Probe Dependency of Segmental Interaction Parameters in Copolymers by Inverse Gas Chromatography

Jan-Chan Huang

Plastics Engineering Department, University of Massachusetts Lowell, Lowell, Massachusetts 01854

Received 27 October 2009; accepted 3 May 2010
DOI 10.1002/app.32739
Published online 27 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Inverse gas chromatography (IGC) has been widely used to determine the Flory-Huggins parameter, χ, between two polymers using a series of solutes as probes. Many studies showed that interaction parameters were probe dependent. In recent studies, it was proposed that the difference in interaction energy between functional groups of solutes and solvent mixtures could lead to an apparent solvent solubility parameter different from the volume average of the components. An equation was derived to relate the probe dependency to the deviation of the solubility parameter. By plotting $\phi_2\phi_3RT(\chi_{23}/V_2)$ vs. the solubility parameter of solutes, a straight line could be obtained with a slope proportional to the deviation of the solvent solubility parameter. The plot was shown to yield negative slopes for miscible polymer blends. When there was an unfavorable interaction between two solvents, an opposite situation would be observed. In this study, the method was tested in two copolymer systems, and the copolymers were considered as mixtures of two homopolymers. The plots showed straight lines with positive slopes when χ_{23} was positive. The technique was shown to apply to copolymer systems also. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 719–725, 2011

Key words: inverse gas chromatography; interaction parameter; solubility parameter; copolymers; poly(vinyl acetate); poly(dimethylsiloxane)

INTRODUCTION

The knowledge of the interaction parameters between two polymers is very important in the study of their miscibility and thermodynamic properties of solutions. Inverse gas chromatography (IGC) has been demonstrated to be an effective tool for measuring the thermodynamic properties of solute (probe) vapors in polymers.[1–4] In IGC measurement, a known amount of nonvolatile stationary phase is dissolved in a volatile solvent and coated on a porous inert support. In the operation of IGC, a carrier gas is passing through the column continuously. When a volatile probe liquid is injected into the column, the liquid vaporizes and flows with the carrier gas. Using Flory-Huggins theory,[5] the Flory-Huggins interaction parameter between a polymer and a probe, χ, can be related to the specific retention volume of the probe, V_g^T, by the following equation[1–4]:

$$\chi = \ln\left(\frac{RTv_2}{V_g^T P_1^0 V_1}\right) - 1 - \frac{P_1^0}{RT}(B_{11} - V_1) \qquad (1)$$

where R is the gas constant, T is the column temperature, v_2 is the specific volume of the stationary phase, and P_1^o, V_1, and B_{11} are the vapor pressure, the liquid molar volume, and the second virial coefficient of the probe, respectively. When a polymer blend is used in an IGC study, the corresponding specific retention volume and density data of blends can be used in eq. (1). The interaction parameter obtained is called $\chi_{1(23)}$. Applying the Flory-Huggins equation of polymer solutions[5] to a ternary system with two polymers and one probe, $\chi_{1(23)}$ can be related to the pair interactions of probe-polymers, χ_{12} and χ_{13}, and polymer-polymer, χ_{23}[3,4]:

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}(V_1/V_2) \qquad (2)$$

Here ϕ is the volume fraction of the two stationary phases. As molar volumes of polymeric solvents may not be accurately known, it is a practice in IGC study to define a probe normalized interaction parameter, $\chi'_{23} = \chi_{23}(V_1/V_2)$. Equation (2) then becomes[3,4]:

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi'_{23} \qquad (3)$$

The advantage of this parameter is that, it can be calculated through the specific retention volume by the following formula without calculating the individual interaction parameters[6]:

$$\ln\left(\frac{V_{g,\text{blend}}^T}{w_2v_2 + w_3v_3}\right) = \phi_2 \ln\left(\frac{V_{g,2}^T}{v_2}\right) + \phi_3 \ln\left(\frac{V_{g,3}^T}{v_3}\right) + \phi_2\phi_3\chi'_{23} \qquad (4)$$

Correspondence to: J.-C. Huang (Jan_Huang@uml.edu).

