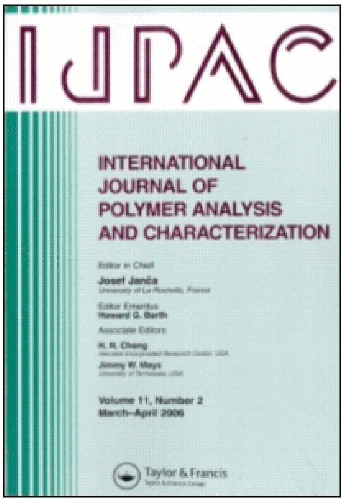
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Review: Inverse Gas Chromatography for the Characterization of Polymer Blends

Zeki Y. Al-saigh[a]
[a] Department of Chemistry & Geology, Columbus State University, Columbus, Georgia

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Review: Inverse Gas Chromatography for the Characterization of Polymer Blends

ZEKI Y. AL-SAIGH

*Department of Chemistry & Geology, Columbus State University,
4225 University Avenue, Columbus, Georgia 31907-5645*

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Inverse gas chromatography (IGC) has been proven to be useful for the characterization of polymer blends in terms of polymer-polymer interaction parameters, polymer-solute interaction parameters, solubility parameters, molar heat of sorption and mixing, melting point depression as an indicator of miscibility, contact energy parameters, and surface characterization. A complete treatment of the theories of polymer blend solution and IGC are illustrated, and the general use of the IGC method is reviewed.

Keywords: Blends, thermodynamics, interactions, inverse gas chromatography

INTRODUCTION

Polymer blends, often called alloys, provide new and unique properties of materials which can be difficult to obtain by synthesizing new polymers. By mixing known polymers, unique properties can be obtained simply by adjusting the combination, composition and the blending process. Frequently, a polymer is needed with specific properties, and since the number of available monomers is limited, synthetic methods may not provide a way of finely adjusting the properties of two known polymers. The concept of blending polymers is similar to that of metal alloys except that polymer blends are less expensive to make and considerably lighter. However, there are differences in mechanical strength and other properties between the two kinds. Economically, it is more advantageous to obtain the desired properties by blending polymers than synthesizing a homopolymer that would provide the same desired properties. Polymer blends have been known for five decades and are industrially important because of the technological interest in multicomponent polymer systems.[1-10]

The characterization of the physiochemical properties of polymer blends is the key for successfully utilizing these systems in industry. The most important quantity for the characterization is the miscibility of the blend, in other words, the compatibility of the polymer pair. Polymer blends can be composed of two or more homopolymers or copolymers. A pair of polymers may exist in a completely homogeneous state where their segments are mixed at the most intimate level or they may segregate into distinct phases. Miscibility occurs when specific interaction forces develop between the polymer-polymer pair in the form of dispersive forces, hydrogen bonding,[11] charge-transfer complexes, acid-base type interactions, dipole moments, and electron donor-acceptor complexes.[12,13] It is generally known that exothermic heat of mixing[7-9] is an indication of the miscibility of polymer blends. Accordingly, several techniques were developed and employed to characterize the thermodynamics of polymer-polymer systems.

To date, there is no comprehensive method for the characterization of polymer blends owing to the high viscosity of polymer blends, and therefore, to the extreme difficulty of handling viscous samples using conventional analytical techniques. In addition, polymer blends are thermodynamically complex mixtures, however, there are numerous direct methods that have been used for characterization: measurement of the glass-transition temperature, thermal and mechanical methods,[14-16] NMR,[17] electron spin resonance,[17] solvent-vapor sorption, heat of mixing measurements, small-angle light scattering,[18] small-angle X-ray scattering, small-angle neutron scattering,[19,20] excimer fluorescence,[21] melting point depression,[22-27] and inverse gas chromatography (IGC).[28-52] Unfortunately, most of these techniques are beset by a number of technical problems. Researchers over the years, have modified these methods and introduced correction factors to minimize the overall error in the thermodynamic quantities. To date, there is an intense effort to improve the accuracy and the versatility of these methods.

In this review, IGC and its applicability to polymer blends will be discussed. The term "inverse" is conveniently used because the chromatographic column consists of the polymer blend coated onto a solid support, therefore, unlike conventional gas chromatography where the chromatographic column is only used for separation and quantitation. In IGC, the stationary phase in the chromatographic column is under study. IGC has been applied widely to homopolymers, copolymers, and polymer blends, however, little data exist on polymer blends as compared to homopolymers. IGC has the potential of obtaining a wealth of information such as: interaction parameters, contact energy parameters, and molar heat of sorption and mixing of solutes. All of these quantities can be obtained experimentally by measuring retention time, weight of the blend, inlet and outlet pressure of the carrier gas, flow rate of the carrier gas, and the column temperature.

In this review, we will show that IGC can be used to characterize polymer blends that contain either a pair of amorphous homopolymers or a pair of amorphous-semicrystalline polymers. Other classes of polymer blends will also be discussed. Research is underway to test the applicability of IGC on more complex polymer blends such as pairs of semicrystalline polymers. We will also show that IGC is accurate and selective when compared with other methods. Advantages and disadvantages will be covered including precautions needed to obtain accurate and reliable data.

THEORY

Thermodynamics of Polymer Blend Mixtures

In a polymer blend, the key term in the miscibility of a polymer-polymer pair is the free energy of mixing ΔG_m

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1}$$

where ΔS_m is the combinatorial entropy of mixing and ΔH_m is the molar heat of mixing. Flory[53] attributed the combinatorial entropy of mixing to the mixing of the segments on a lattice of fixed volume. Because entropy depends on volume, an additional contribution to the entropy of mixing may be needed in Equation (1). Sanchez *et al.*[54] have developed a theory to allow for this effect by considering that all mixtures obey the equation of state when appropriate reducing parameters, such as pressure and temperature, are used for volume. Other "equation-of-state" theories of mixtures yield a combinatorial entropy of mixing similar to that of Flory. However, the combinatorial entropy becomes negligible as the molecular weight of the polymer becomes high. Therefore, in case of high-molecular-weight polymers, only the value of ΔH_m is used for the characterization of the miscibility of the polymer pairs. It is generally accepted that complete polymer-polymer miscibility results when the heat of mixing is exothermic and the negative interaction parameter is negative. However, this is not a sufficient condition since the stability considerations require for binary mixtures, that

$$\frac{\delta^2\,\Delta G_m}{\delta\,\phi_i^2} > 0 \tag{2}$$

where ϕ_i is the volume fraction of ith component. The volume fraction term was first introduced by the Flory-Huggins theory which described polymer solutions with a reasonable success.[53] The free energy of mixing as described by the Flory-Huggins theory, is:

$$\Delta G_{mix} = RT\,\{n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1\phi_2\chi_{12}\} \tag{3}$$

Where n_i is the number of moles of the ith component, RT has its usual meaning, and χ_{12} is a parameter which is inversely proportional to absolute temperature. Parameter χ_{12} was introduced as an enthalpic contact parameter; the two logarithmic terms represent the (combinatory) entropy of mixing. The combinatory entropy of mixing was approximated by Flory[53] to read:

$$\Delta S_m = -R(n_1\,V_1 + n_2\,V_2)\left[\frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2}\right] \tag{4}$$

where V_1 and V_2 are the molar volumes of components comprising the mixture. This model further assumes the heat of mixing is described by the Van Laar expression:

$$\Delta H_m = (n_1 V_1 + n_2 V_2) B \phi_1 \phi_2 \tag{5}$$

where B is a binary interaction energy parameter. B is related to the parameter χ, as

$$\frac{B}{RT} = \frac{\chi_{12}}{V_1} \tag{6}$$

Equation (6) can be extended to multicomponent mixtures as follows:

$$\frac{\Delta H_m}{V} = \Sigma_{i>j} B_{ij} \phi_i \phi_j \tag{7}$$

where V = total volume of mixture = $\Sigma_i n_i V_i$

While the sign of the combinatorial entropy always favors mixing, it is clear from Equation (4) that its magnitude is greatly diminished as molar volumes become very large. Thus, in the limit of high molecular weights, the condition for miscibility of polymer blend can only be satisfied by a negative interaction parameter χ_{23} (subscripts 1, 2 and 3, refer to the solvent, polymer 2 and polymer 3, respectively) leading to the conclusion that exothermic heat of mixing is a requirement for miscibility in high-molecular-weight polymer blends. As a result of the exothermicity principle, a number of miscible polymer blends were identified.[6,7,55,56]

The thermodynamics of IGC can be described in terms of the elution behavior of volatile substances (solutes) in chromatographic columns.[28,45-47] The key term in the calculation of any thermodynamic quantity using IGC is the specific retention volume V_g^o measured directly from chromatographic parameters. V_g^o is commonly used to describe the elution behavior of solutes, and it is defined as:

$$V_g^o = \Delta t \frac{F}{w} \frac{273.15}{T_r} \frac{3}{2} \frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1} \tag{8}$$

Here, $\Delta t = t_p - t_m$ is the difference between the retention time of the solute t_p and of an unretained solute (marker) t_m. F is the flow rate of the carrier gas measured at room temperature T_r, w is the mass of the stationary phase, and P_i and P_o are the inlet and outlet pressures, respectively.

The specific retention volume is related to the partition coefficient c_1^l/c_1^g as

$$V_g^o = \left(\frac{c_1^l}{c_1^g}\right) v_2 \left(\frac{273.15}{T}\right) \tag{9}$$

Here, c_1 is the concentration of the solute, and the superscripts l and g denote the liquid and gas phases, respectively; v_2 is the specific volume of the liquid phase (the polymer) at the column temperature T.

In a chromatographic column, a fast equilibrium between the stationary and mobile phases is usually established. Because of this, V_g^o measured from the chromatographic quantities is amenable to thermodynamic interpretation. However, if the column temperature is not at least 50°C above the glass-transition temperature of the polymer blend, then V_g^o is not amenable for thermodynamic interpretation owing to surface adsorption and kinetic effects.

