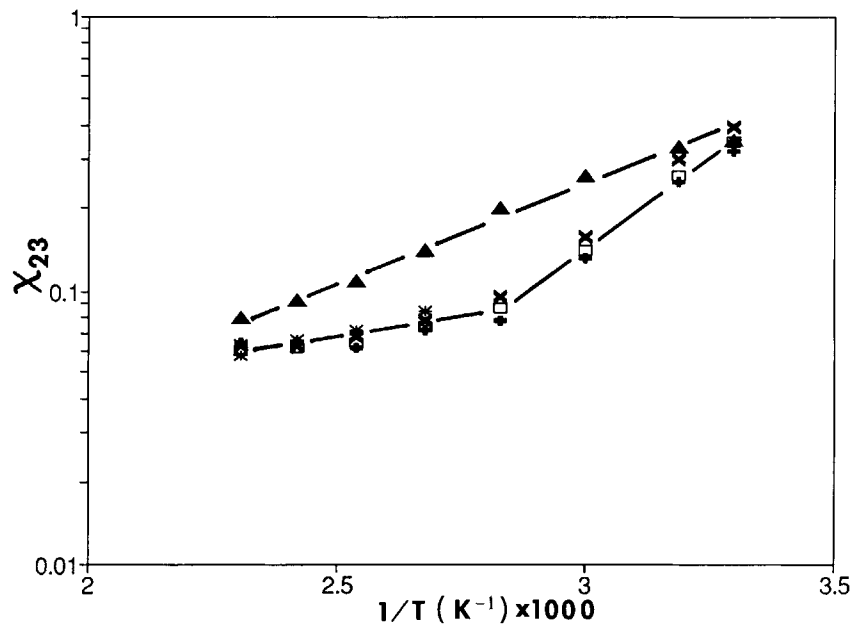
Figure 8 Variation of $X_{23(cal.)}$ and $X_{23(eff.)}$ with reciprocal temperature. ($\triangle$), $X_{23(cal.)}$ at ω = 1–20 wt %; (+), $X_{23(eff.)}$ at ω = 0.1 wt %; ($\square$), $X_{23(eff.)}$ at ω = 1 wt %; ($\times$), $X_{23(eff.)}$ at ω = 10 wt %; (*), $X_{23(eff.)}$ at ω = 20 wt %.

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