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or

$$\ln K_m = \phi_2 \ln K_2 + \phi_3 \ln K_3 + \phi_2\phi_3\chi'_{23} \quad (5)$$

Here v is the specific volume and w is the weight fraction of a solvent. The dimensionless K ($=V_g^T/v$) is the partition coefficient of a solute in a solvent or solvent mixture. Equation (4) has frequently been used to study the interaction of two stationary phases using the IGC method. But many studies have shown that the value of χ'_{23} depends on the probe used.[6–11] In examining literature data, it was found that in many systems, when probe dependency occurred, the values of χ'_{23} were positive when χ_{12} and χ_{13} were positive, and decreased toward negative when χ_{12} and χ_{13} decreased. In most systems that were miscible, some negative χ'_{23} values were generally observed for probes with low values of χ_{12} and χ_{13}. It has been pointed out that χ'_{23} contains V_1, which is probe dependent. What the literature referred to is the probe dependency of χ_{23}, or χ_{23}/V_2 for a polymer system. The comparison of χ_{23} or χ_{23}/V_2 would be more appropriate for studying probe dependency.[12–14]

APPARENT SOLUBILITY PARAMETERS OF SOLVENT MIXTURES

Because of the probe dependency in the IGC method, it was proposed to study the variation of solubility parameter of the mixture as a means to measure the interaction between two polymers.[15,16] If the heats of vaporization of a mixture and its components are known, the heat of mixing can be calculated. The solubility parameter, δ, of a liquid is defined as[17]:

$$\delta = \left(\frac{\Delta E_{\text{vap}}}{V}\right)^{1/2} \quad (6)$$

where ΔE_{vap} is the energy of vaporization and V is the molar volume of the liquid. The ratio $\Delta E_{\text{vap}}/V$ is the cohesive energy density; it represents the energy required to separate the liquid molecules into the ideal gas state. Experimental values of χ have been used to estimate the solubility parameters of polymers using the method of DiPaola-Baranyi and Guillet.[18,19] In their studies, the Flory-Huggins parameter between a solute and a polymer was assumed to have the following expression:

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 + \chi_S \quad (7)$$

Here χ_S is the entropy term. Equation (7) can be changed into the following linear expression[18,19]:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \eta\right) \quad (8)$$

where η is the average value of χ_S/V_1. From a linear regression method δ_2 can be determined. When a mixture is used as the stationary phase, the solubility parameter of the mixture, δ_m, can be compared with the prediction of the regular solution method, which predicts δ_m to be the volume average of the two components[17]:

$$\delta_m = \phi_2\delta_2 + \phi_3\delta_3 \quad (9)$$

If there were a specific interaction between two solvents that produced negative enthalpy of solution, the value of δ_m would be higher than the prediction of eq. (9), to account for the separation of the additional specific interaction between the mixtures and pure components in the vaporization process. A comparison of the solubility parameters of polymer mixtures would be a good indicator to predict their miscibility. In the previous study,[15] this argument was tested using the data of the poly(ε-caprolactone) (PCL)/poly(epichlorohydrin) (PECH) system at 80°C. It was found that the solubility parameter of the mixture was lower than the prediction of eq. (9). This was opposite to the above argument, even though there were some specific interactions between PCL and PECH and the system was miscible. When a deviation from eq. (9) occurs, the deviation of the solubility parameter of the mixture, Δ, can be defined as:

$$\delta_m = \phi_2\delta_2 + \phi_3\delta_{\backslash 3} - \Delta \quad (10)$$

Here Δ is the deviation of the solubility parameter of the polymer mixture. A mechanism was then proposed to explain this observation.[15] When two solvents with specific interactions are brought together, some functional groups interact with each other and are less available to interact with the probes. Compared with the average values based on the nominal composition, the probes will have less specific interaction with the mixture. Therefore, polar probes show a decrease in retention volume compared with the average value of the components, and for n-alkane probes the decrease may be smaller. This difference between probes is exhibited as the probe dependency. The solubility parameters of solvent mixtures measured by the IGC method also decrease to reflect the change in the interaction between the probe and the solvent mixtures. It cannot be related solely to the cohesive energy density of the solvent mixtures. But the extent of such solubility parameter change, as measured by the parameter Δ, could be an indicator of the interaction between the two solvents.

Based on the above arguments a method was proposed to estimate χ_{23}/V_2 and test the miscibility of

the two polymer components.[15] From eqs. (3), (7), and (10) the following equation was obtained in the previous study[15]:

$$\phi_2\phi_3 RT(\chi_{23}/V_2) = \phi_2\phi_3(\delta_2 - \delta_3)^2 - 2\Delta(\delta_1 - \delta_m, r) - \Delta^2 + RT(\phi_2\chi_{s,2} + \phi_3\chi_{s,3} - \chi_{s,m})/V_1 \quad (11)$$

The left-hand side can be plotted vs. the solubility parameter of the probe, δ_1. In the plot, a linear trend with a negative slope was predicted for miscible blends. The slope was proportional to the deviation parameter, Δ, which could be used as a measurement of miscibility. In another study,[16] this approach was also verified in plasticized poly(vinyl chloride) (PVC) and a copolymer, and in poly(vinylidene fluoride) (PVDF) - poly(ethyl methacrylate) (PEMA) blends.