At equilibrium, the difference between the chemical potential of the solute in either phase from that in the reference state is the same,

$$\Delta\mu_1^l = \Delta\mu_1^g \tag{10}$$

If we assume that both c_1^l and c_1^g are very small (ideal dilution) throughout the chromatographic column, then at equilibrium, the chemical potential of the solute in the gas phase is given by:

$$\Delta\mu_1^g = RT \ln \frac{R\,T\,C_1^g}{M_1\,P_1^o} - B_{11}\,P_1^o \tag{11}$$

where M_1 is the molecular weight of the solute, R is the gas constant, P_1^o is the saturated vapor pressure of the solute, and B_{11} is the second virial coefficient of the solute in the gaseous state. It should be noted that the last term in Equation (11) represents the correction for nonideality of the solute in the gas phase and that higher virial terms are usually neglected. The correction for nonideality is important since most IGC experiments are performed between 100–200°C. At this range of temperature, the saturated vapor pressure of low-boiling-point solutes (such as pentane) is very high (and the significance of the last term in Equation (11) is also high) and the truncation of the virial expansion may not be warranted. Extreme care is needed so that the critical temperature of the solute is not exceeded. When the solute saturated vapor pressure is high, the nonideal term should be treated with caution. Later in this analysis, we will show that while this consideration is quite important in the calculations of the interaction parameters of the solute with a homopolymer, in the case of polymer blends, all the axillary parameters, such as P_1^o, will cancel out.

While the chemical potential of the solute in the liquid phase is:

$$\Delta\mu_1^l = \pm V_1 P_1^0 + \left(\frac{\delta \Delta G_{mix}}{\delta n_1}\right)_{n=1,P,T} \tag{12}$$

where n_1 is the number of moles of component 1 in a mixture and V_1 is its molar volume. The derivative $(\delta\Delta G_{mix}/\delta n_1)_{n=1,P,T}$ when evaluated from Equation (3), reads:

$$\left(\frac{\delta\Delta G_{mix}}{\delta n_1}\right)_{n=1,P,T} = RT\left[\ln\phi_1 + 1 \pm \frac{V_1}{V_2} + X_{12}\right] \quad (13)$$

At equilibrium, both chemical potentials are equal to each other. Combination of Equations (9)–(13) yields:

$$\chi_{12} = \ln\frac{273.15Rv_2}{V_g^0 V_1 P_1^0} \pm 1 + \frac{V_1}{M_2 v_2} \pm \frac{B_{11} \pm V_1}{RT} P_1^0 \quad (14)$$

Equation (14) is used routinely for calculation of χ_{12} from IGC experiments.

When a polymer pair is used as a stationary (liquid) phase in a chromatographic column, subscripts 2 and 3 will be used to represent polymers 2 and 3, respectively (subscript 1 refers to the test solute). The interaction between the two polymers is expressed in terms of the free energy of mixing ΔG_{mix} which has the same form as Equation 3, only the subscripts change to 2 and 3. the first two (entropic) terms in this equation are negligible for polymer blends. Thus, for the polymer blend being miscible (ΔG_{mix} being negative), χ_{23} must be negative. When considering IGC of polymer blends, then the free energy of mixing must be written for a three-component system. It is usually expressed as

$$\begin{aligned}\Delta G_{mix} &= RT[n_1\ln\phi_1 + n_2\ln\phi_2 + n_3\ln\phi_3 \\ &\quad + n_1\phi_2\chi_{12} + n_1\phi_3\chi_{13} + n_2\phi_3\chi_{23}]\end{aligned} \quad (15)$$

Equation (15) is considered to be satisfactory for nonpolar mixtures. The interaction coefficients χ are considered to be independent of the composition of the blend. The derivative of ΔG_{mix} Equation (15) is

$$\begin{aligned}\left(\frac{\delta\Delta G}{\delta n_1}\right)_{n=1,P,T} &= RT\left[\ln\phi_1 + 1 \pm \frac{V_1}{V_2}\phi_2 \pm \frac{V_1}{V_3}\phi_3 + \phi_2\chi_{12}\right. \\ &\quad \left. + \phi_3\chi_{13} \pm \frac{V_1}{V_2}\phi_2\phi_3\chi_{23}\right]\end{aligned} \quad (16)$$

In Equation (14), v_2 should be replaced by $(W_2v_2 + W_3v_3)$, where W_2 and W_3 are the weight fractions and v_2 and v_3 are the corresponding specific volumes of the two polymers in the blend. Thus, one can easily derive Equation (17):

$$\ln\frac{273.15R(W_2v_2+W_3v_3)}{V_g^0V_1P_1^0}\pm 1\pm\frac{B_{11}\pm V_1}{RT}P_1^0 = \phi_2\left[\chi_{12}\pm\frac{V_1}{M_2v_2}\right]+\phi_3\left[\chi_{13}\pm\frac{V_1}{M_3v_3}\right]\pm\frac{V_1}{V_2}\phi_2\phi_3\chi_{23} \tag{17}$$

Usually the parameter χ_{23}' is introduced as

$$\chi_{23}=\left(\frac{V_1}{V_2}\right)\chi_{23} \tag{18}$$

Comparison of Equations (14) and (18) suggests that to obtain χ_{23} for blends, χ_{12} and χ_{13} have to be known. Thus, three columns are usually prepared—two from homopolymers and a third from a blend. The three columns should be studied under identical conditions for column temperature, carrier gas flow rate, inlet pressure and the same solutes should be used. All auxiliary parameters (P_1^0, T, M_2, M_3, V_1, v_2, v_3, and B_{11}) will then be identical for the three experiments, and a combination of Equation (14) (taken twice for two homopolymers) and Equation (18) for the blend will yield:

$$\chi_{23}=\frac{\ln\dfrac{V^0_{g,blend}}{W_2v_2+W_3v_3}\pm\phi_2\ln\dfrac{V^0_{g,2}}{v_2}\pm\phi_3\ln\dfrac{V^0_{g,3}}{v_3}}{\phi_2\phi_3} \tag{19}$$

Here, the second subscript of V_g^0 identifies the nature of the column. From Equation (19), χ_{23}' may be calculated even for solutes for which the parameters P_1^0, B_{11}, and V_1 are not known or are known with insufficient accuracy.

The parameter "B" is introduced as a binary interaction energy parameter (also referred to the contact energy parameter or excess cohesive density) and its relationship to the parameter χ_{12} is:

$$\frac{B_{12}}{RT}=\frac{\chi_{12}}{V_1} \tag{20}$$

For polymer blends, one can obtain a similar relationship for B_{23} to that in Equation (20) as follows:

$$B_{23}=RT\frac{\chi'_{23}}{V_1} \tag{21}$$

B_{23} determines the miscibility of the blend with a negative value being necessary for mixing. Munk *et al.*[57] were first to introduce this thermodynamic parameter for the evaluation of the miscibility of blends. B_{23} may also be evaluated directly from the experimental retention volumes and weight fractions w_i by combining Equations 19 and 21,

$$B_{23} = \left(\frac{RT}{V_1\phi_2\phi_3}\right)\left[\ln\frac{V^0_{g,blend}}{W_2v_2 + W_3v_3} \pm \phi_2 \ln\frac{V^0_{g,2}}{v_2} \pm \phi_3 \ln\frac{V^0_{g,3}}{v_3}\right] \tag{22}$$

Munk *et al.*[57] showed that B_{23} values evaluated from experiments depended on the chemical nature of the solute, in contradiction to theory. To correct for this effect, Munk introduced a phenomenological relation developed by Munk and Al-Saigh[28] and suggested by Pouchly *et al.*.[58]

Several issues are still under investigation and need to be resolved which, in turn, will improve the IGC method further. Recently, several researchers cautioned about the inadequacy of Flory-Huggins theory for polymer solution thermodynamics. Several attempts were made to modify Flory-Huggins theory by employing different approaches. For example, Fujisawa *et al.*[59,60] have used a different equation of state based on free volume. Riedle[61] has used the Fujisawa approach and applied it to a system of carbon tetrachloride-poly(vinyl methyl ether). He reported that Fujisawa's approach yielded better agreement over a wide range of temperature, than Flory's equation of state. They concluded that this improvement is due to a more accurate representation of free volume which does not overestimate the solvent-polymer free volume. However, the Riedle experimental approach was not clearly described and there was a good possibility that IGC was not employed to test Fujisawa's theory. It is of interest to note Fujisawa's theoretical approach for the calculation of χ_{12}; however, no similar theories were reported for polymer blends.

Fujisawa's theory is similar to that of Flory, both use the reduced variables, P, V, and T. However, Fujisawa's theory uses a different reduced equation of state. Flory's equation of state is

$$\frac{P*V*}{T*} = \left[\frac{V*^{1/3}}{(V*^{1/3} - 1)}\right] - \frac{1}{V*T*} \tag{23}$$

where P*, V*, and T* are the reduced pressure, volume and temperature, respectively. Fujisawa reduced equation of state is

$$\frac{P*V*}{T*} = \left[\frac{V*^{2}}{(V* - 1)^{2}}\right] - \frac{1}{V*T*} \tag{24}$$

The interaction parameters χ_{12} can be obtained using either of these reduced equations of state as follows:

$$\chi_{12} = \left(\frac{P_1 V_1}{v_1 RT}\right)\left(\frac{A^2 \alpha_1 T}{2} + Y_{12}\right) \tag{25}$$

where α_1 is the thermal expansion coefficient, and Y_{12} and A are terms derived using the molecular surfaces of the solute and the polymer, respectively. For more details about the derivations of these two terms consult ref..[61]

We have shown that IGC yielded different χ_{23} values when the chemical nature of the solutes was varied.[28] This created a debate that several IGC investigators were interested in resolving. Horta *et al.*[62] reported that the equation-of-state does not yield true polymer-polymer interaction parameters on polymer blends. They used the molecular surfaces to obtain the polymer-polymer interaction parameters independent of the solute chemical nature. They reported results in good agreement with those obtained from the vapor sorption method. Shi and Schreiber[63] described a corrective measure to treat this issue. They examined a second contributing factor to this effect, the nonrandom partitioning of vapor phase molecules between the components of a solid's surface layer. Munk *et al.*[57] developed a theory of mixing based on the multidimensional solubility parameter approach.

