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Notes

The "$\Delta\chi$ Effect" and Polystyrene–Poly(vinyl methyl ether) Compatibility in Solution

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It is well-known that most pairs of polymers (components 2 and 3) are incompatible corresponding to a positive value of the χ_{23} interaction[2] larger than 2 for the simple case of equal molecular weights.[3] Since χ_{23}, defined[2] by Flory, is proportional to molecular weights, the value of 2 corresponds, for high polymers, to a very small repulsive interaction. If a common solvent (1) is added to an incompatible pair, the resulting solution is phase-separated but becomes homogeneous for a solvent volume fraction (φ_1) greater than a certain critical value, φ_{1c}. According to Flory–Huggins solution thermodynamics, as applied to such ternary systems by Scott[4] and Tompa,[5] phase equilibrium does not depend on the solvent but only on χ_{23} related to φ_{1c} through

$$\chi_{23} = 2(1 - \varphi_{1c})^{-1} \qquad (1)$$

According to eq 1, solution-phase separation, i.e., φ_{1c} between 0 and 1, indicates $\chi_{23} > 2$ and hence incompatibility in the absence of the solvent. However, eq 1 was derived assuming that $\chi_{13} = \chi_{12}$. Recent treatments[6,7] relax this restriction and *predict that phase equilibrium in ternary systems containing* two polymers and a solvent depends not only on χ_{23} but also on any difference in strengths of the polymer–solvent interactions, i.e., on

$$|\Delta\chi| = |\chi_{12} - \chi_{13}| \qquad (2)$$

Due to this "$|\Delta\chi|$ effect", phase separation is predicted[6,7] even when the polymers are compatible ($\chi_{23} < 2$ or negative) provided that $|\Delta\chi|$ is sufficiently large. The phase diagram shows a closed region in which phase separation occurs, such as is seen in Figures 1 or 2. For zero and small φ_1 the system is homogeneous, then becomes cloudy in an intermediate range of φ_1. Koningsveld and collaborators have studied two systems showing this behavior: benzene/(polyisobutylene + ethylene–propylene–diene terpolymer)[8] and diphenyl ether/linear polyethylene + atactic polypropylene.[9] Unfortunately, it is not obvious that $|\Delta\chi|$ is large in these cases. However, the present work shows that the behavior in certain solvents of the compatible pair polystyrene (PS) + poly(vinyl methyl ether) (PVME) provides definite evidence of the $|\Delta\chi|$ effect.

Recent work[10] shows PS–PVME to be a compatible (2–3) pair at ordinary temperatures, and consistent with this, a GLC study[11] indicates a very small positive χ_{23} value. Thies and collaborators[12] found that the pair PS ($\overline{M}_n \sim 104\,000$–$150\,000$) and PVME ($\overline{M}_n \sim 524\,000$) gave clear solutions when mixed with benzene, toluene, and tetrachloroethene but cloudy solutions with chloroform, dichloromethane, and trichloroethene. Table I shows the χ_{12} and χ_{13} values for the solvents as found by the GLC method at 40 °C. It is apparent that the solutions are either clear or cloudy depending on whether the solvents give small or large values of $|\Delta\chi|$. We have calculated the spinodals for these systems, using $\chi_{23} = 0$ and with the χ_{12} and χ_{13} values found in the table. When chloroform, dichloromethane, and trichloroethene are the solvents, one predicts very large closed two-phase regions, so that although the polymers are compatible, the addition of a few percent of these solvents brings about incompatibility. On the other hand, when toluene and tetrachloroethene are the solvents, compatibility is predicted for these polymers in solution. For benzene, where the $|\Delta\chi|$ value is larger, one predicts a small closed two-phase region, which is not found experimentally and which vanished when χ_{12} was made slightly negative. It is evident that the theory, together with the GLC interaction parameters, gives good qualitative results. One aspect, however, of the observations of Thies and collaborators is inconsistent with this explanation. Whereas clear films are cast from the homogeneous solutions, the cloudy solutions give films which show a microscopic phase separation. The latter systems should show two-phase regions closed at low φ_1. Thus, for solvent evaporation under quasiequilibrium conditions, the solution should become homogeneous at low φ_1 followed by the formation of a clear film. Presumably the viscosity of these high molecular weight systems at low φ_1 is too high for the solution to clear and the film remains in a metastable phase-separated state, as suggested by Nishi and Kwei.[10]

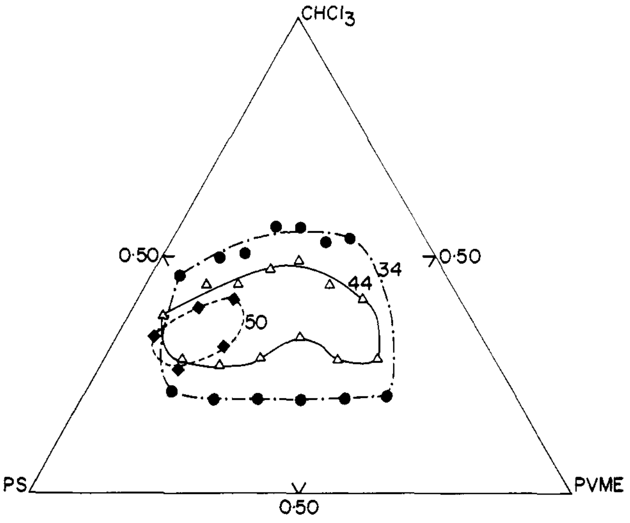

Figure 1. Experimental closed regions of incomplete miscibility for the chloroform/[PS(2100) + PVME(1100)] system at various temperatures in °C. The system is turbid inside the region and clear outside. Solution compositions are in volume fractions.