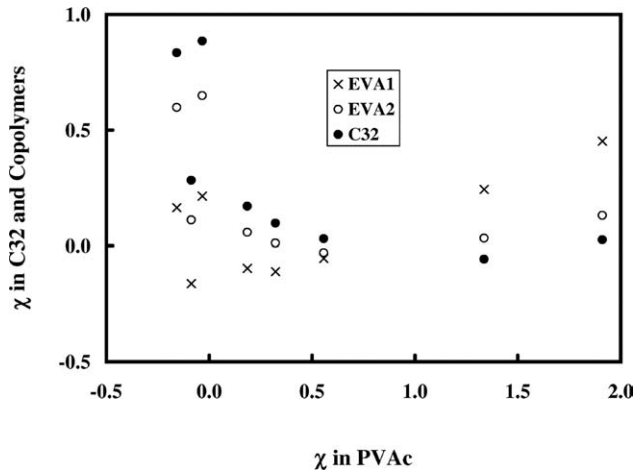

Figure 1 The plot of χ for solutes in dotriacontane (C32) and copolymers vs. χ of solutes in PVAc at 120°C. EVA1: 48.5 wt % VAc; EVA2: 15.4 wt % VAc.

EVALUATION OF X_{23} OF POLYETHYLENE AND POLY(VINYL ACETATE)

When two components are thermodynamically unfavorable in miscibility their interaction parameters will be positive. For polymer mixtures, a small positive χ_{23} could lead to an immiscible system. The IGC technique and eq. (4) could not be used in immiscible systems, because the equation was derived based on the assumption of miscible mixtures. However, two different monomers can be brought together into a one-component system by copolymerization. If the two monomers are randomly polymerized together a copolymer with properties intermediate between the two homopolymers could result. The interaction parameters between solutes and the copolymers should also follow a trend intermediate between the two homopolymers.

In a random copolymer, two types of monomers are joined together near the segmental level. They can be treated as a solution of these two types of monomers. The concept was first proposed in the ASOG (analytical solution of groups) model.[20] In the model, a molecule or a solution is treated as a mixture of groups irrespective of whether these groups are connected in the same or different molecules. For example, a solution of hexane and acetone is considered as a mixture of methyl, methylene, and ketone groups. Methyl groups in acetone are considered to have the same properties as those in n-hexane. The solution properties are determined from the difference of the properties of the mixture and pure components. This is a good approximation when groups are free to contact each other. Based this approach, a random copolymer can be treated as a mixture of two homopolymers, and the interaction parameters between these two homopolymers can be estimated from the results of homopolymers and copolymers by the IGC method.

More recently a similar concept was used in a study by Du and coworkers.[21] In that study dotriacontane, poly(vinyl acetate) (PVAc), and two poly(-ethylene-co-vinyl acetate) (EVA) were used. Dotriacontane was used to represent polyethylene. The segmental interaction parameters between ethylene and vinyl acetate were reported for the two EVAs. A probe dependency was also observed but the composition dependency was small. The results might well be analyzed by eqs. (5) and (11), which will be shown later. Values of $\chi_{1(23)}$ for each composition from the study of Du and coworkers. were reported for 120°C. Figure 1 shows the plot of Flory-Huggins interaction parameters of solutes in dotriacontane and EVAs vs. PVAc. This is similar to the plot of log V_g for different stationary phases.[22–24] This is a convenient method for comparing and scanning interaction between solutes and solvents, particularly in the presence of a specific interaction and when the solvent molecular weights or the vapor pressure of solutes are unknown. The use of the plot of χ requires the knowledge of vapor pressure, but it has a benefit that the effect of vapor pressure, which is affected by the solute liquid state interaction, is removed.

