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THERMODYNAMIC CHARACTERIZATION OF BINARY POLYMER BLENDS BY INVERSE GAS CHROMATOGRAPHY

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ABSTRACT

The gas chromatographic method of characterization of polymer blends with regard to the state of binary polymer mixtures, origin of miscibility in miscible blends, evaluation of the noncombinatorial free energy parameters χ_{23}' and $\chi_{23}^{*\prime}$ for miscible blends, and structural information of microphase-separated copolymer systems, etc. are reviewed with discussions of some selected polymer-polymer systems. A brief discussion of the principle and practice of GC with a polymer stationary phase, of the evaluation of χ and χ^*, of sources of error and accuracy of the method, and of column support materials and support loading is also presented. Preliminary results of an inverse gas chromatography study of the newly reported miscible polymer pair poly(vinyl propionate) and poly(ethyl acrylate) are presented.

I. INTRODUCTION

The gas-liquid chromatographic technique with polymeric stationary phases has found wide application in verious areas of polymer characterization, such as the determination of the first- and second-order transitions [1-3], degree of crystallinity and related physical quantities [4, 5], diffusion coefficients of small molecules in polymers [6], functional endgroup content in oligomers [7], surface areas and adsorption isotherms [8, 9], study of microphase separation and domain size in block copolymers [10, 11], thermodynamics of polymer-small molecules and polymer-polymer systems [12, 13], etc. The references cited represent some of the early work in each of the areas mentioned. For detailed information the reader is referred to the many reviews in this field [14-18]. In all these studies the polymer is used as the stationary phase, and its interaction with known volatile solutes, often called "probes," is measured in terms of retention volume. The shape of the chromatograms and their temperature dependence, the desired information, may be obtained from the magnitude of the retention volume. Because the method yields information about the polymeric stationary phase, it is often called "inverse gas chromatography" (IGC). The present review is concerned with the application of IGC to the characterization of polymer blends.

Very few methods are available for the determination of polymer-polymer interaction parameters, viz., IGC, vapor sorption, analog calorimetry, and melting point depression analysis for blend systems in which at least one of the component is crystallizable [19]. Of the first two applicable to amorphous polymer systems, IGC turned out to be popular because of its rapidity and the general availability of gas chromatographic equipment. However, doubts have been expressed frequently about the quantitative validity of the results obtained by IGC. These will be discussed later in this review. Before that, the principle of the method and its practice in studying polymer solution thermodynamics are dealt with briefly. A detailed discussion of the theory and experimental requirements of GC may be found in many excellent texts and reviews [20-25].

II. PRINCIPLE AND PRACTICE OF IGC

IGC designed to study polymer solution thermodynamics is based on the partition of a low molecular weight solute (Component 1) between a mobile gas phase and a stationary phase of a polymeric liquid (Component 2). The latter is usually used as a thin coat on an inert support. The theory is based on equilibrium bulk sorption, which is achieved at temperatures above about $T_g + 50°C$ for most polymers [26].

Basically, the experiment uses a gas chromatograph, the column of which has been packed with an inert support coated with the polymer under study. A small quantity of a probe along with a marker, such as air or methane, is injected into the carrier gas stream (which may be He, N_2, Ar, or H_2) at the entrance of the column. The times required to elute the plug of the probe substance (t_R) and that of the marker (t_M) are measured. From a knowledge of the volume flow rate of the carrier gas (f_c), the total volume of carrier gas needed to elute the probe minus the dead volume in the column (which is the elution volume of the marker) gives the adjusted retention volume of the probe, the retention time being $t_N = t_R - t_M$. The more favorable the interaction between the polymer and the probe, the greater is the retention volume.

To study polymer-polymer interaction, the retention volumes of a probe are measured for each of two pure polymers and for their blends as stationary phases. If the two polymers are compatible, they interact with one another, and this will reduce the ability of the blend to interact with the solvent, and hence the retention volume for the blend will be smaller than the weight average of the retention volumes for the two homopolymers at the corresponding composition [27, 28].

However, the retention volume as measured above needs correction due to the pressure drop along the column. This is done by converting the adjusted retention volume measured at the column outlet pressure (P_o) to the value corresponding to the mean column pressure ($\bar{p}$),

$$\bar{p} = \frac{2}{3} P_o \; [(P_i/P_o)^3 - 1] / [(P_i/P_o)^2 - 1],$$

where P_i is the column inlet pressure [29]. The retention volume so corrected is called the "net retention volume " (V_N). Littlewood et al. defined a more fundamental retention volume, called the "specific retention volume" ($V_g{}^\circ$), as the volume of carrier gas, measured at 273.2 K and corrected for column pressure drop, required to elute the probe from a column containing 1.0 g of this stationary phase [30].

Thus

$$V_g^\circ = \frac{273.2 f_c (t_R - t_M)}{T_r W_2} \; \frac{P_o - p_w}{P_o} \; \frac{3[(P_i/P_o)^2 - 1]}{2[(P_i/P_o)^3 - 1]}, \tag{1}$$

where f_c is the volume flow rate of carrier gas measured by a soap bubble flowmeter at room temperature T_r and outlet pressure P_o, the second factor in Eq. (1) being the pressure correction for f_c, p_w is the vapor pressure of water at T_r, and W_2 is the mass of the stationary phase. $V_g{}^\circ$ is expressed in units of mL/g.

The retention volume is related to the partition coefficient for the equilibrium districution of the probe between the mobile gas phase and the stationary liquid phase. The partition coefficient is, in turn, related to the activity coefficient of the probe in the stationary phase from which the interaction parameter χ between the probe and the stationary phase can be calculated.

Following Everett, the infinitely dilute activity coefficient of the probe at column temperature T K and zero column pressure for a carrier gas which is insoluble in the stationary liquid phase (under the condition that the probe is infinitely dilute in both phases and that the gas mixture is only slightly imperfect and the molar volume V_1 of the pure probe does not change appreciably with pressure) may be related to V_g° [31]:

$$\ln \gamma_1^\infty = \ln \frac{273.2R}{V_g^\circ p_1^\circ M_2} - \frac{(B_{11} - V_1)p_1^\circ}{RT} + \frac{2(B_{1c} - \bar{V}_1^\infty)P_o J\left(\frac{4}{3}\right)}{RT}, \qquad (2)$$

where

$$J\left(\frac{4}{3}\right) = \frac{3}{4}\left[\frac{(P_i/P_o)^4 - 1}{(P_i/P_o)^3 - 1}\right],$$

p_1° is the vapor pressure of the pure liquid probe, B_{11} is the gas phase second virial coefficient of the probe vapor, B_{1c} is the mixed virial coefficient of the probe vapor and the carrier gas, and $\bar{V}_1^\infty$ is the partial molar volume of the probe at infinite dilution in the stationary phase.

Mixed virial coefficients are difficult to obtain and, in general, at moderate pressures (less than 2 atm) the correction term involving this quantity can be ignored [17]. For a binary mixed stationary phase [2, 3], M_2 in Eq. (2) would be replaced by $x_2M_2 + x_3M_3$ [13].

Note that γ_1^∞ represents a mole fraction activity coefficient at infinite dilution of the solute probe. For a polymeric stationary phase determination of γ_1^∞, Eq. (2) may not be precise because M_2, the number-average molecular weight, may be difficult to evaluate precisely. To overcome this problem, Patterson et al. suggested the use of the weight-fraction or volume-fraction activity coefficient (γ_Φ), which resulted in activity coefficient equations free of the molecular weight of polymers [12, 32]. Covitz and King also used the weight-fraction activity coefficient for the same reason [33]. Thus, for a binary polymer blend stationary phase, it follows from Eq. (2) (with M_2 replaced by $x_2M_2 + x_3M_3$) and using approximations $x_2 + x_3 = 1, x_1 = N_1/(N_2 + N_3)$, etc. that

$$\ln \gamma_\Phi^\infty = \ln\left(\frac{a_1}{\Phi_{1,\text{liq}}}\right)^\infty = \ln \frac{273.2R(w_2v_2 + w_3v_3)}{p_1^\circ V_{g23}^\circ V_1} - \frac{(B_{11} - V_1)p_1^\circ}{RT}, \quad (3)$$

where w_i and v_i are the weight fraction and the specific volume of component i in the polymer blend stationary phase, respectively [13].

The activity coefficient γ_Φ^∞, as expressed by Eq. (3), may be equated to the one derived for this quantity by using the Flory-Huggins theory of polymer solution thermodynamics [34, 35]. For the three-component system under discussion here, the relevant expression at infinite dilution of Component 1 ($\Phi_1 \to 0$) is

$$\ln(a_1/\Phi_1)^\infty = [1 - (r_1/r_2)]\Phi_2 + [(1 - (r_1/r_3)]\Phi_3 + \chi_{12}\Phi_2 + \chi_{13}\Phi_3$$
$$- r_1(\chi_{23}/r_2)\Phi_2\Phi_3, \quad (4)$$

where the r_i's are numbers of segments in the components expressed as $r_i = V_i/V$. V_i and V are, respectively, the molar volumes of component i and of a segment chosen as reference for all components. The χ_{ij}'s are the traditional Flory interaction parameters [36] expressed as

$$(\chi_{ij})_{\text{Flory}} = r_i Z \Delta w_{ij}/kT.$$

Equating Eqs. (3) and (4) and using the symmetrical χ_{ij}/V_i quantities in place of the unsymmetrical χ_{ij},

$$\chi_{1(23)} = \left[\left(\frac{\chi_{12}}{V_1}\right)\Phi_2 + \left(\frac{\chi_{13}}{V_1}\right)\Phi_3 - \left(\frac{\chi_{23}}{V_2}\right)\Phi_2\Phi_3\right]V_1$$
$$= \ln \frac{273.2R(w_2v_2 + w_3v_3)}{p_1^\circ V_{g23}^\circ V_1} - (1 - V_1/V_2)\Phi_2 - (1 - V_1/V_3)\Phi_3$$
$$- \frac{p_1^\circ}{RT}(B_{11} - V_1). \quad (5)$$

In Eq. (5), χ_{ij}/V_i represents the interaction parameter normalized to unit volume of the component i; it is therefore symmetrical and dependent only on the chemical nature of i and j but independent of their chain lengths [37].