Since the effect of the chemical nature of the solutes is important for the miscibility the polymer blends, Munk[57] developed theory based on several types of intermolecular interactions (all mediated by molecular surfaces) that allowed for the evaluation of the actual polymer-polymer interaction coefficients. The parameter B_{23} is used as an indicator for the blends miscibility (B_{23} is related to χ_{23}, see Equation (21)). The apparent B_{23}^{A} is derived as follows:

$$B_{23}^{A} = B_{23}\left[\frac{S_1}{(S_2\phi_2 + S_3\phi_3)}\right] + (B_{12} - B_{13})\left[\frac{S_3 - S_2}{(S_2\phi_2 + S_3\phi_3)}\right] \tag{26}$$

where S_1, S_2, and S_3 are the molecular surface area per unit volume of the solute, polymer 1 and polymer 2, respectively. It is apparent that Equation (26) involves correction factors relating to the molecular surfaces of all entities. However, experiment yields only the apparent values of B_{23}^{A} which are strongly dependent of the nature of the solute used. The reasons for this are:

1. different surface-to-volume ratio of different solute molecules, and
2. the difference in the surfaces-to-volume ratios of the two polymers; this is a major effect. The second term in Equation (26) predicts that the difference between B_{23}^{A} and B_{23} will be larger when both $(B_{12} - B_{13})$ and $(S_3 - S_2)$ differ significantly from zero.

The true value of B_{23}, independent of the chemical nature of solutes, is derived based on the solubility parameters of the two polymers as

$$B_{23} = \frac{C_{23} S_2 S_3}{(S_2 \phi_2 + S_3 \phi_3)} \tag{27}$$

where C_{23} is a correction term based on the solubility parameters as follows

$$C_{23} = [(\delta_{2,w} - \delta_{3,w})^2 + (\delta_{2,p} - \delta_{3,p})^2 + (\delta_{2,a} - \delta_{3,a})(\delta_{2,d} - \delta_{3,d}) \tag{28}$$

where subscripts 2 and 3 are for polymer 2 and 3, respectively; and subscripts W, P, a, and d designate dispersive, polar, electron acceptor, and electron donor intermolecular interactions, respectively.

$$\frac{B_{23}^{A}}{S_1} = \frac{B_{23}}{(S_2 \phi_2 + S_3 \phi_3)} + \left[\frac{(B_{12} - B_{13})}{S_1}\right]\left[\frac{S_3 - S_2}{(S_2 \phi_2 + S_3 \phi_3)}\right] \tag{29}$$

Provided that the S_1 values of all solutes are known, it is possible to plot (B_{23}^{A}/S_1) as a function of $(B_{12} - B_{13})/S_1$ and to obtain $B_{23}/(S_2 \phi_2 + S_3 \phi_3)$ as the intercept and $[(S_3 - S_2)/(S_2 \phi_2 + S_3 \phi_3)]$ as the slope. Equation (29) was applied by Munk *et al.* [57] to three polymer blend systems. They concluded that this theory was able to predict the miscibility of a polymer blend from the multi-dimensional solubility parameters of individual polymers. These parameters were obtained by IGC on samples of pure homopolymers.

Melting Point Depression

For polymer blends containing amorphous and semicrystalline homopolymers, the morphology of the blend is more complex as compared to an amorphous-amorphous polymer pair. Above the semicrystalline polymer melting point, both polymers will be at melt state. However, below the semicrystalline polymer melting point, the structure of the blend contains two domains, amorphous and crystalline. Therefore, the chromatographic retention will involve two mechanisms, one caused by the interaction of solute with the amorphous domain, and the other caused by the interaction of solutes with the crystalline surface. To allow thermodynamic validity of the polymer-polymer interaction coefficient χ_{23}', correction of the specific retention volumes V_g° in Equation (8) is necessary. For a complex blend involve a semicrystalline diluent, it is possible to obtain the polymer-polymer interaction coefficient χ_{23} and the interaction energy parameter B_{23} experimentally in a different way than explained earlier. Melting point depression of a polymer mixture (blend) containing a semicrystalline polymer can be used for quantifying the heat of mixing of the polymer pair.[22-27]

When crystals of the semicrystalline polymer are in equilibrium with the amorphous part of the semicrystalline and the amorphous counterpolymer, the melting point of the semicrystalline polymer will be lower than when the equilibrium is with the amorphous part of the semicrystalline polymer only. This is known as a melting point depression resulting of mixing amorphous polymer with a semicrystalline polymer. In most cases, the amount of the depression of the melting point depends on the weight fraction of the diluent polymer. The melting point depression can be used as indicator for the polymer blend miscibility. Most of the work performed thus far using melting point depression is based on calorimetry, and only a few studies have been reported with IGC.[47] The thermodynamic analysis of polymer-polymer mixtures using melting point depression can be based on the Flory-Huggins theory.[22,25,53] Information can only be obtained at temperature close to the pure semicrystalline polymer melting point. However, the melting point measured is influenced by a number of factors (perfection, size, and environment of crystals) which must be accounted for.

Combining Equations (1), (2) and (4), the free energy of mixing per unit volume of the blend is obtained as follows:

$$\frac{\Delta G_{mix}}{(n_2V_2 + n_3V_3)} = RT\left[\frac{\rho_2\phi_2}{M_2}\ln\phi_2 + \frac{\rho_3\phi_3}{M_3}\ln\phi_3\right] + B_{23}\phi_2\phi_3 \qquad (30)$$

Most of the parameters in equation 30 were defined earlier except for the molecular weights M_2 and M_3 and the densities ρ_2 and ρ_3. Subscripts 2 and 3 refer to polymer 2 (semicrystalline) and 3 (amorphous) in the mixture.

The chemical potentials of the pure semicrystalline polymer (μ_2°) and the semicrystalline polymer in the mixture (μ_2) (both per unit volume) are computed from Equation 30 as follows:

$$\mu_2 - \mu_2^o = \left(\frac{\delta \Delta G_{mix}}{\delta n_2}\right)_{T,P,V_2} \qquad (31)$$

The chemical potential of perfect crystals of the semicrystalline polymer at any temperature relative to the same reference state is $\mu_2{}^c$ and is obtained as follows:

$$\mu_2^c - \mu_2^o = -\left(\frac{\Delta H_{2u}}{V_{2u}}\right)\left(1 - \frac{T_m}{T_m^o}\right) \qquad (32)$$

where T_m and T_m^o are the melting points of polymer 2 (semicrystalline) in the mixture and pure semicrystalline polymer, respectively. The quantity $\Delta H_{2u}/V_{2u}$ is the heat of fusion of the semicrystalline polymer per unit volume.

At equilibrium, the chemical potential of the perfect crystals in the pure semicrystalline polymer is equal to that of the semicrystalline polymer in the mixture,

$$\mu_2^c = \mu_2 \qquad (33)$$

Combining Equations (30–32) yields Equation (34) as an expression of the extent of the depression of the melting point of the semicrystalline polymer after mixing.

$$\frac{1}{T_m} - \frac{1}{T_m^o} = -R\left(\frac{V_{2u}}{\Delta H_{2u}}\right)\left[\frac{\rho_2 \ln \phi_2}{M_2} + \left(\frac{\rho_2}{M_2} - \frac{\rho_3}{M_3}\right)v_3 + \left(\frac{B_{23}}{RT_m}\right)\phi_3^2\right] \qquad (34)$$

The quantities ϕ_2, ϕ_3, ρ_2, ρ_3, M_2, and M_3 are the volume fractions, densities, and molecular weight of the semicrystalline (2) and the diluent polymer (3), respectively. B_{23} is the polymer-polymer interaction energy that is related to Flory-Huggins interaction parameter χ_{23}' as

$$B_{23} = RT_m^o\left(\frac{\chi_2'}{V_3}\right) \qquad (35)$$

where V_3 is the molar volume of component 3 (the amorphous diluent polymer).

The first two terms in Equation (34) are the entropic contribution and the third term is the enthalpic contribution. If the molecular weight of the semicrystalline and the diluent polymers are high, then the entropic contribution represents less than 1°C which would play only a minor role in the melting point depression. Therefore, the values of the first two terms can be neglected, and Equation (34) reads:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = -\left(\frac{V_{2u}}{\Delta H_{2u}}\right)\left(\frac{B_{23}}{T_m}\right)\phi_3^2 \tag{36}$$

Rearrangement yields:

$$\frac{T_m^o - T_m}{T_m T_m^o} = -\left(\frac{V_{2u}}{\Delta H_{2u}}\right)\left(\frac{B_{23}}{T_m}\right)\phi_3^2 \tag{37}$$

which can be rewritten in the following form:

$$\Delta T_m = T_m^o - T_m = -T_m^o\left(\frac{V_{2u}}{\Delta H_{2u}}\right)B_{23}\phi_3^2 \tag{38}$$

ΔT_m in Equation (38) is determined experimentally from IGC. Equation (38) is used to calculate the polymer-polymer interaction energy B_{23} for semicrystalline-amorphous diluent blends.

Finally, there have been several attempts to derive successful equations for the equilibrium and nonequilibrium melting point depression for polymer blends containing a crystallizable diluent[54,57-60] using calorimetry. Some of these equations have been proven to be successful in obtaining information on polymer blend systems, particularly the thermodynamic properties and interaction parameters. However, there have been some arguments concerning the dependence of χ on composition which may lead to an error in the χ parameter[64] Jo and Kwon[64] have derived an equation for the equilibrium melting point depression based on the equation of state theory which eliminated the composition dependence of χ. They reported that their equation yielded a more accurate χ parameter when applied to several blend systems using methods other than IGC.