In Figure 1 it can be seen that the plot between dotriacontane and PVAc was near an inverse trend. Nonpolar solutes such as octane had low χ in dotriacontane but high χ in PVAc. They were located at the right hand side of plot. Strong polar solutes such as dioxane had high χ in dotriacontane but low χ in PVAc. They were located at the left-hand side of the plot. With an increase in vinyl acetate content nonpolar solutes gradually had an increase in χ while polar solutes had a decrease in χ. Such systematic variation indicating this copolymer system might be

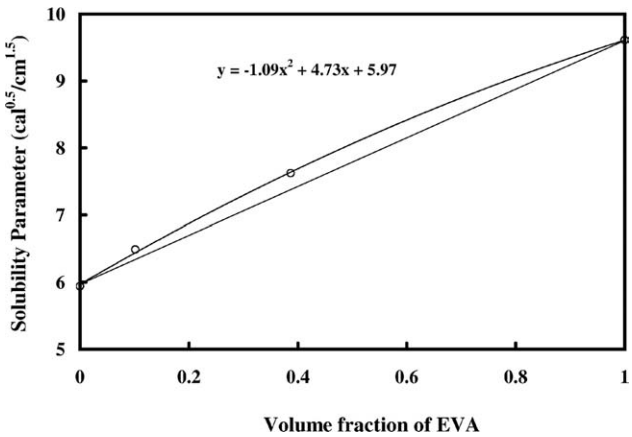

Figure 2 The plot of solubility parameter of EVA copolymers vs. the volume fraction of EVA at 120°C. Upper line is the second order polynomial fit. Lower line is the volume average.

correlated by a single parameter using a nonpolar-polar scale, such as the Hildebrand solubility parameter.

In the mixture of hydrocarbons and EVA the value of χ_{23} is expected to be positive, because the hydrocarbon is nonpolar and EVA is polar. In addition, there may be some self association of acetate groups in EVA. This association shielded some acetate functional groups from interaction with probes. In the mixture of n-alkanes and EVA some of these acetate groups dissociated and were available to interact with solutes. The result of this dilution process was that solute molecules would feel that the mixture had more polar interaction than the volume average estimation based on pure components. This apparently more polar interaction of solvent mixtures, as probed by solutes, was opposite to the situation of miscible blends when a specific interaction was formed between two solvents, and would lead to a negative Δ. Therefore, when the interaction parameter χ_{23} was positive, there was a tendency that the slope of eq. (11) would be positive too, and χ_{23} would increase when solutes became more polar.

From $\chi_{1(23)}$ results reported by Du and coworkers solubility parameters of the polymers were calculated using eq. (8) and plotted in Figure 2. It can be seen that, solubility parameter of the copolymers had a positive deviation from volume average. This indicated a higher apparent solubility parameter in the copolymer, and the possibility of self-interaction of polar acetate groups. In Figure 2, a straight line was also drawn to show the volume averaging rule for solubility parameters of mixtures. From the apparent solubility parameter, one can make an estimation of the effective polarity of the mixture. For example, in a copolymer of 50 vol % VAc the solubility parameter of the copolymer was 8.06 $cal^{0.5}/cm^{1.5}$ rather than 7.77 estimated from volume averaging. A value of 8.06 corresponded to an effective composition of 57.8 vol % in the volume average. Therefore, in 50 vol % VAc, an equivalent of 7.8 vol % of VAc groups might have been dissociated from each other and the solute would feel the mixture to have 57.8 vol % VAc content.

The plot of eq. (11) was made in Figure 3 for two EVA copolymers. It can be seen that, a good linear trend with positive slope was obtained for each copolymer. This indicated that mixing of polyethylene and EVA was unfavorable and would lead to immiscible systems. If both monomers exist as a block or graft copolymer, a multiphase structure could also result. But random copolymerization forced the two monomers to join together and create a solution that exhibited unfavorable thermodynamic properties. The similarity between the EVA system and previous studies on miscible systems[15,16] showed that solution thermodynamic properties of the copolymers could be treated as a solution of two homopolymers and the probe dependency of χ_{23} can also be demonstrated in the IGC study of copolymers.

EVALUATION OF X_{23} OF PHENYLMETHYL SILOXANES

Another copolymer available for this study is the IGC data of phenyl substituted poly(dimethylsiloxane) (PDMS). These compounds had a range of phenyl content. They are common stationary phases for gas chromatographic study because of their thermal stability and low-vapor pressure over a wide temperature range. Different phenyl contents impart chromatographic selectivity for solutes. This series of copolymers can be considered as a copolymer of PDMS and the hypothetical poly(diphenylsilioxane) (PDPS). In this study, the results of Parcher et al.[25] were used for further testing of eq. (5). In the study