When the stationary phase contains a single component, Eq. (5) reduces to Eq. (6) at infinite dilution of Component 1 ($\Phi_2 \to 1$).

$$\chi_{12} = \ln \frac{273.2Rv_2}{p_1{}^\circ V_{g2}{}^\circ V_1} - (1 - V_1/V_2) - \frac{p_1{}^\circ}{RT}(B_{11} - V_1). \tag{6}$$

Similarly,

$$\chi_{13} = \ln \frac{273.2Rv_3}{p_1{}^\circ V_{g3}{}^\circ V_1} - \left(1 - \frac{V_1}{V_3}\right) - \frac{p_1{}^\circ}{RT}(B_{11} - V_1). \tag{7}$$

Combining Eqs. (5), (6), and (7), one obtains [27, 28]

$$\chi_{23}{}' = \frac{\chi_{23} V_1}{V_2} = \frac{1}{\Phi_2 \Phi_3} \ln \left[\frac{(v_2)^{\Phi_2} (v_3)^{\Phi_3}}{w_2 v_2 + w_3 v_3} \frac{V_{g23}^\circ}{(V_{g2}{}^\circ)^{\Phi_2} (V_{g2}{}^\circ)^{\Phi_3}} \right]. \tag{8}$$

Ward et al. pointed out that the ratio of the geometric to the weight-average specific volume in Eq. (8) would be close to unity [27]. For a compatible blend, $\chi_{23}{}'$ should be approximately zero or negative. From Eq. (8) it follows that this requirement is met when the retention volume of the probe in the blend is equal to or less than the volume-fraction-weighted geometric mean of its retention volumes in the two homopolymers. This may be taken as the rule of thumb for ascertaining polymer-polymer miscibility by IGC.

From the IGC experiments for Components 2 and 3 separately and their mixtures as stationary phases, χ_{12}, χ_{13}, and $\chi_{23}{}'$ may be determined by using Eqs. (5), (6), and (7). It is common practice in the literature to express the 2,3 interaction parameter normalized to the size of the probe used, i.e, $\chi_{23}{}' = \chi_{23} V_1/V_2$. The 2,3 interaction parameter so normalized helps the comparison of the interchange free energy for 2,3 segments with those for 1,2 and 1,3 segments in the same scale.

The χ parameters thus derived are based on the lattice model which makes no allowance for a change in volume due to mixing or equation-of-state effects. Modern theories of polymer solution thermodynamics aim at remedying this situation [38-43]. The modern theories differ from the Flory-Huggins theory in many respects. According to the modern theories, the Gibbs free energy of mixing consists of three contributions originating from (i) the combinatorial entropy of mixing; (ii) the exchange interaction energy which reflects the energy involved when *i-i* or *j-j* contacts are replaced by *i-j* contacts; and (iii) the equation-of-state or free volume differences between the components. The latter leads to a volume change during the mixing process. These theories associate the interaction between molecules with surfaces of their hard-core volumes (volumes at 0 K) rather than with volumes, and express the combinatorial entropy of mixing in terms of segment fractions rather than volume fractions used in the Flory-Huggins theory. The segment numbers are determined by using the hard-core volumes instead of the macroscopic volumes used in the Flory-Huggins theory. This approach gives rise to segment fraction $\Phi_i^* = w_i v_i^* / \Sigma w_i v_i^*$, where v_i^* are reduction parameters per gram for volume, i.e., the specific core volumes [13]. Thus, on correcting the combinatorial free energy of mixing, the appropriate noncombinatorial free energy of mixing parameter represented by χ^* can be derived from the Gibbs free energy of mixing [44, 45]. In IGC, χ^* is easily obtained by replacing the specific volumes by core specific volumes and the volume fractions (Φ_i) by segment fractions in Eqs. (5) through (7).

Using the corresponding-states formulation of the Flory-Prigogine theory, Patterson and Delmas [46, 47] arrived at the following relation for χ_{ij}^*, which shows the exchange interaction contribution and the free volume contribution explicitly. Thus, for the binary mixture (1,2) with Component 1 at infinite dilution, as in GLC,

$$\Delta\mu_{1(\text{noncomb})} = RT\chi_{12}^* = \frac{V_1^* X_{12}}{\tilde{V}_2}$$

$$+ P_1^* V_1^* \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_2} + 3\tilde{T}_1 \ln \frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_2^{1/3} - 1} \right], \qquad (9)$$

free volume term **interactional term**

where P_1^* and V_1^* are the pressure and volume reduction parameters, $\tilde{V}_i = V_i / V_i^*$ and $\tilde{T} = (\tilde{V}^{1/3} - 1)\tilde{V}^{-4/3}$. Similarly, for a ternary system with a mixed stationary phase, the corresponding equations are

$$RT\chi_{1(23)}^* = \frac{s_1 V_1^*}{\tilde{V}_0} \left[\left(\frac{X_{12}}{s_1} \right) \theta_2 + \left(\frac{X_{13}}{s_1} \right) \theta_3 - \left(\frac{X_{23}}{s_2} \right) \theta_2 \theta_3 \right]$$

$$+ P_1^* V_1^* \left[\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_0} + 3\tilde{T}_1 \ln \frac{\tilde{V}_1^{1/3} - 1}{\tilde{V}_0^{1/3} - 1} \right], \qquad (10)$$

free volume term **interactional term**

where $\tilde{V}_0$ is the reduced volume of the mixed stationary phase, X_{ij} is the interchange energy parameter of the Flory-Prigogine theory, s_i is the molecular surface-to-volume ratio, and θ_i is the surface fraction [13]. The X_{ij} terms, like their χ_{ij} counterparts, are not symmetrical, being proportional to s_i. On the other hand, the X_{ij}/s_i terms, like the χ_{ij}/V_i terms, are independent of the molecular size.

Calculation of the X_{23} parameter follows an involved procedure. The method followed by Su is given here [48]. Values of P^* and V^* at a fixed temperature, say 25°C, are obtained from the literature. These same values are used at all experimental temperatures. The reduced volumes are then calculated at the same temperature 25°C by the equation

$$\tilde{V}^{1/3} = 1 + \frac{\alpha T}{3(1 + \alpha T)}, \tag{11}$$

where α is the coefficient of cubic expansion at 25°C, obtainable from the literature for some polymers and most solvents. Then $\tilde{T}$ (for 25°C) is calculated from the relation

$$\tilde{T} = (1 - \tilde{V}^{-1/3})/\tilde{V}. \tag{12}$$

The value of T^* at 25°C is then obtained by using the relation

$$\tilde{T} = T/T^*. \tag{13}$$

Like P^* and V^*, T^* is taken as constant at all temperatures.

Values of $\tilde{V}$ at any experimental temperature are then obtained by iteration with Eq. (12). By using these data in Eq. (9), X_{12} may be evaluated.

Similarly, for the ternary system, X_{23} is calculated in the following way. $\tilde{T}_0$ is obtained from Eq. (14), taking $X_{23} = 0$ as the first approximation:

$$\tilde{T}_0 = (\psi_2\tilde{T}_2 + \psi_3\tilde{T}_3)/(1 - \psi_2\theta_3X_{23}/P_2{}^*), \tag{14}$$

where $\psi_2 = \Phi_2{}^*P_2{}^*/(\Phi_2{}^*P_2{}^* + \Phi_3{}^*P_3{}^*)$ and $\psi_3 = 1 - \psi_2$. $\tilde{V}_0$ corresponding to $\tilde{T}_0$ is obtained by using Eq. (12). By using this $\tilde{V}_0$ value along with X_{12} and X_{13} calculated from Eq. (9) and the like, an approximate value of X_{23} is obtained by using Eq. (10). This new X_{23} is used in Eq. (14) to get a new $\tilde{T}_0$ and thence a new $\tilde{V}_0$ value and next a new X_{23} value. This process is repeated several times to obtain an accurate X_{23} value.

III. SOURCES OF EXPERIMENTAL ERROR AND ACCURACY

It is evident from Eqs. (5) through (7) that the accuracy of χ_{ij} would be dependent on the accuracy of the V_g°. V_g° is experimentally obtained with the help of the Eq. (1). The volume flow rate of carrier gas (f_c) is usually measured with a soap bubble flowmeter. The inlet pressure P_i of the carrier gas immediately before its entry into the column is measured with a mercury manometer. The outlet pressure P_o is assumed equal to that of the atmosphere and measured by a barometer. The distance between the marker peak and probe peak is measured with a scale. To obtain $t_R - t_M$ from this distance, it is divided by the speed of the strip-chart recorder. The relative error will be large if the two peaks are quite close. W_2 is determined either by using the calcination or the extraction method [49]. Errors from all such sources can add up to a large value. However, accuracy of the order of 2% is obtainable. Klotz et al., however, claim to have achieved an accuracy of 0.5 to 1% by optimizing the experimental conditions [50].

During the initial stages of the development of the IGC method, interlaboratory comparison revealed poor agreement between V_g° values obtained with columns prepared by different workers [51]. Subsequently, the origin of the most of this discrepancy was traced to inaccurate estimates of the amount of polymer coated on the support [49]. In fact, the error in the determination of the amount of polymer on the support has also been identified by other groups [52, 53] as the single most important factor leading to disagreement between the χ parameters determined by IGC and the vapor sorption method reported in the literature [54]. It is therefore pertinent to discuss the recommended methods of estimation of W_2. Two methods are commonly followed. The calcination method completely decomposes the polymer and burns up the volatile products with no residue left. It is therefore not applicable to polymers like poly(dimethylsiloxane), which leaves silica as residue. For the latter kind of polymer, prolonged extraction with a Soxhlet apparatus is adhered to. However, the calcination method is preferred when possible. With both methods, suitable blank corrections with the uncoated support must be made. Another method, frequently the method of choice for low molecular weight stationary phases, computes the percentage of loading directly from the amounts of polymer and support originally brought together. This latter method is prone to large errors due to losses in coating vessels. However, Patterson et al. found that, with polystyrene as coating material, the calcination and the computation method give results which are in agreement within 1 to 12% [49]. At high loadings the computation method gives poor results because of considerable loss of polymer in the coating vessels, while at low loading the calcination method becomes inaccurate because of the relatively large blank correction.