DATA REDUCTION

The solute specific retention volumes V_g^o, the interaction coefficients χ_{12} and χ_{13}, and the true polymer-polymer interaction coefficients χ_{23} are calculated according to Equations (8), (14) and (19). The vapor pressure P_1^o calculated from the Antoine equation

$$\log P_1^o = \frac{A - B}{(t + C)} \tag{39}$$

where T is the temperature in °C, and the constants, A, B, and C are taken from Dreisbach's compilation.[65] The molar volumes of the solutes V_1 were calculated using Equations (40–42),

$$V_1 = \frac{M_1}{\rho_L} \tag{40}$$

$$\rho_L + \rho_V = a - bt \tag{41}$$

$$\rho_V = \frac{P_1^o M_1}{RT} \tag{42}$$

where ρ_l and ρ_v are the are the respective solute densities in the liquid and saturated vapor state, M_1 is the molecular weight of the solute, and P_1^o is the pressure calculated from Equation (39). The constants a and b are from Dreisbach's compilation.[65] Second virial coefficients B_{11} are computed using:[66]

$$\frac{B_{11}}{V_c} = 0.430 - 0.886\left(\frac{T_C}{T}\right) - 0.694\left(\frac{T_C}{T}\right)^2 - 0.0375\ (n-1)\left(\frac{T_C}{T}\right)^{4.5} \tag{43}$$

where V_c and T_c are the critical molar volume and the critical temperature of the solute, respectively, and n is the number of carbon atoms in alkanes number of corresponding groups in non-alkane solutes.

The molar heat (enthalpy) of sorption of the solutes absorbed by the amorphous part of the blend (ΔH_1^s) is[67]

$$\Delta H_1^s = -R\,\frac{\delta \ln V_g^o}{\delta\left(\frac{1}{T}\right)} \tag{44}$$

The average partial molar heat of mixing at infinite dilution of the solute calculated as follows:

$$\Delta H_1^\infty = R\,\frac{\delta \ln \Omega_1^\infty}{\delta\left(\frac{1}{T}\right)} \tag{45}$$

where Ω_1^∞ is the weight fraction activity coefficient of the solute at infinite dilution, which is calculated from

$$\Omega_1^\infty = \frac{273.15\,R}{V_g^o\,P_1^o\,M_1}\,\exp[-P_1^o(B_{11} - V_1)]RT \tag{46}$$

where P_1^o, V_1, and B_{11} were defined in equation (14). Equation (46) was developed by Patterson *et al.*[68] to replace the original equation for infinite dilution activity coefficient developed by Everett.[69] The original equation depended on an uncertain quantity: the molecular weight of the polymer.

The partial molar free energy of mixing at infinite dilution is calculated from the weight fraction activity coefficient of the solutes

$$\Delta G_1^\infty = R\,T \ln \Omega_1^\infty \tag{47}$$

The partial molar free energy of sorption at infinite dilution is calculated

$$\Delta G_1^s = -RT \ln\left[\frac{M_1\, V_g^o}{273.15\, R}\right] \tag{48}$$

The entropy of sorption of solutes is calculated by incorporating Equations (44) and (48).

$$\Delta G_1^s = \Delta H_1^s - T\Delta S_1^s \tag{49}$$

The specific volumes of semicrystalline polymer (the inverse of ρ_{sc}) in the temperature range of study can be calculated as follows:

$$\frac{\rho_{sc}}{\rho_a} = 1 + 0.13X_c \tag{50}$$

$$\rho_{sc} = 1.74(1 + 0.13X_c) \tag{51}$$

where ρ_{sc} and ρ_a are the densities of semicrystalline and amorphous states of the semicrystalline polymer, and X_c is the degree of crystallinity.

EXPERIMENTAL

Column Preparation

In IGC experiments, the polymer-polymer interaction parameter needs to be calculated with high precision. χ_{23} represents the difference between various polymer-solute interactions that are usually of the same order of magnitude. Small absolute error in these quantities can result in a large relative error in the calculated χ_{23} parameter. Each of homopolymer and blend sample should be weighed carefully and dissolved in appropriate solvents (about 100 mL). The polymer samples can then be used to coat the solid support using our suggested method (soaking method).[28] This coating technique was developed to reduce the error associated with inaccurate determination of the polymer mass on the column. The polymer mass determination is one of the chief sources of the systematic error in the specific retention data. Solvent residue may be removed by drying overnight in a vacuum oven at 100°C. Prior to any retention measurements, each new column may be conditioned in the chromatograph at 120°C for 8 h, during which the carrier gas is sweeped through the system until a low and steady base-line signal is obtained.

A minimum of three columns should be prepared; the first containing pure polymer 1, the second containing pure polymer 2, and the third containing the blend. The three columns should be studied under identical conditions allowing measurements of the interaction parameters χ_{12}, χ_{13}, and χ_{23}. If the effect of composition of the blend on the interaction parameter needs to be studied, then six blend columns of different weight fractions of each polymer and counter polymer need to be prepared, ranging from 0 to 100% wt. The complete procedure for the chromatographic measurements are reported in ref.[70] Low molecular-weight-solutes of different chemical natures are injected onto the packed column.

Experiments show that the equilibrium (diffusion across the layer) is established reasonably fast when the polymer is kept at a temperature significantly higher (by about 50–70K) than the glass-transition temperature.[71] However, polymers below their glass-transition temperature are not penetrated by solute molecules under GC conditions.

Data Acquisition

Measurements are usually made on a conventional GC equipped with a flame ionization (FID) or thermal conductivity (TC) detector. Thermal conductivity is often preferred because it offers continuous monitoring of the carrier gas. The flow rate of the carrier gas is controlled by a precision needle valve and is measured by a thermostated soap-bubble flow meter. The flow rate of the carrier gas is monitored frequently to ensure consistent stability of the flow rate. The flow rate is varied within a range of 1–30 mL/min to explore its dependence on V_g° values. The inlet and outlet pressures are frequently monitored by a precision mercury manometer. The outlet pressure is generally atmospheric while the inlet pressure is in the range of 900 mm Hg in conventional IGC experiments. Methane is used to serve as a marker for retention time (if a FID detector is used), otherwise air can be used for the TC detector, to measure dead volume in the column.

Control of Experimental Artifacts

The main complicating factors in IGC are: 1. concentration effects associated with larger solute injections; 2. slow diffusion of the solute through the polymer layer; 3. adsorption of the solute onto the surface of the polymer.

The following steps are recommended to obtain meaningful values for the specific retention volume: (1) data should be either extrapolated to vanishing amounts of injected solute or measured by using injection amounts arbitrarily defined as vanishingly small; (2) the data should be extrapolated to infinite polymer loading to eliminate the effect of the adsorption of the solute onto the surface of the polymer; (3) the data should be extrapolated to zero flow rate to compensate for slow establishment of phase equilibrium. The reader is referred to ref.[45] for additional details.

APPLICATION

Although this article focuses on polymer blends, it would be beneficial to review the general uses of IGC, which followed the pioneering work of Smidsord and Guillet.[72] Tait and Abushihada[73] among other groups, compared IGC results to those obtained by different methods. They compared the ability of IGC and vapor sorption techniques to measure polymer-solvent interaction parameters. Their finding was that the IGC method is capable of obtaining data in the region (concentration and temperature) above which vapor pressure measurements became difficult and IGC generally required less experimental time. Grajek and Witkiewicz[74] compared IGC with the static method in their study for the determination of the adsorption isotherms of argon and benzene on activated carbons. Al-Saigh and Munk,[28] concluded that IGC is capable of sufficient accuracy to be of great value in measuring interaction parameters at infinite solvent dilution, and that solvent dependency of the measured polymer-polymer interaction parameter is a result of weakness in the thermodynamic theories used, and not a fault of the IGC technique itself. Reviews on IGC are given in refs.[67,70,75-77]. Examples of the applications of IGC to polymers and polymer blends are listed in Table I & II, respectively.

Amorphous-Amorphous Polymer Blends

Most of the work performed in this area has focused on polymer-polymer interaction parameters. This stemmed from the fact that knowledge of compatibility is most significant when studying polymer blends. Measurement of χ_{23} are reported in a temperature range in which the two polymers are in a melt state; the solid state is avoided even though the possibility exists that the polymer pair can be compatible in the solid or semisolid state. Deshpade *et al.*[78] were the first to apply IGC to a blend of poly(dimethyl siloxane)/n-tetracosane and di-*n*-octyl phthalate/n-tetracosane. Although these blends consist of low-molecular-weight polymers, their results indicated that IGC is useful in characterizing a mixture of low-molecular-weight polymers, and applicable to a ternary stationary phase. They calculated χ_{23} by using the Prigogine-Flory theory and showed that the

TABLE I Applications of IGC to Polymer Systems

Partition and activity coefficients	
a. Infinite solvent dilution	30,35,37,51,119–121
b. Finite concentration	68,78,83,98,99,101,115,117,122–133
Polymer-solvent or polymer-polymer interaction parameters	
a. Infinite solvent dilution	109–111
b. Finite concentration	134
Enthalpy of mixing	46,47,120
Solubility parameter	135–139
Glass-transition and melting temperatures	43,46,71,119,140,141–144
Crystallinity of polymer phase	45,47,71,145–148
Solute diffusion coefficients	149–160
Cross-linking studies	161–164
Interfacial studies	76, 165
Methodology	57,62,63,166–171
Surface characterization	74,92,96,145,156,159–164,172–233
Hydrogen-bonding studies	234
Acidity studies	235
Food	227–230,236
Plasticizers	226
Surfactants	231
Epoxy-resin curing	237
Paints and coatings	238
Microstructure studies	239
Conducting polymers	240–242