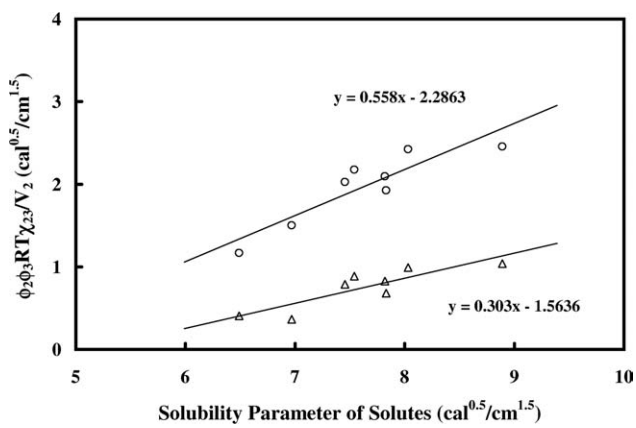

Figure 3 The plot of $\phi_2\phi_3 RT\chi_{23}/V_2$ vs. the solubility parameter of probes at 120°C for EVA copolymers. Symbols: O: EVA-1 with 48.5 wt % VAc; Δ: EVA-2 with 15.4 wt % VAc.

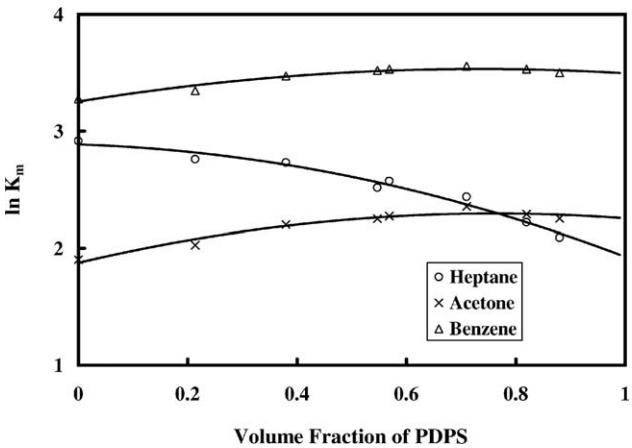

Figure 4 The plot of ln K_m vs. the volume fraction of PDPS for n-heptane, acetone, and benzene, in PDMS-PDPS system at 100°C. Solid lines are correlation based on eq. (5).

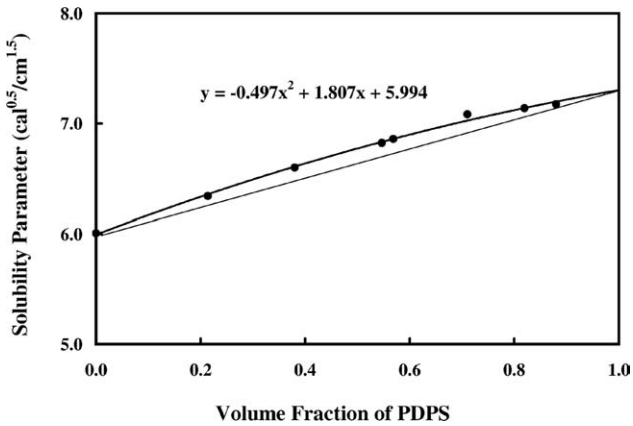

Figure 5 The plot of solubility parameter of PDMS-PDPS copolymer vs. the volume fraction of PDPS at 100°C. Upper line is the second order polynomial fit. Lower line is the volume average.

of Parcher et al., 10 solutes with different polarity were used for 8 polymers with phenyl content ranging from zero to 75 mole percent. Retention volumes were reported for 66, 100, and 150°C. Densities of the copolymers were also reported for 25°C by Parcher et al.[25] The density of polymers at high temperature was estimated with a thermal expansion coefficient of 0.0009 K^{-1}.[26]

Figure 4 showed the plot of ln K_m for heptane, benzene, and acetone vs. the volume fraction of PDPS at 100°C. The volume fractions of PDPS were calculated based on the mole fraction of phenyl substitution and van der Waals volume from the table of Bondi.[27] It can be seen that the results could be correlated by a second order polynomial using the volume fraction of PDPS as the variable. The convex curve in Figure 4 gave a positive value for χ_{23}. The values of ln K in PDMS and the hypothetical PDPS, and χ_{23} are shown in Table I for each solute in 100°C. It can be seen that n-alkanes had higher K values in PDMS than in PDPS. For other solutes the reverse was true. That was because other solutes were aromatic or polar and better interacted with the phenyl groups in PDPS. Also shown in Table I is the relative error in fitting eq. (5). N-Pentane and ethanol had the highest error. This might be because they had the lowest specific retention volume and ln K, which magnified the relative error in experimental measurement. Ethanol may also have the effect of surface adsorption, which is discussed later.