Munk et al. reported a new procedure called by them "the soaking method" for depositing the entire amount of polymer on a support and into the column so that the loading is obtainable by computation [55].

When coating the support with polymer mixtures, it should be ensured that the solvent used to dissolve the blend results in blend films that remain miscible at all compositions. Ingress of moisture into the system during support coating should also be carefully prevented.

Regarding the accuracy of the χ_{23} or χ_{23}^* values, it should be noted that these are obtained by subtracting $\chi_{1(23)}$ from suitably weighted χ_{12} and χ_{13} (vide Eq. 5). Errors in these values would therefore show up as a larger error in the 2,3 interaction parameter.

IV. SUPPORT AND LOADING

The solid support widely used in GC is one of the Chromosorb materials. These are diatomaceous earth in origin, but because of their surface silanol groups, they give asymetric peaks with polar solvents and a dependence of V_g° on sample size. To eliminate these problems, Chromosorbs are acid washed and the surface made nonpolar by silanizing the silanol groups with dimethyldichlorosilane or other silanizing reagents. Most frequently, Chromosorb W (60-80 or 80-100 mesh, acid washed, and DMCS treated) is used as the support material. Since this treatment does not eliminate the surface polar groups completely [56], the adsorption of polar compounds at the support-polymer interface is not completely prevented and, according to Klein et al., V_g° for polar compounds should always be determined by extrapolation of V_g° data to infinite column loading (see below) [57].

Card et al. found in a recent study that Chromosorb W, acid washed and DMCS treated, is not inert, and considerable interaction of the probes (both polar and nonpolar) with this support occurs [58], especially with polar probes. The authors surmised that the origin of this interaction lies in the small amount of PDMS which the support may contain following treatment with DMCS and a number of highly polar residual surface groups (probably hydroxyl) which remain unconverted even after DMCS treatment [56]. These latter groups interact strongly with polar probes, making a very large contribution to V_g° for very small probes and a small contribution for large probes. These retention characteristics do not change when the supports are coated with polymers, polar or nonpolar. By subtracting the contribution to V_g° due to interaction with uncoated support from V_g° values obtained with coated supports, true V_g° values are obtained, independent of the amount of probe injected, polymer loading, and flow rate. The correction was found to be particularly important for polar probes and for probes that interact poorly with the polymers. However, in subsequent work the authors showed that the dependence of V_g° on column loading cannot be eliminated in this way [59].

Alternatively, a nonpolar support Fluoropak-80 made from poly(tetrafluoroethylene) has been successfully used [60-62]. However, Conder indicated that PTFE could not be considered inert [63]. Also, according to Walsh et al., the porous nature of PTFE makes it an unsuitable support material. They found kaolin to be a good support material which is nonporous and has a high surface area [64]. Glass bead supports have also been used by many workers [11, 27, 65].

In determining the amount of polymer W_2 to be used for coating a given amount of support material, Υ, the following factors are to be taken into consideration. In general, the net retention volume arises out of two effects: (i) adsorption of the probe on the polymer surface and the polymer-support interface, and (ii) absorption of the probe in the stationary phase. For the gas-liquid partition of concern here, the contribution of adsorption to V_g° should be eliminated and equilibrium condition must prevail.

The variation of V_g° with temperature over a range encompassing T_g as well as T_m of a semicrystalline polymer has the shape shown in Fig. 1, as has been discussed in detail by Guillet et al. [4, 5, 15, 17, 66, 67]. In the temperature region AB below T_g, the retention volume is due to equilibrium adsorption on the polymer surface and the polymer-support interface. Above T_g, the probe penetrates the polymer, and bulk sorption begins to contribute to V_g°, but the rate of diffusion of the probe into the polymer is low so that equilibrium is not maintained. This continues up to the region CD, where the diffusion rate becomes sufficiently large so that equilibrium conditions are restored, provided the coating is not too thick and retention is predominantly due to bulk sorption. This stage is reached at temperatures about 50°C above T_g for most polymers in packed columns [26]. Exceptions do exist, however. For example, for polyisobutylene and poly(vinyl acetate) the equilibrium sorption state was found to be reached at temperatures exceeding T_g by 150 and 80°C, respectively [26, 68].

Section DE of the curve reflects the melting process. The linear section EF following DE represents the whole polymer in a liquidlike state. Working in the various regions of the curve helps obtain various kinds of information about the polymeric stationary phase [15]. The relations connecting V_g°

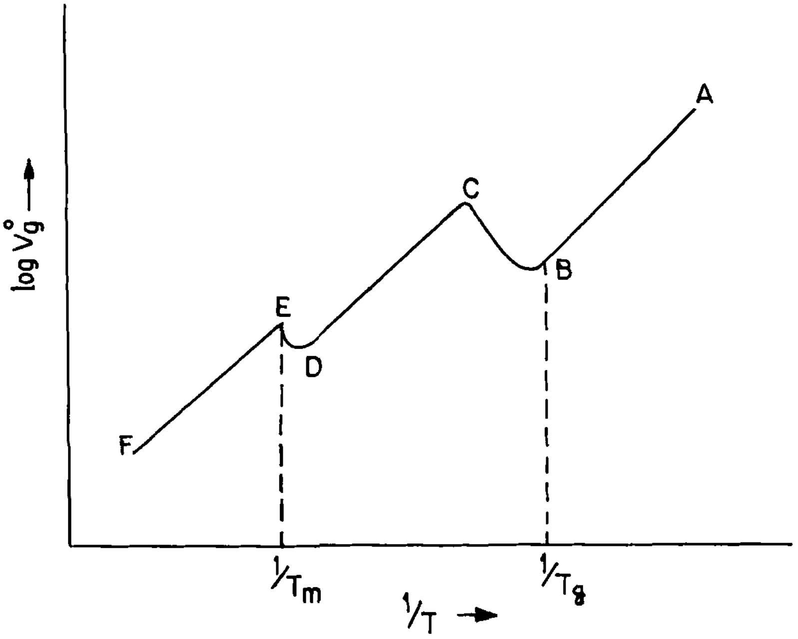

FIG. 1. Generalized retention diagram for a semicrystalline polymer used as a stationary phase in IGC.

with the thermodynamic interaction parameters are based on the bulk sorption model. It is therefore imperative that for the evaluation of thermodynamic quantities, one should work in the region CD for a completely amorphous polymer or in the region EF for a semicrystalline polymer (above T_g + 50°C and above T_m).

However, even in these regions there may be significant surface and interface adsorption, depending on the column loading. In order to eliminate the effect of Υ adsorption on V_g°, use is made of the relation due to Martin [69] :

$$V_g^\circ = K_b + K_A(A_2/W_2) + K_i(A_i/W_2), \qquad (15)$$

where K_b, K_A, and K_i are partition coefficients for bulk sorption, polymer surface adsorption, and support-polymer interfacial adsorption, respectively; W_2 and A_2 are the weight of the polymer and its surface area; and A_i is the polymer-support interfacial area. At low column loading the last two terms in Eq. (15), which represent the contribution of adsorption to V_g°, may be significant. These contributions would decrease with increasing W_2. Since A_2 and A_i change very little with increasing W_2, the last two terms in Eq. (15) may be made insignificant at sufficiently high W_2 and, in this high column loading region, V_g° should be independent of W_2. V_g° free from adsorption effects may therefore be obtained by extrapolating V_g° vs $1/W_2$ to infinite column loading according to Eq. (15) [67]. However, for extrapolation purposes the V_g° data should conform to equilibrium conditions

At high column loading the coating may be too thick to allow penetration of the probe through the whole thickness during its passage through the column. Only a fraction of the polymer is therefore involved in the partition process. Under such nonequilibrium conditions, V_g° is grossly underestimated and highly dependent on the flow rate. V_g° therefore has to be extrapolated to zero flow rate and zero probe size [67]. However, this way of eliminating adsorption effects is very tedious. Munk et al. recently made a theoretical analysis of the variation of V_g° with the amount of probe injected and developed a method for obtaining V_g° corresponding to zero probe size from a single small injection [59]. Also, these authors cautioned that the extrapolation to zero flow rate can be very harmful if the flow rate is not measured correctly [71].

In search of a simple procedure for obtaining V_g° free from the Υ adsorption effect, Galin and Rupprecht observed that, with polystyrene columns at around 8% column loading, the opposite effects of Υ adsorption and nonequilibrium diffusion cancel each other so that this column loading may be used to determine V_g° by using small probe sizes and moderate flow rates (10-15 mL/min) without going through the process of extrapolation to zero flow rate and infinite column loading [70]. On the other hand, Newman and Prausnitz considered that this situation obtains at 15% column loading [72]. According to Summers et al., the contribution of Υ adsorption effects to V_g° becomes insignificant at column loadings greater than 6.5% [32]. However, in order to ensure operation at equilibrium, V_g° data should be extrapolated to zero flow rate. Furthermore, Galin and Rupprecht showed that the contribution of Υ adsorption at a given column loading is greater for nonsolvent probes than for solvent probes and, in using polystyrene as the stationary phase, they found that it became zero at column loadings as high as 20% for nonsolvent probes [70]. Thus, suitable loading depends on many factors such as surface area of support, type of polymer, and diffusion coefficient of solvent in the polymer. It is common practice to use a column loading of about 8-10%, a small probe size, and extrapolate V_g° data to zero flow rate.