TABLE II Polymer Blends Studied by IGC

Poly(dimethyl siloxane)/polycarbonate	32–34
Poly(methyl acrylate)/poly(epichlorohydrin)	28, 57, 89
Poly(methacrylates)/poly(vinyl chloride)	31
Polystyrene/poly(dimethyl siloxane)	37
Polystyrene/poly(n-butyl methacrylate)	30, 81, 92
Polystyrene/poly(acrylic acid)	243
Polystyrene/polybutadiene	84
Polystyrene/poly(vinyl methyl ether)	35, 120, 244
Poly(vinyl chloride)/poly(ε-caprolactone)	10, 79, 110, 117, 243, 245
Poly(vinyl chloride)/polyacrylates	31
Poly(vinyl chloride)/poly(methyl methacrylate)	31
Poly(vinyl chloride)/plasticizer	117
Poly(vinyl chloride)/chlorinated polyethylene	83
Poly(vinylidene fluoride)/poly(methyl methacrylate)	29, 92
Poly(vinylidene fluoride)/poly(ethyl methacrylate)	47
Poly(vinylidene fluoride)/poly(ethyl acrylate)	104
Poly(vinyl acetate)/poly(*n*-butyl methacrylate)	39
Poly(vinyl acetate)/poly(vinyl isobutylether)	41
Poly(vinyl acetate)/poly(epichlorohydrin)	40, 57
Poly(vinyl acetate)/poly(vinyl isobutyl ether)	41
Poly(vinyl acetate)/poly(4-hydroxystyrene)	82,86
ε-caprolactone/poly(epichlorohydrin)	44, 57, 126, 245
Poly(4-hydroxystyrene)/ε-caprolactone	91
Polyethylene glycol/polypropylene glycol	80
Polyethylene glycol/polypropylene glycol adipate	80
Poly(dimethyl phenylene oxide)/polystyrene	89, 246
Poly(dimethyl phenylene oxide)/poly(methyl styrene)	246
Poly(ethylene oxide)/polystyrene	90
Poly(ethylene oxide)/phenoxy resin	247
Poly(ethylene oxide)/poly(epichlorohydrin)	57
Poly(ethylene oxide)/poly(2-hydroxypropyl acrylate)	57
Poly(ethylene oxide)/poly(methyl methacrylate)	91, 92
Triblock copolymer of poly(ethylene oxide)/ poly(methyl methacrylate)	108
Poly(methyl methacrylate)/poly(methyl methacrylate-co-butyl methacrylate)	114
Polystyrene/poly(styrene-*co*-*n*-butylmethacrylate)	113
Polystyrene/Poly(styrene-*co*-*iso*-butyl methacrylate)	113
Poly(hydroxy ether of bisphenol A)/poly(vinyl methyl ether	87, 89
Poly(styrene-*co*-acrylic acid)/polymethacrylates	112
Poly(styrene-*co*-acrylic acid)/poly(methacrylate-*co*-4-vinylpyridine)	112
Poly(vinyl chloride)/poly(ethylene-*co*-vinyl acetate)	38
Poly(isobutyl methacrylate)/poly(styrene-*co*-acrylic acid)	116
Poly(isobutyl methacrylate)/poly(styrene-*co*-N,N-dimethyl aminoethyl methacrylate)	116
Poly(methyl methacrylate)/poly(vinylidene chloride)	248
Polypropylene/fluorochemical additive	63
Poly(ethyl acrylate)/poly(vinyl propionate)	84
Poly(methyl acrylate)/poly(vinyl acetate)	85

interaction parameters depended on the chemical nature of the solute. They attempted to eliminate this dependence either by using the molar volumes of the solutes or the molar surfaces.

Olabishi,[79] applied IGC to a blend of several compositions poly(ε-caprolactone)/poly(vinyl chloride) at 120°C. These findings supported Deshpande's results[78] in attributing the solute dependency to the inability of the Flory-Huggins theory to account for all the polymer-solute interactions. Olabishi[79] concluded that the complementary dissimilarity is the rule of polymer miscibility when specific interaction forces are involved. The parameter χ_{23} yielded negative values (–0.77 to –0.15) for polar solutes and slightly positive values (0.1 to 2.2) for nonpolar solutes. He cautioned that the reliability of these values depends strongly on the effectiveness of each solute in revealing different contributions to the polymer-polymer interaction energy. This dependence is the actual contributing factor in the variation of χ_{23} values with the chemical nature of the solutes. These values were compared with those obtained from static vapor sorption, and the IGC data yielded lower χ_{23} values than the sorption method.

IGC was applied to low-molecular-weight oligomers ranging from 2000 to 40,000 g/mol.[80] Mixtures of poly(ethylene glycol) with poly(propylene glycol) and poly(ethylene glycol adipate) were examined at a temperature range of 53° to 115°C. The parameters χ_{23} were found to be temperature dependent, ranging from –17 to +12. This study showed a complex thermodynamic behavior. The interaction parameters depended on temperature which led to the conclusion that this dependence is not a general indication of the existence of the critical temperature of mixing, particularly lower critical standard temperature (LCST). Also, χ_{23} values depended on the composition of the polymer pair because of the specific interaction between components. This phenomenon was explained on the basis of aggregation or association in mixtures. The experimental values of χ_{23} showed essential differences, especially for enthalpy and entropy, from those calculated theoretically using Flory's theory.

In similar studies, one of the mixture components was a low-molecular-weight oligomer. This mixture represents a composition somewhere between a mixture with one low molecular-weight component and two "true" high-molecular weight polymers. Su and Patterson[35] studied a blend of polystyrene (M_n = 600) with poly(vinyl methyl ether) (M_w = 10000). This mixture was found to be compatible. They avoided the difficulties associated with the high-glass transition temperature of polystyrene by selecting a polystyrene oligomer. The polymer-polymer coefficient χ_{23} parameters were obtained in the range of –0.10 and to 0.30. However, isopropyl alcohol (poor solvent for both polymers) yielded values as high as 1.47, while chloroform yielded 0.65. However, when higher molecular weight polystyrene was used, the blends were incompatible. The highest average value for χ_{23} was 0.42 when 30% of polystyrene was used, and the lowest average value of 0.23 when 35% polystyrene was used.

DiPaola-Baranyi[29,81] and Al-Saigh and Munk[28] applied IGC to a variety of polymer blends. A blend of poly(methyl acrylate)-polyepichlorohydrin was examined and the measured values of χ_{23} varied between –0.09 and +0.49 with an experimental error of about 0.01.[28] Values within each family of solutes were clustered together. Thus, the dependence of the interaction parameters on the chemical nature of solutes was real. They showed that χ_{23} may contain other solute-dependent contributions to the free energy of mixing which are not properly accounted for by the polymer solution thermodynamic theories. In addition, they pointed out in the same study, the variation of χ_{23} from solute to solute is partly due to the experimental errors and artifacts. A series of critical and corrective procedures were undertaken that considerable reduced experimental errors.[42,82]

The thermodynamic miscibility of several polystyrene-poly(butyl methacrylate) mixtures was studied as a function of composition, temperature, and molecular weight of polystyrene.[30] No strong attractive forces between these two polymers were found. Values of χ_{23} ranged from –0.4 at lower temperatures to slightly positive at higher temperatures. However, the IGC results indicated the miscibility of this blend when low-molecular-weight polystyrene was used over the entire range of composition. With high-molecular-weight polystyrene, the blend was immiscible. The resultant miscibility arose from a more favorable entropic effect when the molecular weight of polystyrene was lowered. The IGC results were tested successfully by using differential scanning calorimetry (DSC) on the same blends.

One of the developments made to the theory of IGC was the ability to calculate B_{23}, the binary interaction energy parameter or the contact energy parameter, Equation (22). Munk *et al.*[44] calculated B_{23} of poly(ε-caprolacton)-poly(epichlorohydrin) (PCL-PECH) blend and correlated this parameter with the Hildebrand solubility parameter of the solute. This correlation was a successful attempt, for the first time, to obtain a manageable way by which binary interaction data could be determined for a polymer blend.

This correlation was used to estimate the true B_{23} for the blend based on the experimental data. This study was conducted at 100 °C above the glass transition of PECH to ensure ideal chromatographic behavior over the entire composition range. With 25 solutes, the compositional dependence on χ_{23}, as well as the overall data reproductivity, was assessed. PCL-PECH blends were found miscible at all composition, by IGC and other methods, because of the favorable interaction between chlorine in PECH and the carbonyl group in PCL. To assess the overall reproducibility among independent experiments, two identical columns were prepared for each composition. The V_g° values for each pair of columns were found to differ by 0.5–1.5%. The χ_{23} values ranged between –2.3 to +0.12 depending on the polarity of the type of solutes. Miscibility of PECH-PCL was favored when the composition of PECH-PCL was 50-50 by weight. This was apparent when ln V_g° was plotted versus the composition of the blend; a downward curvature was obtained which reflected the strength of the interaction between the two polymer pairs. Similar results were obtained on poly(vinylidene fluoride)-poly(ethyl methacrylate) blend (see the next section for more details). Such plots revealed insight regarding the behavior of hypothetical noninteracting blends by obtaining the average of the ln V_g° of the two pure homopolymers (Fig. 1).

Tyagi *et al.*[41] obtained similar results, and found a real dependence of the chemical nature of the solutes and the composition of the blend on χ_{23}. In their application of IGC to a blend of poly(vinyl acetate)/poly(n-butyl methacrylate) at 100° and 120°C, poly(vinyl acetate)/atactic poly(vinyl isobutyl ether) at 70°C and poly(n-butyl methacrylate)/poly(vinyl isobutyl ether) at 70°C, miscibility of these blends was favored at a ratio 0.4–0.6 weight fraction. El-Hibri and Munk[40] reported that there are erratic variations in χ_{23} for polymer blends in literature because of experimental artifacts and errors. Nevertheless, χ_{23} bears a real dependence on the chemical nature of the solutes which has a fundamental thermodynamic origin. The dependence is smaller than previously thought and appears to be related to the strength of interactions between the solute and the individual homopolymers forming the blends.