TABLE I
The Values of ln *K* for PDPS (Component 2) and PDMS (Component 3), χ_{23}, and % Error in Fitting eq. (5) at 100°C

	ln *K* (PDPS)	ln *K* (PDMS)	χ_{23}	% Fit
n-Pentane	1.25	2.18	0.75	1.68
n-Hexane	1.93	2.89	0.81	1.42
n-Heptane	2.57	3.53	1.02	1.15
n-Octane	3.20	4.19	1.18	1.15
Ethanol	1.80	1.59	0.39	1.94
Acetone	2.25	1.88	0.72	1.15
Acetonitrile	2.72	1.80	0.94	0.77
Nitromethane	3.28	2.37	0.99	0.83
Methyl ethyl ketone	2.99	2.67	0.77	0.81
Benzene	3.50	3.25	0.52	0.50

Figure 5 shows the plot of solubility parameters of copolymers vs. the volume fraction of PDPS. It can be seen that the solubility parameters also showed a positive deviation similar to Figure 2. The results could also be represented as a second order polynomial. A good fit in second order polynomial for solubility parameter indicated that the deviation parameter was proportional to $\phi_1\phi_2$, and there was no need to assume a concentration dependenct χ_{23}. The magnitude of the solubility parameter deviation was smaller than that in Figure 2. This was because both PDMS and PDPS were nonpolar and dominated by dispersion type interaction, which had a difference of solubility parameters of about 1 $cal^{0.5}/cm^{1.5}$, as can be seen in Figure 5. But for EVA, the solubility parameters of homopolymers differed markedly in polarity, by about 3 $cal^{0.5}/cm^{1.5}$, as can be seen from Figure 2.

The plot of eq. (11) for 100°C using χ_{23} from Table I and a value of $\phi_2 = 0.5$ is shown in Figure 6. The results at other temperatures had similar trends and were not shown. It can be seen that data could be correlated by a straight line with a positive slope. Ethanol showed a deviation from the trend of other solutes. It might happen because ethanol had surface adsorption on nonpolar solvents.[28] When different loading was used for different copolymers in chromatographic packings the variation of surface-to-volume ratio might cause a change in the specific

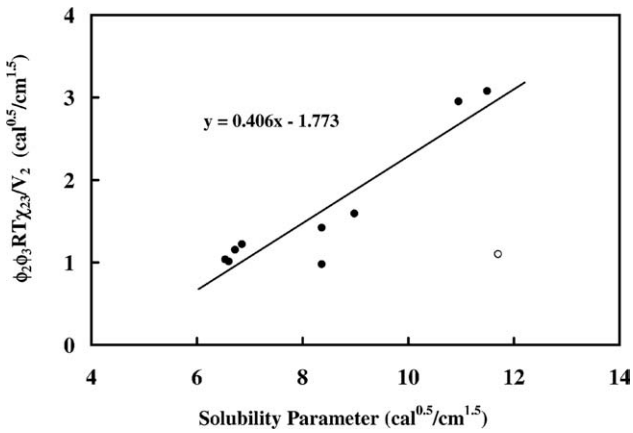

Figure 6 The plot of $\phi_2\phi_3RT\chi_{23}/V_2$ vs. the solubility parameter of solutes for PDMS-PDPS copolymers at 100°C and $\phi_1 = 0.5$. The open symbol is ethanol.

retention volume and K of ethanol. Ethanol was not used in the determination of the slope in Figure 6. The values of Δ were determined to be -0.406 cal$^{0.5}$/cm$^{1.5}$ for 100°C. The corresponding estimation using the curve in Figure 5 gave -0.497 cal$^{0.5}$/cm$^{1.5}$. The difference might occur because in Figure 5, when eq. (8) was used, each solubility parameter was determined from different solutes in a particular copolymer, whereas in Figure 6, the value of χ_{23} for each solute was determined from the same solute in different copolymers. It is also possible that selection of solute samples might affect the results of slope, especially when strong polar solutes were used, because their interaction with solvents might deviate from the Hildebrand solubility parameter model. The true value might be between these two numbers, and they were both negative. Therefore, both figures indicated positive deviation of volume average of solubility parameters and a thermodynamically unfavorable system between PDMS and PDPS.