V. IGC CHARACTERIZATION OF POLYMER-POLYMER SYSTEMS

Many binary polymer blend systems, as well as block and graft copolymers, have been characterized by IGC with regard to (a) the state and origin of miscibility, (b) the evaluation of the noncombinatorial free energy parameters χ_{23} and χ_{23}^*, (c) the structural information of microphase-separated copolymer systems, etc. Table 1 lists the polymer-polymer systems including polymer-plasticizer systems and block and graft copolymers studied by IGC. All binary polymer blend systems can be grouped in three classes: $\chi_{23}^{*\prime} = 0$, <0, >0. Most investigators report χ_{23}' instead of $\chi_{23}^{*\prime}$. The latter provides better insight into the nature of exchange interactions and is finding increasingly greater usage. However, since the difference in the thermal expansion coefficients of polymers is rather small, the correction due to equation-of-state effects is small for polymer-polymer systems, and χ_{23}' therefore often gives an adequate measure of the strength of exchange interactions. There are, of course, exceptions. For example, the results of the PCL-PVC system discussed below [61]. In what follows we shall discuss some representative systems of each class.

Patterson and Robard made a detailed analysis of situations leading to polymer-polymer miscibility and of the origin of the critical solution temperatures [73]. The critical value of χ_{23}^* which may be derived from Scott's application of the Flory-Huggins theory to systems containing two polymers [35] is

$$\chi_{23,\mathrm{cr}}^{*\prime} = \frac{M_1 v_1^*}{2}\left[\frac{1}{(M_2 v_2^*)^{1/2}} + \frac{1}{(M_3 v_3^*)^{1/2}}\right]^2 . \tag{16}$$

Blend systems for which $\chi_{23}^{*\prime}$ is less than or equal to the critical value are miscible. Equation (9) indicates that this parameter is a composite quantity with contributions from (i) exchange interactions arising out of the formation of 2,3 contact pairs from the respective homo-contact pairs, (2,2) and (3,3), and (ii) the difference in free volume of Components 2 and 3. The latter, although it may be small for polymer-polymer systems, is a positive quantity. In addition, in the usual case of dispersion forces, the unlike contacts are relatively weak, so that the X_{23} parameter has a positive value. For example, a value of X_{23} of the order of 10 J/cm^3 originating from dispersion interaction could be quite common, so that $\chi_{23}^{*\prime}$ would easily exceed its critical value, which is very small. In general, miscible polymer-polymer systems involving similar polymers are rather scarce for this reason. Nevertheless, some miscible polymer-polymer systems do exist in which the polymers are very similar [74].

TABLE 1. Polymer-Polymer and Polymer-Plasticizer Systems Studied by Inverse Gas Chromatography

System	Ref.
Oligo(dimethylsiloxane) + tetracosane	13
Dioctyl phthalate + tetracosane	13
Oligostyrene + poly(vinyl methyl ether)	77
Polystyrene + poly(vinyl methyl ether)	50
PVC + dioctyl phthalate	81
PVC + alkyl stearate lubricants	101
PVC + poly(ϵ-caprolactone)	61
PVC + polyesters	87
PVC + polyacrylates	62
PVC + polymethacrylates	62
PVC + polystyrene	102
PVC + chlorinated polyethylene	64
Chlorinated polyethylene + poly(methyl methacrylate)	28
Chlorinated polyethylene + poly(*n*-butyl methacrylate)	28
Chlorinated polyethylene + poly(ethyl methacrylate)	28
Chlorinated polyethylene + poly(ethylene-*co*-vinyl acetate)	93
Poly(epichlorohydrin) + poly(methyl acrylate)	55
Poly(2,6-dimethyl-1,4-phenylene oxide) + polystyrene	103, 104
Poly(2,6-dimethyl-1,4-phenylene oxide) + poly(4-methylstyrene)	103
Poly(vinyl acetate) + nitrocellulose	105
Poly(vinyl acetate) + poly(methyl acrylate)	74
Poly(vinyl acetate) + poly(*n*-butyl methacrylate)	107
Poly(vinyl acetate) + polyacrylonitrile	108
Poly(vinyl propionate) + poly(ethyl acrylate)	84

(continued)

TABLE 1 (continued)

System	Ref.
Poly(ethylene oxide) + poly(vinyl alcohol)	106
Poly(styrene-*b*-tetrahydrofuran)	10
Poly(styrene-*b*-dimethylsiloxane)	11
Polystyrene + poly(dimethylsiloxane)	11
Polycarbonate + poly(dimethylsiloxane) (blends, alternating block copolymers, and randomly coupled copolymers)	27
Poly(methyl methacrylate) and poly(stearyl methacrylate) (blends, graft copolymers, and random copolymers)	98
PDMS-PEO-PDMS triblock copolymers	99
Poly(styrene-*co*-2-hydroxyethyl methacrylate)	100
Poly(styrene-*g*-2-hydroxyethyl methacrylate)	100
Oligostyrene + poly(*n*-butyl methacrylate)	97
Polystyrene + poly(*n*-butyl methacrylate)	97
Polystyrene + polybutadiene	57, 85
Polystyrene + polystyrene $(\bar{M}_n = x)$, $(\bar{M}_n = y)$, $x \neq y$	111
Polystyrene + poly(ethylene glycol)	109, 110
Polystyrene + poly(ethylene glycol) adipate	109, 110
Poly(ethylene glycol) + poly(ethylene glycol adipate)	65
Poly(ethylene glycol) + poly(propylene glycol)	65
Poly(propylene glycol) + poly(ethylene glycol adipate)	65
Poly(ethylene glycol) (200) + poly(ethylene glycol) (4000)	65
Poly(ethylene-*co*-vinyl acetate)	112

The similarity in the chemical nature of the polymers in these systems is so great that $X_{23} \simeq 0$.

On the other hand, if there exist specific interactions between the polymers, the contact energy parameter X_{23} (dispersion + specific interaction) could be close to zero or assume significantly negative values, depending on whether the specific interaction is very weak ($\Delta H_m \simeq 0$) or strong ($\Delta H_m < 0$). But specific interactions bring about nonrandomness in the system, so that a negative contribution to ΔS_m arises.

The interactional part of the experimental $\chi_{23}{}^*$ (Eq. 9) takes into account both these enthalpic X_{23} and the associated noncombinatorial entropy, so that the experimental $\chi^*_{23,\text{interactional}}$ alone could be positive even when the enthalpic X_{23} is negative (exothermic mixing). This is why it is difficult to predict polymer-polymer miscibility. Patterson and Robard cite some examples of mixtures of small molecules to clarify the point [73]. Thus, although benzene + dioxane and CCl_4 + dioxane have equimolar heats of mixing of -150 and -250 J/mol, signifying large negative values of X_{12}, the excess free energies of mixing of these systems turn out to be positive. Similarly, the excess free energies of mixing for the systems CCl_4 + *n*-propyl ether and $CHCl_3$ + *n*-propyl ether turn out to be less negative than the excess heats [75]. Nevertheless, the majority of the miscible polymer blends reported in the literature owe their miscibility to the existence of specific interactions between them. Free energy experiments, such as IGC, lead to X_{23} as a contact free energy parameter (vide Eq. 9) distinct from the contact energy parameter (which can be determined calorimetrically) and incorporates the unfavorable entropy arising out of the order created by specific interactions [13]. X_{23} from enthalpic data would therefore always be more negative than the value calculated from GLC data.

A. Class 1: $\chi_{23}{}^{*\prime} \simeq 0$

Three miscible polymer pairs belonging to this class have been chosen for discussion. These are: polystyrene (PS) + poly(vinyl methyl ether) (PVME), poly(vinyl acetate) (PVAc) + poly(methyl acrylate) (PMA), and poly(vinyl propionate) (PVPr) + poly(ethyl acrylate) (PEA).

1. Polystyrene + Poly(Vinyl Methyl Ether)

This miscible blend system has received wide attention, and a number of methods were used for the determination of the $\chi_{23}{}'$. Results of different groups of workers varied even when the same method was adopted. Thus, by using the vapor sorption method, Kwei et al. obtained significantly negative χ_{23}' values, e.g., -0.75 for PVME/PS 35/65 wt/wt at 30°C [76]. However, the high molecular weight polystyrene used in this work was in a glassy state at this temperature, and Patterson et al. reasoned that χ_{23}' may turn out to be too negative in such a situation [77]. On the other hand, by the same technique, Panayiotou and Vera obtained χ_{23}' values ranging between slightly negative to pronounced positive at 25°C for oligostyrene ($\bar{M}_w$ 800) and PVME ($\bar{M}_w$ 14 000) [78].

Small-angle neutron scattering by the deuterium substitution technique revealed that χ_{23}' has only a very small negative value for a 50 wt% mixture of PS ($\bar{M}_w$ 63 000) and PVME ($\bar{M}_w$ 10 000) at 120°C, indicating that the system was near the demixing temperature [79].

Lastly, this blend system was studied by the IGC method by two groups of workers. Su and Patterson used two blend compositions, viz., PS ($\bar{M}_n$ 600)/PVME ($\bar{M}_v$ 10 000) 45/55 and 62.5/37.5 (wt/wt) at 40°C [77]. χ_{23}' values varied significantly with the probe. Anomalously large positive values were obtained with probes for which the differences between χ_{12} and χ_{13} were large. An explanation for this high result with probes that interact preferentially with one of the polymers was provided by Su et al. The effect was greater when the concentration of the preferred polymer in the blend was higher. Leaving aside the anomalously large positive values, χ_{23}' was found to lie in the range -0.1 to 0.1 for the blend composition with lower PVME concentration. The χ_{23}' values for blends with lower PVME concentration were given greater weight by them for justifiable reasons. Using the literature LCST data of PVME + PS systems of different polymer molecular weights [80] and calculating the $\chi_{23,cr}'$ values corresponding to these critical temperatures from the Flory-Huggins theory by an equation corresponding to Eq. (16), Su et al. obtained a plot of χ_{23}' vs temperature. In this way χ_{23}' was found to have small positive values (<0.015) at 200°C, which decreased with decreasing temperature and extrapolated to a slightly negative value at 40°C. The situation would not have changed appreciably even if the composition dependence of χ was taken into account. On the other hand, the reported existence of an UCST at low temperature [76] in these blend systems suggested that the extrapolated negative χ_{23}' value at 40°C might not have been valid. These two facts, viz., LCST at high temperatures and the UCST at low temperatures, indicated that χ_{23}' may remain positive over the whole temperature range [73].