Walsh and McKeown[31] investigated the effect of an ester side chain of polyacrylates and polymethacrylate with poly(vinyl chloride). Their results showed low interaction parameters indicating a strong interaction between the polymer pair, especially for polymethacrylate and polyacrylate with shorter ester side chains. These results agreed well with their earlier find-

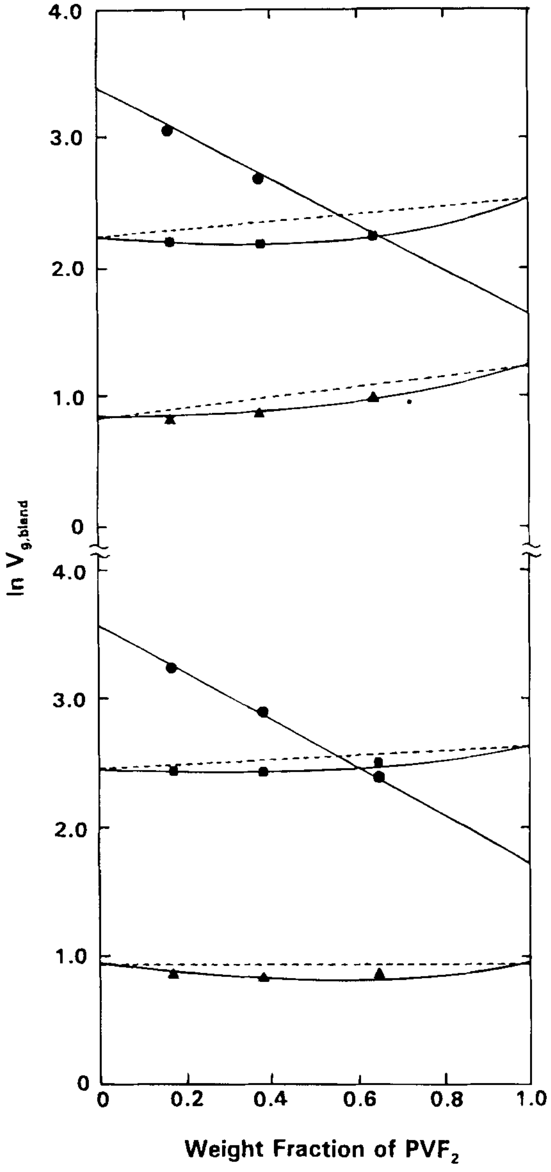

FIGURE 1 (_____) the dependence of V_g° on poly(vinylidene fluoride) (PVF2) volume for selected solutes at 175° (lower) and 185°C (upper): ● dodecane, ■ n n-butyl acetate, △ ethanol; (------) the hypothetical average for pure PVF2 and poly(ethyl methacrylate). (Reprinted with permission from Z.Y.Al-Saigh and P. Chen, Macromolecules, 24, 3788 (1991). Copyright (1991) American Chemical Society.)

ings where polymers with longer ester side chains were found to be not compatible with PVC and phase separated on heating. Walsh[83] also investigated the compatibility of PVC with chlorinated polyethylene. Average χ_{23} values of 0.001 for 25% PVC, –0.009 for 75% PVC, and –0.009 for 85% PVC were obtained indicating that the miscibility was favored at a composition range of 50 to 85% of PVC. Average values of χ_{23} were used in this work, however, the absolute values depended on the nature of solutes and ranged between 0.002 to –0.0002.

Bhattacharyya *et al.* have studied several polymer blends by the IGC: poly(ethyl acrylate)/poly(vinyl propionate)[84] and poly(methyl acrylate)/poly(vinyl acetate)[85] as a function of temperature, composition, and the chemical nature of solutes. Their findings showed that PMA and PVA are miscible in all proportions and the miscibility is not affected by specific interactions between the polymer pair. The absence of specific interactions has been inferred from IGC, which shows a lack of complementary dissimilarity between the polymer pair and that the polymer-polymer interaction parameter has a small but positive value. This system did not exhibit a dependence of miscibility on molecular weight of the polymer pair. Their results were in agreement with the view that the exchange interaction energy is positive but small, as must be the free volume contribution to the free energy of mixing. It is interesting to note that they were able to produce ternary phase diagrams for the polymer pair PMA/PVA in a poor and good solvent. These diagrams contain closed immiscibility loops; the region inside the loop is phase separated while the miscibility region of the blend is outside the loop.

Several attempts were made to eliminate the so-called "solute effect" and to obtain polymer-polymer interaction parameters independent of the chemical nature of solutes, which was addressed by Prolongo and co-workers.[86] They used Scott-Flory-Huggins theory for the calculations of the interaction parameters of poly(vinyl acetate)-poly(4-hydroxystyrene). The interaction parameters showed dependence on the chemical nature of solutes. They attributed the weakness of Scott-Flory-Huggins theory to the fact that this theory assumes that the Gibbs mixing function for the ternary polymer-polymer-solute system is additive with respect to the binary contributions. They adopted the Prolongo *et al.* theory[62] and recalculated the interaction parameters, obtaining negative values of χ_{23}, thus, confirming the miscibility of this blend by hydrogen-bond interaction. The solute-dependence was minimized and only a slight variation with the blend composition was found.

In another study[87] on a blend of poly(hydroxy ether bisphenol A) and poly(vinyl methyl ether), two methods of data analysis were applied; the Prolongo *et al.* method[62] and the Farooque and Deshpande method.[88] Minor differences were found for the interaction energy density B_{23} using both methods. The experimental data were reasonably consistent with the theoretical predictions of an associated model. However, Shi and Shreiber[63] investigated the solute dependency and reviewed several experimental results that support the fact that there is a difference between surface and bulk compositions. Etxeberria *et al.*[87] commented on Shreiber's finding and believe that, if this difference is correct, IGC accurately gives information on the surface interaction in a binary stationary phase. They further believe that avoiding solutes with similar or small V_g° values, the Farooque and Deshpande method[88] can provide a rapid estimation of interaction parameters with a confidence interval close to other more sophisticated methods of the IGC data analysis. In recent studies, Etxeberria *et al.*[89] have applied the lattice fluid theory (the basis of Sanchez's method[90]), in an attempt to eliminate the solute dependence on the miscibility of poly(epichlorohydirn)/poly(methyl acrylate) and poly(hydroxy ether of Bisphenol A) (phenoxy, PH)/poly(vinyl methyl ether) blends. Their conclusion was that lattice fluid theory did not work well for these blends. They recommended to adequately select solutes having only very different V_g° with the pure components of the blend in order to minimize the solute dependence on χ_{23}. They also concluded that Farooque-Deshpande method[88] for data analysis is easier to use, since it does not need the large number of of parameters required for the method based on free volume theories, as in the case of Sanchez's method.[90] In a similar study, Lezcano *et al.*[91] have reached a conclusion similar to Etxeberria *et al.*[89] regarding the usefulness of the Deshpande's method[88] for the minimization of the solute dependence on the polymer-polymer interaction parameters. They applied two theoritical methods: Horta's method[62] and Deshpande's method,[88] and obtained χ_{23} for poly(4-hydroxystyrene)/poly(ε-caprolactone) blend. The values of χ_{23} obtained are reliable which showed an agreement between the two methods. Furthermore, a good concordance has been found between the interaction parameters calculated by the two methods (using IGC) and those obtained by measuring the melting point depression (using DSC) of poly(ε-caprolactone) in binary blend. As Deshpande's method can be derived from that of Horta and because it is simpler, it could be preferentially used in systems in which the surface-to-volume ratios of the polymers are similar and no large differences in the free volumes are present.

Polymer Blends Containing Semicrystalline Diluent

Few results are available on the characterization and the thermodynamics of blends containing semicrystalline polymers using IGC. However, blends containing semicrystalline diluents, particularly fluorinated polymers such as poly(vinylidene fluoride) (PVF_2) and poly(trifluoroethylene) (P_3FE) have been the subject of several studies using calorimetry method.[14-18,24,32,50-52,88] IGC has only been applied to a few polymer blend systems (PVF_2-PMMA),[29,92] (PVF_2-PEMA),[47] Poly(vinylidene fluoride)/poly(vinyl methyl ketone),[70] PEO/polystyrene,[93] PEO/poly(methyl methacrylate),[94] PEO/poly(epichlorohydrin),[57] PEO/poly(2-hydroxypropyl acrylate),[57] and PEO/poly(methyl methacrylate).[95] The miscibility of the blend was increased in the melt using χ_{23} parameters.

DiPaola-Baranyi *et al.*[29] were first to apply IGC to a blend of molten (PVF_2) and (PMMA). Negative interaction parameters were obtained in agreement with the well-known miscibility of this blend above the PVF_2 melting point. The effect of the blend composition on the miscibility were conducted which was in agreement with those obtained by small-angle X-ray scattering and calorimetry. In addition, the glass-transition and melting-point depression data were also measured and used as an indicator of the miscibility of the blend. Al-Saigh and Chen[47] conducted experiments at a temperature range below the melting temperature of the semicrystalline diluent; as expected, melting-point depression of the crystalline component had occurred. The melting point depression was used to measure the miscibility by calculating B_{23}, and was applied to a blend of PEMA and semicrystalline PVF_2. Thermodynamic quantities were in excellent agreement with those obtained by calorimetry on the same blend. For example, the B_{23} parameter for PVF_2-PEMA using DSC was –3.18 cal/mL,[96] as compared to –3.15 cal/mL using IGC.[47] This is the only data available on semicrystalline polymer blends using the melting point depression by IGC. Other polymer blends, such as PVF_2-PEMA and PVF_2-PMMA, exhibited values of –2.98[97] and –0.30[98] cal/mL respectively, using melting point depression by DSC.

If a polymer blend with a semicrystalline polymer diluent is used, below the melting point of the semicrystalline polymer, the morphology of the blend is complex and careful analysis is required to account for the mass of polymer. The morphology of these types of blends depends on kinetic and thermodynamic factors. It has been shown that the amorphous polymer can penetrate into the amorphous phase of the counter polymer between the crystalline lamella.[99,100] However, this interface depends on the strength of the intermolecular interactions between the two polymers.[101] Kumar and Yoon[102,103] have developed a lattice model for interphases in binary semicrystalline-amorphous polymer blends that describes the structure and composition of the crystal-amorphous interface and the size of the interphase and its dependence on the energy of interaction between the polymer pair.