RELATION BETWEEN X_{23} AND X OF PURE COMPONENTS

The probe dependency made it difficult to evaluate the true value of χ_{23}. An additional analysis method is suggested here by examining the physical meaning of eq. (4). In the equation, $\chi_{1(23)}$ represents the specific free energy of a solute in the solvent mixture and $(\phi_2\chi_{12} + \phi_3\chi_{13})$ represents the volume average free energy of the solute in the components. The latter quantity also represents the free energy of solution when no specific interaction occurs between two components in the stationary phase. The quantity $\phi_2\phi_3\chi_{23}/V_2$ then represents the free energy of transfer for a solute to move from the interacted solvents mixture to the linear combination of the pure components. It also represents the difference a solute molecule would experience in the polymer mixtures, when the interaction between the two polymers is "charging up" from the ideal solution state. For polar-nonpolar solvent mixtures, this difference is likely a function of the difference of the interaction parameters of the solute between the two solvents, $\chi_{12} - \chi_{13}$. This phenomenon was called the $\Delta\chi$ effect in an earlier study.[9] Although it was proposed for the study of miscible mixtures, it is also applicable to an unfavorable, but miscible, mixture. The best solute that can be used to evaluate χ_{23} would be the one that has small or zero $\Delta\chi$. This conclusion is similar to miscible systems.

Figure 7 shows the plot of χ_{23}/V_2 vs. $\Delta\chi/V_1$ of solutes in the two systems studied here. The more polar homopolymers were assigned as component 2. The plot was made on χ_{23}/V_2 vs. $(\chi_{12} - \chi_{13})/V_1$ because the system was polymeric, making χ_{23} difficult to define. It can be seen that, there was a small dependence of χ_{23}/V_2 on $\Delta\chi/V_1$. This, of course, was another way to demonstrate the probe dependency. Polar solutes and n-alkanes gave different signs for $\Delta\chi$. Polar solutes had negative $\Delta\chi/V_1$ but higher values of χ_{23}/V_2. A higher value of χ_{23}/V_2 happened because polar solutes could compete with polar functional groups of solvents even though they were associated. The interaction of polar solutes gave more negative enthalpy of solution than nonpolar solutes, and more positive entropy of solution because of a decrease of self association order of solvent in the solution, and therefore gave lower $\chi_{1(23)}$ and higher χ_{23} through eq. (2). The ability of a polar solute to interact with solvents can also be measured by the value of $\Delta\chi/V_1$ of the solute. A more polar solute had a smaller χ value in the polar homopolymer, component 2, and led to a more negative $\Delta\chi/V_1$. Thus, χ_{23}/V_2 and $\Delta\chi/V_1$ depended on the same mechanism and will have a mathematical relationship. For the EVA system the dependency was gentle and a linear regression could be used. From the

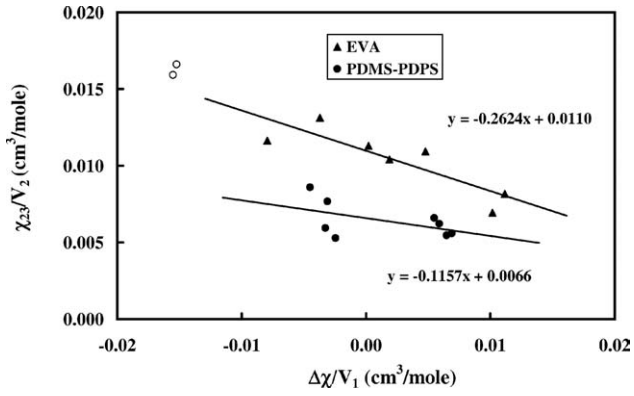

Figure 7 The plot of χ_{23}/V_2 vs. $\Delta\chi/V_1$ of solutes for EVA copolymers at 120°C and PDMS-PDPS at 100°C. Open symbols are acetonitrile and nitromethane in PDMS-PDPS.

plots the best values of χ_{23}/V_2 were 0.011 mol/cm^3 for EVA system at $\Delta\chi/V_1 = 0$.

For the PDMS-PDPS system polar acetonitrile and nitromethane were also located at the left-hand side but showed a deviation from the linear trend. This deviation might be a result of specific interaction between solutes and one of the components. Despite the deviation of two polar solutes, they still showed positive deviations for χ_{23}/V_2 indicating an unfavorable PDMS-PDPS system. Using other solutes the value of χ_{23}/V_2 was determined to be 0.0090, 0.0066, and 0.0051 mol/cm^3 for 66, 100, and 150°C, respectively. The rate of decreasing was higher than thermal expansion of polymers. The decrease was mostly the result of decreasing χ_{23}. When temperature increased thermal energy overcame the mutual interaction between functional groups and made χ_{23} smaller. For systems with negative χ_{23} a decrease in the magnitude of χ_{23} might also be observed if data over a wide temperature range were available.