Su et al. [81] pointed out that their GLC estimate of χ_{23}' was consistent with a very small positive or negative value for this quantity. Considering the accuracy of the method, it was not possible to ascertain whether the value is positive or negative. A small positive χ_{23}' value does not rule out the existence of specific interactions, however. Considering the sizable positive contribution of dispersion force to χ_{23}', specific interactions associated with negative enthalpy were indirectly predicted for $\chi_{23}' \simeq 0$. Presumably, this interaction occurs between the ether oxygen and phenyl group of the polymer pair. In support of this, they pointed out that the GLC-determined χ_H for the interaction of benzene and toluene with PVME is small. A direct estimate of the enthalpy of interaction could have been available from the determination of the variation of χ_{23}' with T since

$$\chi_H = -T\left(\frac{\delta\chi}{\delta T}\right)_P. \tag{17}$$

But the authors refrained from making any inference about the sign of $d\chi/dT$ in view of the inaccuracies of the χ_{23}' values.

On the other hand, Klotz et al., who studied this system recently, claimed far greater accuracy and drew several conclusions which can only be reached if the χ_{23}' values are very accurate [50]. They studied four blend compositions, viz., PS/PVME = 15/85, 25/75, 50/50, and 75/25 (wt/wt) from 120 to 210°C. The molecular weights and polydispersity index D of the polymers PS ($\bar{M}_w$ 17 500, D 1.06) and PVME ($\bar{M}_w$ 68 500 and D 1.86), were different from those used by Su et al. Although their χ_{23}' values also varied with the probe, the variation was not too wide. The values increased with increasing temperature for all compositions, indicating phase separation was taking place at higher temperatures. The χ_{23}' values varied significantly with blend composition, e.g., at 135°C the average values for the nonpolar probes were - 0.45, 0.16, and -2.89 for 3/1, 1/1, and 1/3 PS/PVME, respectively. Klotz et al. remarked that the value for the 1/3 blend is unusually large and negative. These data were interpreted to indicate that, at 135°C, miscibility was most favored for the 1/3 blend, the 1/1 blend was phase separated, and the 3/1 blend was again miscible although miscibility for this blend was less favorable than for the 1/3 blend. They derived the demixing temperatures for each blend composition by plotting χ_{23}' vs temperature and extrapolating to zero. The phase diagrams determined on the basis of these demixing temperatures were in agreement with those determined by other workers by other methods.

However, the pattern of variation of χ_{23}' with blend composition observed by Klotz et al. was different from that found by Kwei et al. for this system. The latter found χ_{23}' to increase continuously from a large negative value of -0.75 for a blend containing 35 wt% PVME to -0.17 for 65 wt% PVME.

However, these results were obtained by the vopor sorption method at a low temperature (30°C) [76].

Furthermore, positive χ_{23}' values obtained by Klotz et al. for the 1/1 blend by IGC have no quantitative validity since the blend was phase separated at the experimental temperature. Equation (4) and hence Eq. (5) are not valid [11, 12] for a phase-separated blend. Under such circumstances, unrealistic values are expected. Hence, the use of the positive χ_{23}' values and its temperature variation to determine the demixing temperature of the 1/1 blend, as was done by Klotz et al., is not justified.

Considering the more reliable binary interaction parameter, it was found that X_{12} for ethylbenzene (1) and PVME (2) at 150° is negative, -4.16 J/cm^3, indicating the existence of specific interactions. Because ethylbenzene is the hydrogenated monomer of PS, this result indicated that there would be specific interactions between PS and PVME as well.

a. Variation of χ_{23}' *with the Nature of the Probe.* As has been mentioned above, χ_{23}' varies significantly with the nature of the probe. Since χ_{23}' is normalized with respect to the molar volume of the probe, some variation in its value with probe size is expected. However, the variation observed is much more predicted from the probe volume difference [13, 77, 81]. Particularly large χ_{23}' values are obtained with probes that interact preferentially with one of the polymers [77, 81]. Su et al. provided a qualitative explanation for this effect; Munk et al. gave a quantitative explanation [55]. From a careful study of the probe dependence of χ_{23}' for the polymer pair poly(epichlorohydrin) + poly(methyl acrylate), Munk et al. concluded that the probe dependence is real and not an experimental artifact. In order to explain the probe dependence, they used a parameter γ_{ij} (analogous to X_{ij} of the Flory theory) in place of χ_{ij} and replaced volume fractions by surface fractions in the noncombinatorial part of the activity coefficient of Eq. (4), thus obtaining

$$\ln \gamma_{\Phi}^{\infty} = RT\left[1 - \frac{V_1}{V_2}\Phi_2 - \frac{V_1}{V_3}\Phi_3 + \theta_2\gamma_{12} + \theta_3\gamma_{13} - \frac{S_1\theta_1\theta_2\gamma_{23}}{S_2}\right], \quad (18)$$

where θ_i is the surface fraction and S_i is the molar interacting surface. Relating γ_i in Eq. (18) with Φ_i with the help of s_i (the surface-to-volume ratio), they showed that χ_{23}', as determined with Eq. (8), may be related to γ_{23}' (which is $\gamma_{23}S_1/S_2$) in the following way (provided s_2/s_3 is close to 1, so that the approximation $1/[1 - \Phi_3(1 - s_3/s_2)] = 1 + \Phi_3(1 - s_3/s_2)$ applies):

$$\chi_{23}' = \gamma_{23}'\left(\Phi_2 \frac{s_2}{s_3} + \Phi_3 \frac{s_3}{s_2}\right) + \gamma_{12}\left(1 - \frac{s_3}{s_2}\right) + \gamma_{13}\left(1 - \frac{s_2}{s_3}\right). \tag{19}$$

Equation (19) shows how χ_{23}' depends on γ_{12} and γ_{13}, representing interaction of the probe with the individual polymers. This dependence varies with the difference in the surface-to-volume ratios s_2 and s_3 for the blend components. If s_2 and s_3 are very nearly the same, the probe dependence of χ_{23}' would not be significant. Otherwise, χ_{23}' would differ appreciably from γ_{23}', especially if the interaction coefficients γ_{12} and γ_{13} are very different, i.e., if the probe interacts preferentially with one of the polymers. However, it is our view that replacement of χ_{ij} by γ_{ij} in Eq. (4) is not justified since the latter ignores the free volume difference between components *i* and *j* (see Eq. 10).

Nevertheless, from the experimental observations discussed above, it is advisable to give more weight to χ_{23}' values for probes (particularly nonpolar) that are solvents for polymers and do not interact with either polymer very preferentially, i.e., the difference between χ_{12} and χ_{13} is small. With polar probes, as well as with nonsolvent probes, V_g° values are subject to appreciable errors because of adsorption problems with the former and low V_g° with the latter, as discussed in Section IV [57, 58].

2. Poly(Vinyl Acetate) + Poly(Methyl Acrylate)

These two polymers are chemically very similar, the repeating unit of both being isomeric esters differing only in the orientation of the –COO group. No specific interactions are expected to exist between them. The two polymers also do not differ much from each other in respect to chain flexibility. Their T_g's differ by about 30°C, and they have very similar *P-V-T* properties. Hence both the exchange interaction energy and equation-of-state effect would be small and, according to McMaster's analysis, such a system should exhibit both UCST and LCST [82]. However, neither of these was detected, the LCST probably occurring above the decomposition temperature near 300°C and UCST below the T_g and, hence, both being experimentally inaccessible.

The next higher homologs of these polymers, viz., PVPr and PEA, were also considered to be miscible from T_g studies [83]. The similarity in chemical and physical properties of these two polymers is analogous to that of the PVAc + PMA system discussed above. It should be noted that no other binary pair from these four polymers, PVAc, PVPr, PMA, and PEA, was found to be miscible. However, one factor is common between the two miscible blend pairs PVAc + PMA and PVPr + PEA: in each pair the repeating units are isomeric esters differing only in the orientation of the –COO group. This factor is of utmost importance, which perhaps helps to keep the exchange interaction energy close to zero and thus effects miscibility in the absence of specific interactions.

The noncombinatorial interchange free-energy parameters χ_{12}, χ_{13}, and χ_{23}' for PMA ($\bar{M}_v$ 707 000) (Component 2) and PVAc ($\bar{M}_v$ 141 000) (Component 3) are reproduced in Tables 2 and 3. Fractionated polymer samples were used. In the original work, results at 80 and 100°C were reported [74]. However, we reproduce here only the results at 100°C because no definite trend with temperature was noted, and this temperature is well above the recommended IGC working temperature, viz., $T_g + 50°C$. However, because the *P-V-T* properties of the two polymers are not very different, the contribution of the equation-of-state effect to χ_{23}' is small and, accordingly, there is practically no difference in the two interaction parameters χ_{23}' and $\chi_{23}^{*\prime}$. This is evident from the values in Table 3, which vary with the probe and include both negative and positive values.

In the light of the discussion in the preceding section on probe dependence of χ_{23}', it will be appropriate to ignore the values obtained with the three nonsolvent probes: *n*-octane, cyclohexane, and ethanol. With the former two probes, V_g° is much smaller (2 to 5 times) than with the others. They therefore give a more inaccurate estimate of χ_{23}'. Ethanol is not only a nonsolvent but also a hydrogen-bonded polar substance. Hence, V_g° and χ_{23}' with this probe also tend to be less accurate. These considerations lead to χ_{23}' values ranging from +0.1 to -0.1, with one or two exceptions. Because the two polymers are very similar, the χ_{12} and χ_{13} values are close to each other. There is no preferential interaction of any of the probes with either polymer.