Al-Saigh and Chen[47] showed, below the melting point of the semicrystalline polymer, there are two retention mechanisms: adsorption on the crystalline surfaces (kinetic effect), and absorption into the amorphous layer. Since the latter is thermodynamically important, the mass of the amorphous part of the semicrystalline polymer should only be used in Equation (8). This can be accomplished by subtracting the mass of the crystalline part using the percent crystallinity, calculated from Equation (52) from the original mass used

$$\%X_c = 100\left[1-\left(\frac{V_{g,sample}}{V_{g,amorphous}}\right)\right] \tag{52}$$

Equation (8) then reads,

$$V_g^o = \frac{273.15\Delta t.F.J}{w(1-X_c)T_{room}} \tag{53}$$

where J is the pressure correction factor given in Equation (8). Values of V_g° obtained from Equation (53) are corrected for crystalline surfaces and are amenable for the thermodynamic calculations below the melting point of the semicrystalline polymer. However, above the melt, Equation (8) should be used to calculate the specific retention volumes. Figure 1 shows the dependence of PVF_2-PEMA interactions on the w/v fractions of the homopolymer, which reveals that the miscibility of the blend is greatly enhanced when the composition of the blend is at 50:50 w/w. Furthermore, hypothetical lines for the logarithmic average of the ln V_g° of the two pure polymers were obtained that characterized the behavior of hypothetical noninteracting blends. The strength of the polymer-polymer interaction was attributed to the deviation of the experimental lines from the hypothetical line.[47] However, Galin and Maslinko[104] reported that the miscibility of PVF_2-PEMA was favored at 80% of PVF_2, in contrast to results given in ref.[47] Their average χ_{23} was –0.32 which showed only a slight sensitivity to temperatures between 60° and 200°C.

A similar plot to Figure 1 was obtained on PVF_2—poly(vinyl methyl ketone) blends (Fig. 2) which showed that the miscibility is also favored at 50-50 w/v fractions of PVMK. Above the melting point of the semicrystalline polymer, the effect of temperature on V_g° for the same blend was obtained as shown in Figure 3. A linear relationship was obtained at all temperatures used and for all solutes by plotting the specific retention volumes of the blend versus temperature. Both polymers are in the melt at this temperature range and therefore, the thermodynamic quantities are amenable for interpretation at this region. The straight lines in Figure 3 are meaningful, in which many thermodynamic parameters, like the molar heat of sorption and mixing of solutes into the blend layer, could be calculated.

Amorphous-Copolymer Blends

Thermodynamic properties of copolymers were measured for the following copolymers: dimethyl siloxane-carbonate,[33] ethyl-propylene,[105] ethyl-vinyl acetate,[106,107] styrene-butyl methacrylate,[30] styrene-dimethyl siloxane,[37] triblock copolymer of PEO/PMMA,[108] vinyl acetate-vinyl chloride,[109-111] blend of poly(styrene-*co*-acrylic acid)/series of polymethacrylates[112] and blend of poly(styrene-*co*-acrylic acid)/poly (methacrylate-*co*-4-vinylpyridine).[112] DiPaola-Baranyi[113] studied the miscibility of molten blends of poly(styrene-*n*-butyl methacrylate) and poly(styrene-isobutyl methacrylate) blended with homopolymers with various polar and nonpolar solutes. The thermodynamic interaction parameters obtained for these systems were self-consistent; the miscibility of the copolymer was in qualitative agreement with the interpolated behavior of the parent homopolymer, which reflected the effect of the nearest-neighbor segment interactions on the solution thermodynamics of the copolymer. The homopolymer properties was compared to that of the copolymers which revealed only minor differences between molten poly(*n*-, *iso*, and *sec*-butyl methacrylates).

The blends of PMMA and the copolymer of methyl methacrylate and 10% wt butyl methacrylate were also studied by IGC.[114] Values of χ_{23} ranged from –0.29 to –2.58 to 423 K and depended strongly on the chemi-

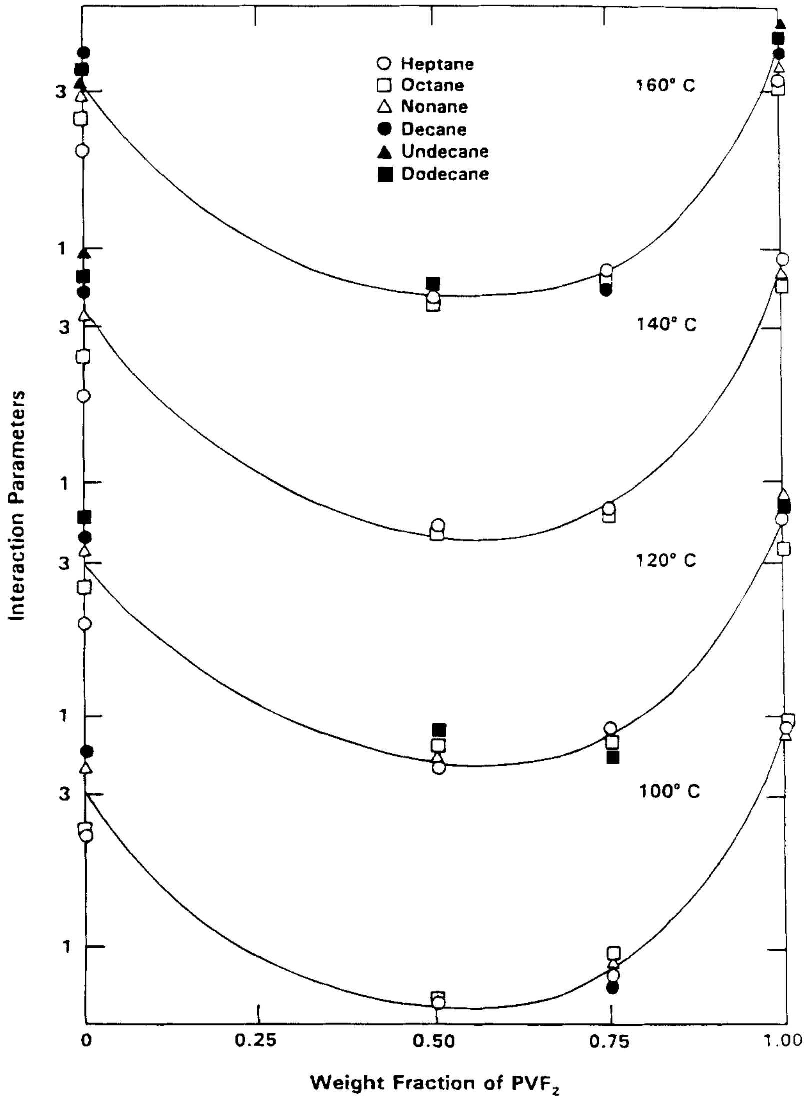

FIGURE 2 The dependence of the polymer-polymer interaction parameter on poly(vinylidene fluoride)-poly(vinyl methyl ketone) blend composition at several temperatures.

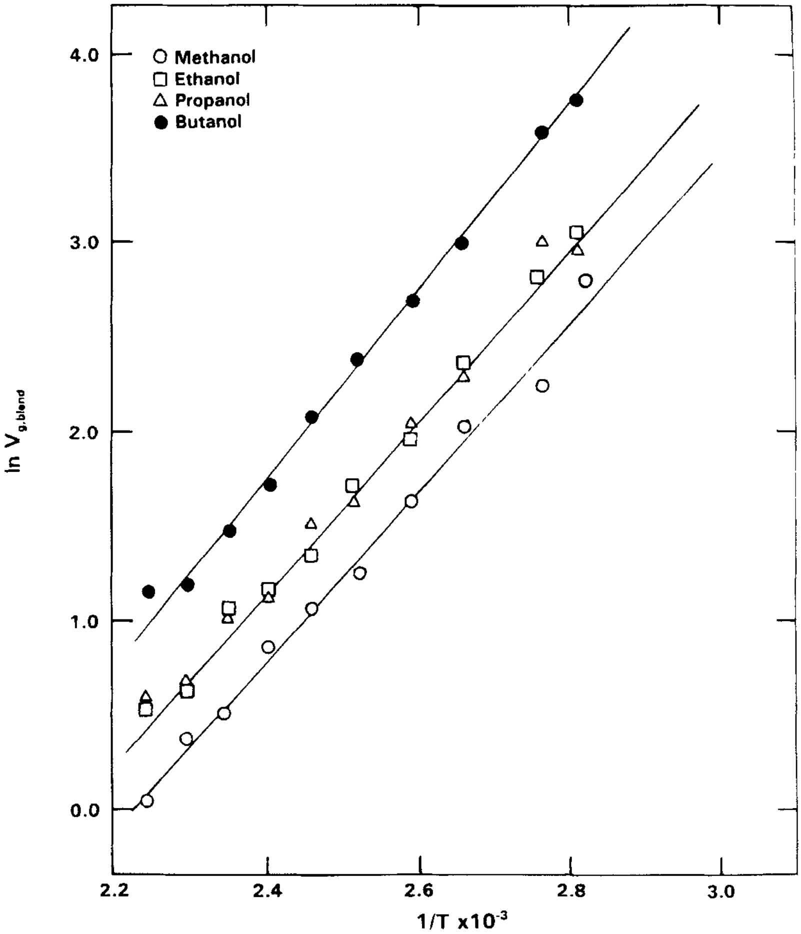

FIGURE 3 The dependence of the specific retention volumes of alcohols on temperature for a 50:50 w/w poly(vinylidene fluoride)-poly(vinyl methyl ketone) blend.

cal nature of solutes. Their results indicated that the miscibility of these blends were in good agreement with those obtained by the static sorption method. The variation of χ_{23} values with solutes were attributed to the imperfection of the Flory-Huggins theory. Their findings revealed some insights into the effect of the chemical nature of solutes on the miscibility of the blend. If the solute interacts equally with both polymers, their mutual solubilities would be improved. If the solute interacts better with one of the polymers in the blend, then their mutual solubilities will decrease, thus, careful selection of solutes for the IGC experiments is necessary. Solutes should be selected to be close to the ideal solvent for both polymer pairs in order to minimize perturbating the behavior of both polymers.