On a volume basis, the EVA copolymers had about twice the χ_{23}/V_2 compared with the PDMS-PDPS system. This may have been because in the latter system the homopolymer pairs were structurally similar as pointed out earlier. The result of this study, again demonstrated the mechanism of probe dependency, and that the best probes for IGC study to estimate χ_{23} would be those with small $\Delta\chi$ and without a specific interaction to the components. A series of solutes with a range of $\Delta\chi$ near zero could also help to determine the value of χ_{23}/V_2 more accurately for polar-nonpolar copolymer systems.

CONCLUSIONS

A mechanism previously proposed for the probe dependency of polymer-polymer interactions was tested using two copolymers. Each copolymer was considered as a mixture of two homopolymers. The plot of $\phi_2\phi_3RT(\chi_{23}/V_2)$ vs. δ_1 gave positive slopes for mixtures. The signs of the slopes were in agreement with the sign of χ_{23}. The results again affirmed the mechanism of probe dependency and demonstrated that the plot of eq. (11) could also be used for a thermodynamically unfavorable system. Using a series of solutes, the plot of χ_{23}/V_2 vs. $\Delta\chi/V_1$ at $\Delta\chi/V_1 = 0$ gave a better estimation on the value of χ_{23}/V_2.

The author would like to express his special thanks to Dr. R. D. Deanin of the Plastics Engineering Department at the University of Massachusetts Lowell for his invaluable help and useful discussion.

References

1. Conder, J. R.; Young, C. L. Physicochemical Measurement by Gas Chromatography; Wiley: New York, 1979.
2. Lloyd, D. R.; Ward, T. C.; Schreiber, H. P., Eds. Inverse Gas Chromatography: Characterisation of Polymers and Other Materials, ACS Symposium Series, No. 391, American Chemical Society: Washington, DC, 1989.
3. Al-Saigh, Z. Y.; Guillet, J. E. Encyclopedia of Analytical Chemistry: Instrumentation and Applications, Meyers, R., Ed.; Wiley: Chichester, 2000; p 7759.
4. Vilcu, R.; Leca, M. Polymer Thermodynamics by Gas Chromatography, Vasilescu, V., Ed.; Elsevier: Amsterdam, 1990.
5. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Ithaca, New York, 1953.
6. Al-Saigh, Z. Y.; Munk, P. Macromolecules 1984, 17, 803.
7. Deshpande, D. D.; Patterson, D.; Schreiber, H. P.; Su, C. S. Macromolecules 1974, 7, 530.
8. Su, C. S.; Patterson, D.; Schreiber, H. P. J Appl Polym Sci 1976, 20, 1025.
9. Hsu, C. C.; Prausnitz, J. M. Macromolecules 1974, 7, 320.
10. Su, C. S.; Patterson, D. Macromolecules 1977, 10, 708.
11. Farooque, A. M.; Deshpande, D. D. Polymer 1992, 33, 5005.
12. Huang, J. C. J Appl Polym Sci 2003, 89, 1242.
13. Huang, J. C. J Appl Polym Sci 2003, 90, 671.
14. Huang, J. C.; Deanin, R. D. J Appl Polym Sci 2004, 91, 146.
15. Huang, J. C. Eur Polym J 2006, 42, 1000.
16. Huang, J. C. J Appl Polym Sci 2007, 106, 4110.
17. Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. Regular and Related Solutions; Van Nostrand Reinhold Co.: New York, 1970.
18. Dipaola-Baranyi, G.; Guillet, J. E. Macromolecules 1978, 11, 228.
19. Ito, K.; Guillet, J. E. Macromolecules 1979, 12, 1163.
20. Wilson, G. M.; Deal, C. H. Ind Eng Chem Fundam 1962, 1, 20.
21. Gou, Y.; Gu, B.; Lu, Z.; Du, Q. J Appl Polym Sci 1999, 71, 693.
22. Langer, S. H.; Purnell, J. H. J Phys Chem 1963, 67, 263.
23. Langer, S. H.; Purnell, J. H. J Phys Chem 1966, 70, 904.
24. Langer, S. H.; Sheehan, R. J.; Huang, J. C. J Phys Chem 1982, 86, 4605.
25. Parcher, J. F.; Hansbrough, J. R.; Koury, A. M. J Chromatogr Sci 1978, 16, 183.
26. Allen, G.; Gee, G.; Mangaraj, D.; Sims, D.; Wilson, G. J. Polymer 1960, 1, 467.
27. Bondi, A. Physical Properties of Molecular Crystals, Liquids, and Glasses; John Wiley and Sons, Inc: New York, 1968.
28. Nitta, T.; Morinaga, K.; Katayama, T. Ind Eng Chem Fundam 1982, 21, 396.