Nandi took an average of the 2,3 interaction indices obtained with all the probes and found the standard deviation to be greater than the average value, which is small and positive at all the compositions studied. In view of the inherent inaccuracy of the IGC-determined χ_{23}', the values falling in the range +0.1 to -0.1 may well be taken as indicative of $\chi_{23}' \approx 0$ [77]. The variation of χ_{23}' with blend composition also may not be real. Further reasoning to this effect is given in our discussion for the PVPr + PEA system below.

It was pointed out earlier that the accuracy of χ_{1i} is far better than that of χ_{23}', and much information is obtained from a consideration of these values. The closeness of χ_{12} and χ_{13} reveals that the polymers are of very similar chemical nature and of similar *P-V-T* properties. The miscibility in this blend system is therefore surely not due to complementary dissimilarity,

TABLE 2. Thermodynamic Quantities of Interaction of Probes with PMA (2) and PVAc (3) at 100°C[a]

Probe	χ_{12}	χ_{12}^*	$X_{12}/s_1 \times 10^8$, J/cm^2	χ_{13}	χ_{13}^*	$X_{13}/s_1 \times 10^8$, J/cm^2
Benzene	0.045	0.54	11.6	0.40	0.50	10.5
Toluene	0.55	0.63	16.7	0.51	0.59	16.0
n-Octane	2.24	2.33	44.0	2.14	2.23	42.6
Cyclohexane	1.65	1.74	54.5	1.64	1.74	55.3
Ethanol	1.09	1.17	54.7	0.96	1.05	48.6
Acetone	0.61	0.74	26.3	0.52	0.66	23.1
Methyl ethyl ketone	0.48	0.59	10.9	0.45	0.56	10.5
Ethyl acetate	0.48	0.61	8.3	0.45	0.68	8.2
1,2-Dichloroethane	0.09	0.18	-0.0	0.04	0.13	-1.8
Chloroform	-0.16	-0.11	-6.9	-0.18	-0.14	-8.0

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TABLE 3. Thermodynamic Quantities for Polymer-Polymer Interaction at 100°C for Different Polymer Ratios (W/W)[a]

	3:1 PMA + PVAc			1:1 PMA + PVAc			1:3 PMA + PVAc		
Probe	χ_{23}'	$\chi_{23}^{*\prime}$	$X_{23}/s_2 \times 10^8$, J/cm^2	χ_{23}'	$\chi_{23}^{*\prime}$	$X_{23}/s_2 \times 10^8$, J/cm^2	χ_{22}'	$\chi_{23}^{*\prime}$	$X_{23}/s_2 \times 10^8$, J/cm^2
Benzene	0.06	0.06	2.3	0.06	0.06	2.4	-0.04	-0.04	-1.5
Toluene	0.16	0.16	5.8	0.05	0.04	1.4	0.09	0.09	3.4
n-Octane	0.16	0.16	3.1	0.12	0.12	2.3	0.00	0.01	0.1
Cyclohexane	0.24	0.24	7.9	-0.11	-0.11	-3.4	-0.11	-0.11	-3.4
Ethanol	0.02	0.02	0.9				0.15	0.15	7.0
Acetone	0.07	0.07	3.0				-0.03	-0.00	-1.2
Methyl ethyl ketone	0.14	0.14	4.8	0.11	0.11	3.9	0.07	0.07	2.3
Ethyl acetate	-0.02	-0.02	-0.5	0.06	0.06	1.9	-0.00	-0.01	-0.1
1,2-Dichloroethane	0.08	0.08	3.3	0.07	0.07	2.9	0.09	0.09	3.6
Chloroform	-0.09	-0.10	-4.0	0.10	0.09	3.6	-0.03	-0.04	-1.7
Average		0.081	2.66		0.055	1.875		0.021	0.85
Standard deviation		0.099	2.89		0.072	2.29		0.078	3.16

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which is the general feature for miscible polymer-polymer systems [61]. The two chlorinated hydrocarbons 1,2-dichloroethane and chloroform proved to be very powerful solvents having negative χ^* and X. Negative X indicates the existence of specific interactions, presumably hydrogen bonding between the ester oxygen in the polymers and the acidic hydrogen in the chlorinated solvents and charge transfer of the n-σ^* type between O in the polymers and Cl in the probes. Of all the probes, χ_{1i} data for ethyl acetate are of particular interest since it is the hydrogenated monomer of a segment of PVAc it approximates and one would expect X_{12}/s_1 to be zero for this probe. The experimental value, however, is small and positive. Indeed, as expected, X_{12}/s_1, which should depend only on the chemical nature of the probe and be independent of its size, is lowest for this probe except for the two chlorinated solvents, which have strong specific interactions with the polymers. The nonzero X_{12}/s_1 value, however, should not be taken as indicative of an unfavorable 1,2 interaction because X_{13}/s_1 also has the same small positive value. If ethyl acetate truly represented a segment of PVAc, X_{13}/s_1 should have been zero. However, according to Patterson et al., the nonzero X_{1i}/s_1 may arise from an error in accounting for the free volume term in the theory. Also, X_{1i}, as determined here, is the interactional free energy (and not the energy) parameter [13].

3. Poly(Vinyl Propionate) + Poly(Ethyl Acrylate)

Recently we completed the thermodynamic characterization of this blend system for which intuitively $\chi_{23}' \approx 0$ but may not be negative (due to lack of complementary dissimilarity and hence of specific interactions) [84]. The $V_g{}^\circ$ data in Table 4 reveal that $V_{g2}{}^\circ$ and $V_{g3}{}^\circ$ are so close that their arithmetic mean (AM) and geometric mean (GM) are almost the same. Since the densities of the two polymers are also very close ($\rho_{\mathrm{PVPr}} = 1.106$, $\rho_{\mathrm{PEA}} = 1.112$, both at 32° [84]), $w_i \approx \Phi_i$, it follows from Eq. (8) that for χ_{23}' to be zero, the GM of $V_{g2}{}^\circ$ and $V_{g3}{}^\circ$ should be equal to V_{g23}° for the 1/1 blend. On the other hand, it has been shown by many workers that for a phase-separated system V_{g23}° should be equal to the weight average [27, 28, 85] of the $V_g{}^\circ$'s for the pure polymers. For a phase-separated 1/1 blend, V_{g23}° should therefore be equal to the AM in this case. Given the 2% error in V_{g23}° and the closeness of the AM and GM in the present case, it is not possible by IGC to establish whether the blend is homogeneous (because $\chi_{23}' \approx 0$) or phase separated (because χ_{23}' is positive).

The data in Table 4 show that V_{g23}° values are lower than the GM for a great majority of the probes which give rise to negative values of χ_{23}'. Disregarding the values obtained with the nonsolvent probes *n*-heptane and ethanol

TABLE 4. $V_g°$ Data for PEA (2), PVPr (3), and Their 1:1 Blend [23] at 60°C

Probes	$V_{g2}°$	$V_{g3}°$	$V_{g23}°$	$\frac{1}{2}(V_{g2}° + V_{g3}°)$	$(V_{g2}° V_{g3}°)^{1/2}$	χ_{23}'
n-Heptane	37.3	41.6	40.6	39.45	39.39	0.12
Benzene	139.0	146.8	142.8	142.90	142.85	0.00
Toluene	305.4	334.0	315.7	319.70	319.39	-0.05
Methyl propionate	111.5	116.6	113.7	114.05	114.02	-0.01
Acetone	52.4	53.8	53.7	53.10	53.09	0.04
Methyl ethyl ketone	109.8	114.8	110.9	112.30	112.27	-0.05
Ethyl acetate	96.6	103.6	99.1	100.10	100.04	-0.03
Ethyl propionate	181.2	202.0	188.0	191.60	191.32	-0.07
Chloroform	165.7	176.1	170.4	170.90	170.82	-0.01
1,2-Dichloroethane	231.4	240.0	232.7	235.7	235.66	-0.05
Ethanol	76.8	80.1	77.04	78.45	78.43	-0.07

(which are polar besides being nonsolvents) for reasons discussed earlier, we find that, at least with acetone as the probe, V_{g23}° is greater than even the AM, leading to a small positive value of χ_{23}'. Considering the inaccuracy of the method, the small negative χ_{23}' values may not be true and χ_{23}' may as well be considered to be zero.

B. Class 2: $\chi_{23}{}^{*\prime} < 0$

1. Poly(Vinyl Chloride) (PVC) + Other Polymers

a. PVC + Polyesters. Olabisi studied the PCL-PVC system and determined the $\chi_{23}{}^{*\prime}$ parameters for two different blend compositions, PCL/PVC = 50/50 and 70/30 at 120°C [61]. Eight different probes were used: ethanol, chloroform, methyl ethyl ketone, pyridine, acetonitrile, fluorobenzene, carbon tetrachloride, and hexane. He found that, except for the nonpolar probes benzene and CCl_4, $\chi_{23}{}^{*\prime}$ and X_{23} have negative values. This indicates the existence of specific interactions [hydrogen bonding involving the acidic H in PVC and ester oxygen in PCL and charge transfer (n-σ^* type) interaction between Cl in PVC and O in PCL] expected for this blend system. Spectroscopic evidence is available of this effect for analogous systems [86]. Interestingly, the interaction parameter $\chi_{ij}{}^*$ and X_{ij} have negative values only for the PCL-chloroform system, which again suggests similarity in the nature of the specific interactions in PCL-PVC and PCL-chloroform. Although $\chi_{23}{}^{*\prime}$ was negative, χ_{23}' was positive for many probes. This difference between $\chi_{23}{}^{*\prime}$ and χ_{23}' illustrates the significant positive contribution of the equation-of-state effect which the former eliminates, at least partially. The positive values obtained with the nonpolar probes were deemed to reflect noncomplexing unlike-contact interactions. It was also observed that as the amount of PCL in the blend increased, $\chi_{23}{}^{*\prime}$ decreased, indicating that the blend was becoming more favorable with regard to miscibility. The interaction parameters at 100°C differed little from those at 120°C.