Walsh *et al.*[115] studied the compatibility of blends containing ethylene-vinyl acetate copolymer and chlorinated polyethylenes. The interaction parameters showed negative values at lower temperatures (70°C) indicating miscibility; however, these values changed to positive at higher temperatures (100°C). This observation is consistent with their phase separation results upon heating. The IGC results agreed well with those obtained by the phase separation technique within the accuracy of these methods.

Galin and Rupprecht[37] studied the compatibility of blends containing a series of dimethylsiloxane-styrene block copolymers using a variety of methods. Positive values of interaction parameters were obtained at 120°, 150° and 180°C indicating the incompatibility of the block copolymer; this incompatibility was reduced, as expected, for low-molecular weight-chains and triblock copolymers. These values were expected from the well-known incompatibility of PS and PDMS chains. The variations of the χ_{23} parameter with polymer structure have been studied using only a good solvent for both polymers. The interaction parameters were found slightly dependent on copolymer composition with a significant decrease for the PS-rich copolymers. The χ_{23} values showed decreasing dependence of temperature. The compatibility of PS-PDMS increased with increasing temperature. Nevertheless, χ_{23} remained positive even at the highest temperature of 180°C, suggesting that the block copolymers should behave, always, as biphasic systems with segregated domains of PS and PDMS. This observation was examined by studying block copolymers films by polarizing microscopy; a well-defined birefringence was noticed up to 300°C. IGC was also applied to these blends in the glassy state ($50° < t < 80°C$) using selective solutes of PDMS (*n*-decane). The results were analyzed and used to calculate the contribution of solute adsorption at the surface of the PS domains to the total specific retention volume. IGC lead to meaningful values of the surface area of PS domains for the copolymers characterized by a dispersion of PS rods in a PDMS matrix, or by a lamellar structure.

Ward and Sheehy[33] studied the compatibility of a blend containing poly(dimethyl siloxane) -poly(carbonate) block copolymer. Their results revealed the incompatibility of this blend, as expected. In addition, the specific retention data of the random copolymer blend (macrophase separated) and block copolymer blend (microphase separated) were found to be approximately the same for a given composition, indicating that the degree of mixing of the PDMS-PC systems cannot be determined by its retention behavior. Values of χ_{23} were found to be dependent on the chemical nature of solutes (depended on their selectivity of the stationary phase), composition of the blend, and temperature. The interaction parameters decreased as the temperature increased. This behavior was attributed to two factors: the decrease in selectivity of some solutes and therefore less preferential interaction at higher temperatures, and the increase of the compatibility of the polymer pair at higher temperatures. The effect of composition on the interaction parameters indicated that the interaction of the PDMS and PC was best at 40:70% wt, respectively. These results were compared with those obtained by small angle X-ray scattering and DSC.

In recent studies, The IGC agreed well with the DSC in detecting the immiscibility of poly(isobutyl methacrylate)/styrene-acrylic acid copolymer blends.[112] IGC obtained positive values of the polymer-polymer interaction parameters, while DSC obtained two separate glass transition temperatures. Both methods also agreed well on the miscibility of poly(styrene-co-acrylic acid) with a series of polycarbonates via negative values for χ_{23} and single glass transition temperature.[112] Although, polystyrene is immiscible with poly(isobutyl methacrylate) due to the absence of specific interactions, it has been shown that a blend consisting of a random copolymer (poly(styrene-co-acrylic acid)) and a homopolymer (poly(methyl methacrylate)) can be miscible in the absence of specific interactions, provided sufficient replution between the two comonmers.[116] Both methods, IGC and DSC, have confirmed the miscibility of a blend of poly(isobutyl methacrylate) with poly(styrene-co-acrylic acid) containing 32 mol% acrylic acid and of poly(isobutyl methacrylate-co-acrylic acid) containing 22 mol% acrylic acid with poly(styrene-co-N,N-dimethyl aminoethyl methacrylate) containing 12mol% of basic comonomer.

Amorphous-Plasticizer Blends

Few studies are available on the characterization of blends containing amorphous-plasticizers using IGC. One of the early studies done on these blends was by Patterson and Schreiber.[117] They applied IGC to a blend of PVC plastizied by di-*n*-octyl phthalate (DnOP) in a temperature range of 100°–130°C. The interaction parameters were strongly negative, indicating high compatibility as expected. However, the interaction parameters became less negative and finally positive at 0.55 vol fraction of DnOP, suggesting a lower compatibility limit. The composition dependence of χ_{23} reflected a nonrandom solution of the solute in the stationary phase and/or nonrandom mixing of PVC-DnOP, particularly for DnOP in the limited compatibility range.

Inorganic-Polymer Blends

IGC data on this class of blends are scanty. No data were reported on traditional inorganic polymers, however, Murakami,[95] studied the interaction between PEO and PMMA in the presence of pulverized porous silica gel. This blend was selected because it contains hydrophobic and hydrophilic polymers. Their results indicated that PEO and PMMA were incorporated into the pores of the silica gel in contrast to earlier studies on PEO/PS blends[118] in which PEO was selectively incorporated into silica gel pores; this incorporation increased with increasing surface area of the silica gel. IGC yielded valuable information on transition phenomena, compatibility and thermal treatment. These data could not be obtained using DSC for this kind of polymer blend.

CONCLUSION

To date, the IGC method has been used to characterize over forty polymer blend systems. Most of the research performed was focused on the miscibility of the polymer blends, others on the morphology of polymer blends. It is evident that IGC is versatile, accurate, and selective in obtaining a wealth of data on polymer blends as compared to other methods. However, theoretical work still needs to be established to eliminate the solute chemical dependency on the interaction parameters of the polymer pairs. With more modification to the theory and more application to complex polymer blend systems, it is envisioned that IGC may become a comprehensive method for polymer blends characterization.

SYMBOL TABLE

A, B, C	Antoine constants
B	Binary interaction energy parameter
B_{11}	Second virial coefficient

B_{12}	Binary interaction energy parameter of solute 1 and polymer 2
B_{13}	Binary interaction energy parameter of solute 1 and polymer 3
B_{23}	Binary interaction energy parameter of polymer 2 and polymer 3
B_{23}^A	Apparent binary interaction energy parameter of polymer 2 and polymer 3
C_1^l	Concentration of the solute in the liquid phase
C_1^g	Concentration of the solute in the gas phase
C_{23}	Correction term based on solubility parameter of polymer 2 and polymer 3
F	Carrier gas flow rate
M_1	Molecular weight of solute 1
M_2	Molecular weight of polymer 2
M_3	Molecular weight of polymer 3
n_i	Number of moles of the ith component
P_1^o	Saturated vapor pressure
P^*	Reduced pressure
P_i	Inlet pressure
P_o	Outlet pressure
R	Universal gas constant
S_1	Molecular surface area of solute 1 per unit volume
S_2	Molecular surface area of polymer 2 per unit volume
S_3	Molecular surface area of polymer 3 per unit volume
t_r	Retention time of marker
t_p	Retention time of solute
T	Temperature in kelvin
T^*	Reduced temperature
T_c	Critical temperature
T_m	Melting temperature of the semicrystalline polymer in the mixture
T_m^o	Melting temperature of the pure semicrystalline polymer
T_r	Room temperature
V^*	Reduced volume
V_c	Critical volume
V_i	Molar volume of the ith component
V_{2u}	Unit volume of the semicrystalline polymer

V_g^o	Specific retention volume of solute
$V^o_{g,2}$	Specific retention volume of solute on polymer 2
$V^o_{g,3}$	Specific retention volume of solute on polymer 3
$V^o_{g,\,blend}$	Specific retention volume of solute on polymer blend
X_c	Degree of crystallinity of the semicrystalline polymer
W	Mass of the polymer or polymer blend
α_1	Thermal expansion coefficient
$\delta_{2,w}$	Dispersive intermolecular interactions of polymer 2
$\delta_{3,w}$	Dispersive intermolecular interactions of polymer 3
$\delta_{2,p}$	Polar intermolecular interactions of polymer 2
$\delta_{3,p}$	Polar intermolecular interactions of polymer 3
$\delta_{2,a}$	Electron acceptor intermolecular interactions of polymer 2
$\delta_{3,a}$	Electron acceptor intermolecular interactions of polymer 3
$\delta_{2,d}$	Electron donor intermolecular interactions of polymer 2
$\delta_{3,d}$	Electron donor intermolecular interactions of polymer 3
ΔG_m	Molar free energy of mixing
ΔG_1^∞	Molar free energy of mixing of solute 1
ΔG_1^s	Molar free energy of sorption of solute 1
ΔH_m	Molar heat of mixing
ΔH_{2u}	Molar heat of fusion of the semicrystalline polymer
ΔH_1^∞	Molar heat of mixing of solute 1
ΔH_1^{s}	Molar heat of sorption of solute 1
ΔS_m	Molar entropy of mixing
ΔS_1^s	Molar entropy of sorption of solute 1
ΔT_m	Melting point depression of the semicrystalline polymer in the mixture
μ_1^1	Chemical potential of solute in the liquid phase
μ_1^g	Chemical potential of solute in the gas phase
μ_2	Chemical potential of the semicrystalline polymer in the mixture
μ_2^o	Chemical potential of the pure semicrystalline polymer
μ_2^c	Chemical potential of perfect crystals of the semicrystalline polymer
ν_2	Specific volume of polymer 2
ν_3	Specific volume of polymer 3
ρ_2	Density of polymer 2
ρ_3	Density of polymer 3
ρ_1	Density of the solute in the liquid phase

ρ_v	Density of the solute in the vapor phase
ρ_{sc}	Density of the semicrystalline polymer
ρ_a	Density of the semicrystalline polymer in the amorphous state
ϕ_i	Volume fraction of the ith component
χ_{12}	Interaction parameter of solute 1 and polymer 2
χ_{13}	Interaction parameter of solute 1 and polymer 3
χ_{23}	Interaction parameter of polymer 2 and polymer 3
Ω_1^∞	Weight fraction activity coefficient of solute 1

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