Riedl and Prud'homme determined χ_{23}' at 120°C for blends of PVC ($\bar{M}_n$ 41 000, $\bar{M}_w$ 85 000) with a number of polyesters: poly(*D,L*-lactide) (PL) ($\bar{M}_n$ 26 000, $\bar{M}_w$ 63 000), poly(ethylene succinate) (PES) ($\bar{M}_n$ 4100, $\bar{M}_w$ 9100), poly(ethylene adipate (PEA) ($\bar{M}_w$ 2600), poly(butylene adipate (PBA) ($\bar{M}_n$ 9500, $\bar{M}_w$ 22 000), poly(ϵ-valerolactone) (PVL) ($\bar{M}_n$ 17 000, $\bar{M}_w$ 46 000), poly(ϵ-caprolactone) (PCL) ($\bar{M}_w$ 36 000), and poly(hexamethylene sebacate) (PHMS) ($\bar{M}_w$ 30 000) [87]. The methylene-to-carbonyl ratio, $[CH_2]/[COO]$, varies from 1 to 7 in the above polyesters as one passes from PL to PHMS. Because of degradation of PES in the columns, χ_{23}' for its blend with PVC could not be determined. χ_{23}' varied with the $[CH_2]/[COO]$

ratio, reaching a minimum for a ratio of 5. Earlier, Paul et al. found similar trends in χ_{23}' by using methods like melting-point depression analysis and analog calorimetry [88]. For the blend systems PVC-PL, PVC-PEA, and PVC-PVL with $[CH_2]/[COO]$ ratios of 1, 3, and 4, respectively, values of χ_{23}' turned out to be positive, indicating that these blends are immiscible. This result, except for PVC-PVL, is in conformity with that obtained by other methods such as thermal analysis and dynamic mechanical properties [88, 89]. For PVC-PCL systems, and also to some extent for PVC-PBA blends, χ_{23}' was found to vary with blend composition, the values becoming more negative with increasing concentration of polyesters in the blends. This result is in accord with that found by Olabishi [61] as mentioned above.

b. PVC + Polyacrylates or Polymethacrylates. Values of χ_{23}' at 120°C for 1/1 mixtures of PVC ($\bar{M}_n$ 35 000) with ethyl ($\bar{M}_n$ 40 000), *n*-propyl ($\bar{M}_n$ 70 000), *n*-butyl ($\bar{M}_n$ 95 000), and *n*-pentyl ($\bar{M}_n$ 80 000) polymethacrylates and with *n*-propyl ($\bar{M}_n$ 95 000) and *n*-butyl ($\bar{M}_n$ 100 000) polyacrylates were reported by Walsh et al. [62]. Considering the variation in the values of χ_{23}' with different probes, the authors opined that the absolute values are not reliable.

However, the data were useful for comparative purposes. For example, χ_{23}' was negative for blends with the polymethacrylates. The value increased with increasing alkyl chain length from an average value of -3.03 for poly(ethyl methacrylate) to -0.02 for poly(*n*-pentyl methacrylate), indicating that the miscibility becomes increasingly poor with increasing alkyl chain length of the poly(alkyl methacrylates). The χ_{23}' values for the blends with the two polyacrylates studied were appreciably positive; however, the blends were close to the phase-separation temperatures, but here again the value of χ_{23}' was found to increase with the alkyl chain length of the poly(alkyl acrylate). These qualitative conclusions agree well with miscibility studies by dynamic mechanical measurements and optical clarity [90]. The X_{23} values for the PVC-polyacrylate systems were determined by analog calorimetry, and negative values were obtained, indicating the existence of specific interactions [91, 92].

2. Chlorinated Polyethylene + Other Polymers

Chlorinated polyethylene (CPE) was found to be miscible with PVC, poly(ethylene-*co*-vinyl acetate) (PEVA), poly(methyl methacrylate) (PMMA), and poly(ethyl methacrylate) (PEMA) by Walsh et al. [28, 64, 93, 94]. Miscible blends with PVC are due to the very close chemical similarity of the two polymers, while the complementary dissimilarity rule for polymer-polymer miscibility applies to the others, i.e., these miscible blends result from specific interactions between CPE and these polymers, all of which contain ester groups. The specific interactions are of the type discussed for the PVC + PCL system.

a. CPE + Acrylates or Methacrylates. The following polymers were used: CPE contained 62.1 wt% chlorine ($\bar{M}_w$ 242 000, $\bar{M}_n$ 25 800), PMMA ($\bar{M}_w$ 72 800, $\bar{M}_n$ 29 000), PEMA ($\bar{M}_w$ 235 000, $\bar{M}_n$ 70 700), and PBA ($\bar{M}_w$ 119 000, $\bar{M}_n$ 33 000).

With PMMA or PBA as a blend component, $V_g{}^\circ$ was found to be a linear function of blend composition, i.e., $V_{g23}^\circ = w_2 V_{g2}{}^\circ + w_3 V_{g3}{}^\circ$ [28]. This result is characteristic of a phase-separated blend. A large positive $\chi_{23}{}'$ was calculated, which decreased with temperature. This result contradicted the analog calorimetry result, which indicated a negative X_{23} [94] and hence a negative or small $\chi_{23}{}'$. The result also went against the LCST observed, which required $\chi_{23}{}'$ to increase from negative to positive values with increasing temperature. Differential thermal analysis and dynamic mechanical measurements revealed that CPE with about 50% chlorine is miscible with PMMA.

Immiscible blends result when the level of chlorination is low (~27%) [94]. For the PEMA-CPE blend, however, a negative $\chi_{23}{}'$ was obtained by IGC which increased toward zero with rising temperature, indicating the existence of a LCST. The error in $\chi_{23}{}'$ was estimated to be ±0.2, corresponding to an error of ±5% in $V_g{}^\circ$. For the PMMA/CPE and PBA/CPE blend systems, it was presumed that phase separation occurred either during the process of support coating or during the heating of the columns (at 100°C for several hours during column conditioning). It was not independently determined, however, whether a phase-separated film results on evaporating the solution of the two polymers in the common solvent (which was MEK) from which the blend was deposited on the support, or whether phase separation occurs on heating to 100°C (the LCST was above 100°C, however).

b. CPE + PEVA. The following polymers were used: CPE ($\bar{M}_n$ 22 900, $\bar{M}_w/\bar{M}_n = 5.22$, 52 wt% Cl) and PEVA ($\bar{M}_w$ 256 000, $\bar{M}_w/\bar{M}_n = 5.16$, 45 wt% VA).

For the CPE + PEVA system, $\chi_{23}{}'/V_1$ was determined to be negative at 70°C but small and positive at 100°C [93]. The results were in agreement with the demixing observed in these blend systems on heating (LCST ≈ 90°C) and with the negative heat of mixing found in analog calorimetry [93, 95]. The heat of mixing became less negative with increasing temperature.

c. CPE + PVC. The following polymers were used. CPE (Hypalon 48, Du Pont, U.K.) ($\bar{M}_w$ 180 000, $\bar{M}_w/\bar{M}_n = 7.6$) contained 44% wt% Cl by weight and 1 wt% S as the SO_2Cl group, PVC ($\bar{M}_w$ 170 000). For the CPE + PVC system, $\chi_{23}{}^*/V_2$ (averaged for all probes) was found to be close to zero, being slightly positive for 25% and 75% PVC in the blends and slightly negative for 85% PVC at 120°C [64]. It was earlier observed that the LCST is close to 120°C for a 1/1 blend [96]. Additionally, discontinuity in the $V_g{}^\circ$ vs temperature plots was observed, indicating demixing. For a given blend composition, the onset of deviation from linearity in the $V_g{}^\circ$ vs T plot was the same, irrespective of the nature of the probe. The temperature for the onset of deviation from linearity when plotted against composition gave a phase diagram which was in agreement with the phase diagram determined by other methods.

However, it is surprising to find that $V_g{}^\circ$ vs T plots were linear for the pure polymer columns. Theory requires that log $V_g{}^\circ$ should show a linear relationship with $1/T$ and not $V_g{}^\circ$ with T [15-17]. The positive $\chi_{23}{}^{*\prime}$ results may indicate the absence of specific interactions. Compatibility may be due to the close similarity of the two polymers so that $X_{23} \approx 0$ and $\chi_{23}{}^{*\prime} \approx 0$ and less than $\chi^*_{23,\mathrm{cr}}$, which has a small positive value. A low negative heat of mixing, 0.15 cal/g at 120°C, was calculated for the 1/1 blend from the endotherm of demixing in the DSC trace. However, the authors pointed out that this heat did not owe its origin to specific interactions but to the volume change on mixing [96].

C. Class 3: $\chi_{23}{}^{*\prime} > 0$

1. Phase-Separated Blends or Copolymer Systems

IGC has also been used to study polymer systems which are determined to be incompatible by other methods. These include: (a) poly(dimethylsiloxane) (PDMS) + tetracosane [13]; (b) blends and block copolymers of PDMS and PS [11]; (c) PS + polybutadiene (PB) [57, 85]; (d) PS + poly(*n*-butyl methacrylate) (PBMA) [97]; (e) blends and alternating $\text{-(}A\text{—}B\text{)-}_n$ block as well as randomly coupled block copolymers of PDMS and polycarbonate (PC) [27]; (f) poly(St-*b*-THF) copolymers [10]; (g) poly(MMA-*g*-stearyl methacrylate) [98]; and (h) PDMS-PEO-PDMS triblock copolymers [99].

Equations (5) through (7), which are used to determine $\chi_{23}{}'$, are rigorously applicable to homogeneous systems. For this reason Patterson et al., as well as DiPaola-Baranyi et al., used oligomer blends (which are homogeneously miscible) in IGC work for the determination of $\chi_{23}{}'$ of incompatible blend systems. For the oligo(dimethylsiloxane)-tetracosane system, positive $\chi_{23}{}'$ values were obtained, consistent with the observed incompatibility of the blend components of higher molecular weights [11]. DiPaola-Baranyi et al. determined the compatibility of the PS-PBMA system by T_g studies with IGC. They found blends of oligostyrene ($\bar{M}_n$ 1709) and PBMA ($\bar{M}_w$ 320 000, $\bar{M}_n$ 73 500) to be compatible in that the blends showed single T_g's [97]. However, the blends become incompatible when oligostyrene is replaced by polystyrene. Thus, blends of PBMA with PS ($\bar{M}_w$ 110 000, $\bar{M}_w/\bar{M}_n < 1.06$) showed two T_g's. They determined χ_{23}' for this system for the compatible blends and found it to have a small positive value for most compositions rich in oligostyrene at 120-140°C. However, a peculiar composition dependence of χ_{23}' was observed that was inexplicable. For example, the average value of χ_{23}' at 75% PBMA was -0.23 while it was 0.44 at 70% PBMA. These workers also used incompatible mixtures of PS-PBMA in IGC and determined a small positive (~0.1) value for χ_{23}'.

In general, when a phase-separated blend was used in IGC, V_{g23}° was found to be equal to the theoretical value of the weight-average V_g° values of the pure components [28]. Thus,

$$V_{g23}^{\circ} = w_2 V_{g2}^{\circ} + w_3 V_{g3}^{\circ}. \tag{20}$$

It was pointed out earlier that for a compatible blend, V_{g23}° should be equal to or less than the volume-fraction-weighted geometric mean of V_{g2}° and V_{g3}°. This mean is close to the weight average if V_{g2}° and V_{g3}° are not very different from each other. Under such circumstances it would not be possible to use Eq. (8) to ascertain compatibility.

It should be noted that although Eq. (5) is strictly applicable only to homogeneous systems, it has been used to determine χ_{23}' for phase-separated blends. However, unrealistic values for χ_{23}' (even negative for some systems) were obtained for many systems in such applications [11, 13]. Working with PDMS and PS block copolymers, Galin et al. obtained χ_{23}' values which were positive and of a reasonable magnitude, confirming the basic incompatibility of PS and PDMS [11]. When three homopolymer blends differing in polymer molecular weights and composition were examined, positive χ_{23}' values were obtained for two blends containing lower molecular weight polymers than the third, for which a negative χ_{23}' was found. This negative value is unrealistic for an incompatible blend. From these results Galin considered that Eq. (5), though strictly applicable only to a homogeneous system, may still be used for a highly dispersed microphase-separated block copolymer but it not valid for incompatible blends in which macrophase separation in very large domains occurs.

Ward et al. noted that V_{g23}° for the PDMS-PC system conformed to Eq. (20) for block copolymers as well as blends. They derived positive χ_{23}' values for both copolymers and blend systems, consistent with the known incompatibility of PDMS and PC in copolymers and blends.

By far the most important application of IGC to the study of highly dispersed microphase-separated block copolymers is concerned with the estimation of the domain sizes. For this application the column was maintained at a temperature between the T_g's of the phases such that $V_g{}^\circ$ results from the adsorption *on* the glassy phase and bulk absorption *in* the liquidlike phase [11]. The assumption was made that the access of the probe to each phase is not influenced by the presence of the other. Thus, for the PS-PDMS system at temperatures below the T_g of PS, bulk sorption is negligible in PS for a *n*-decane probe which is a nonsolvent for PS but a good solvent for PDMS. In such a situation [11],

$$V_{g\,\mathrm{exp}}^{\circ} = wV_{g\mathrm{s}}{}^\circ(\mathrm{PS}) + (1 - w)V_{g\mathrm{b}}{}^\circ(\mathrm{PDMS}), \tag{21}$$

where w is the weight fraction of PS in the PDMS-PS copolymer, $V_{g\mathrm{s}}{}^\circ(\mathrm{PS})$ is the specific retention volume exclusively due to adsorption on PS, and $V_{g\mathrm{b}}{}^\circ(\mathrm{PDMS})$ is the $V_g{}^\circ$ exclusively due to bulk sorption in PDMS. Knowing $V_{g\mathrm{b}}{}^\circ(\mathrm{PDMS})$ for a pure PDMS column, $V_{g\mathrm{s}}{}^\circ(\mathrm{PS})$ was calculated by Eq. (21).

$V_{g\mathrm{s}}{}^\circ$ is related to the surface area A of the PS domains accessible to the probe by the relation

$$\ln A = \ln V_{g\mathrm{s}}{}^\circ + \ln W_2 - \ln K + \Delta H_s/RT, \tag{22}$$

where W_2 is the weight of PS, K is the surface partition coefficient of *n*-decane in the PDMS-PS system, and ΔH_s is the adsorption enthalpy. The authors assumed that K and ΔH_s for the adsorption layers in the copolymer have the same values as for the pure PS-*n*-decane system, which was determined independently [70]. This assumption allowed estimation of A by Eq. (22). If the microphase structure is represented by dispersion of PS rods in a PDMS matrix, the diameter of the PS cylinders can be calculated from A. Galin et al. found that the diameter of the PS cylinders so determined agreed well with the value determined by other methods such as EM and SAXS for a PDMS-rich composition, for which the latter methods revealed this morphology [11].

Ward et al. applied this technique to the estimation of the diameter of polycarbonate (PC) cylinders in PDMS-PC block copolymers in the PDMS-rich region for which a similar morphology was established by EM [27]. However, IGC-estimated diameters were far larger than those estimated by EM or SAXS, because phase separation in this system was not complete. There was some intermixing of PDMS in the PC domains and vice versa, as was evident from the T_g results. Under such circumstances the PDMS embedded inside the PC domains would not be accessible to the probe, so that (1 - w) in Eq. (21) should be lower than the actual composition. Use of the actual composition data gives an underestimate of V_{gs}° (PC) and hence of the surface area, which eventually leads to too large an estimate of the PC cylinder diameter.

A similar situation also obtained for the PS-PDMS copolymers for a composition in which, apart from dispersion of PS rods in the PDMS matrix, a low fraction of PDMS was also found in microdomains surrounded by PS and hence remained inaccessible to the probe. On the other hand, at a somewhat lower PDMS fraction in both copolymers, the film structure is lamellar and the thickness of the lamellae determined for both copolymers was in good agreement with the results of EM and SAXS. Agreement for a PDMS-PC copolymer in the lamellar film structure region was possible because T_g studies now showed that phase separation was complete in this region. Decreasing the PDMS percentage still further resulted in phase inversion where the rubber domains are dispersed in the continuous plastics matrix. In this region the PDMS became largely inaccessible to the probe, resulting in a sharp fall in V_g°. Determination of V_g° as a function of the PDMS content in the block copolymer therefore enables one to determine the stage of phase inversion.

It is thus evident that IGC can provide valuable information about the microphase structure of the block copolymers, and with the help of structural information from EM and/or SAXS it can give a quantitative estimate of lamellar thickness or of the diameters of the glassy domains, depending on the microphase morphology. The results are for situations where phase separation is complete and the phases are accessible to probes.

Ito et al. determined retention diagrams (plots of V_g° vs $1/T$) for n-dodecane as the probe with the random and graft copolymers of stearyl methacrylate (SMA) and MMA as well as for homopolymer blends at 65 to 160°C (T_m of PSMA 36-38°C, T_g of PMMA ≈ 105°C [98]). The retention diagrams for the graft copolymers (with PSMA branches $\bar{M}_n$ 4460) covering a range of $\bar{M}_n$ from 65 000 to 118 000 (depending on the number of PSMA branches per polymer molecule, which varied from 1.3 to 18.3, corresponding to 9.1 to 69 wt% of SMA) did not exhibit the T_g of PMMA segments above about 20 wt% SMA. This indicated that a microphase inversion occurred around this composition where the PSMA segments (which have a lower surface energy) formed a continuous phase essentially covering the copolymer surface. Decreasing the chain length of SMA segments caused phase inversion at higher SMA content.

Surprisingly, the homopolymer blends, although phase separated, gave almost linear retention diagrams with the same slope independent of the composition from 10 to 50 wt% SMA, and deviation from linearity due to the T_g of PMMA was absent above 10 wt% PSMA. This happened because the molten PSMA covered the PMMA phase due to its lower surface energy so that *n*-dodecane as the probe interacted only with the former without interacting with the PMMA phase which has a repulsive interaction with the probe. This view was supported by the fact that the $V_g°$ corrected for the SMA content in the blend was the same as that of a PSMA homopolymer. On the other hand, the retention diagrams of the random copolymer conformed to the behavior of a single-phase system with T_g increasingly lowered with increasing SMA content.

Similar studies with poly(St-*b*-THF) copolymers showed that they behave more like PTHF (which has a lower surface energy) than like PS when used as a stationary phase in IGC [10].

VI. CONCLUSIONS

Ascertaining polymer-polymer miscibility (from the sign of $\chi_{23}^{*\prime}$) with IGC is possible for systems associated with strong specific interactions such as the ones existing between PVC and PCL [61]. The absolute values of $\chi_{23}^{*\prime}$ determined by IGC, however, are not reliable. Nevertheless, in systematic work using several binary blends of which one component is common and the other belongs to a homologous series, such as the blends of PVC with methacrylates or PVC with polyesters, much information can be gained about the relative miscibility from an examination of the absolute $\chi_{23}^{*\prime}$ values [62, 87]. The method is not accurate enough to allow determination of compatibility in systems with $\chi_{23}^{*\prime}$ near zero. The inaccuracy inherent in IGC has been emphasized by all workers with the exception of Klotz et al. [50].

IGC has also proved useful in the study of microphase-separated block and graft copolymer systems. It provides a method for determining the diameters of glassy domains in a rubber matrix, lamellar thickness in a lamellar microphase-separated system, the composition at the point of microphase inversion, etc. It is expected that the accuracy of the method will improve in the future through sustained research, and its usefulness will increase correspondingly.

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