In the present work, low molecular weights of PS and PVME were taken, respectively 2100 and 11 000. Solutions of different concentrations were made up and the tempera-

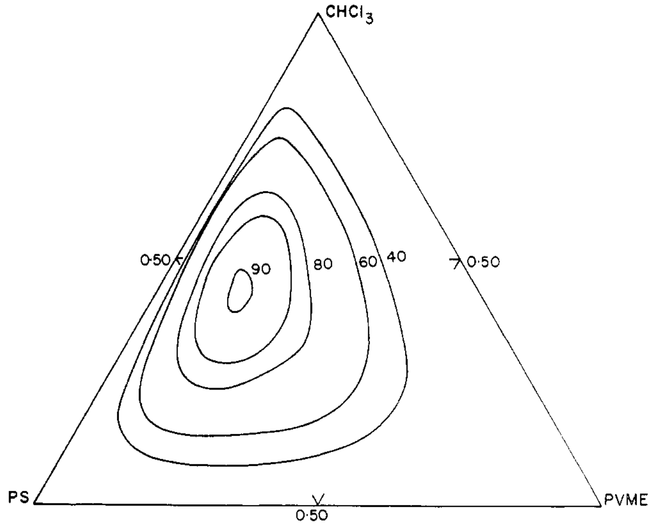

Figure 2. Theoretical spinodals following ref 6 for the experimental chloroform/[PS(2100) + PVME(11 000)] system. The various temperatures are in °C. Values of the polymer-solvent interaction parameters χ_{12} and χ_{13} as in Table I and ref 11, $\chi_{23}' = 0$ and $m_1 = 1$, $m_2 = 25$, $m_3 = 130$, corresponding to the molar volumes of the solvent and polymers. Solution compositions are in volume fractions.

tures corresponding to cloud-points were recorded. Figure 1 gives the cloud-point diagram for chloroform/(PS + PVME) at several temperatures, showing clearly the closed two-phase region predicted from the $|\Delta\chi|$ effect. With increase of temperature, the region disappears, so that above 55 °C the solution is completely homogeneous, i.e., in the three-dimensional (T, composition) space the region becomes a dome closed at high T. (Very similar behavior is found with trichloroethene as solvent instead of chloroform.) This behavior is consistent with the decrease of $|\Delta\chi|$ with increasing temperature, as found in Table I. It is important to note that an increase of miscibility with T cannot be explained if the PS–PVME incompatibility in solution is attributed to χ_{23}. Mixtures of PS and PVME phase separate[10] with increase of T. Thus χ_{23} must increase with T, and would lead to PS–PVME compatibility in solution followed by incompatibility at high T, i.e., the reverse of the experimental behavior. In Figure 1, the closed region at 44 °C seems to have a curious re-entrant boundary. This would indicate that at constant solvent concentration, the (T, polymer composition) cut would be bimodal. Such bimodal cloud-point curves have been found for other polymer–polymer systems in the presence[13] and absence[8] of solvent. However, in the present case the effect is at the limit of the experimental error and needs confirmation. It has not been found with trichloroethene as solvent.

Figure 2 shows the theoretical spinodals calculated following ref 6 with $\chi_{23} = 0$ and with the number of segments in each polymer given by the ratio of its molar volume to that of chloroform. The values of χ_{12} and χ_{13} at 40 °C were as in Table I, and the values at higher temperatures were found using $d\chi_{1i}/dT$ data in ref 11. Although the temperature at which the two-phase region disappears is rather too high (90 °C), it is clear that the predictions are qualitatively correct. The re-entrant boundary at 44 °C is not predicted, but this requires an unconventional free energy–composition relation not explained by current theory.[9] The theoretical treatments in ref 6 and 7 are based on the Flory–Huggins theory where the χ parameters are independent of concentration. Quantitative agreement with experiment should be improved by going ultimately to concentration-dependent parameters.

Table I
Interaction Parameters at 40 °C for Solvent(1)/PS(2) + PVME(3) Systems

Solvent	$\chi_{12}{}^a$	$\chi_{13}{}^a$	$\lvert\Delta\chi\rvert$	$10^3\, d\lvert\Delta\chi\rvert/dT$, deg^{-1} ^{b}
Benzene	0.26	0.15	0.11	−0.6
Toluene	0.19	0.14	0.05	−1.0
Tetrachloroethene	0.36	0.34	0.02	−2.2
Chloroform	0.13	−0.92	1.05	−7.7
Dichloromethane	0.34	−0.39	0.73	−4.8
Trichloroethene	0.19	−0.26	0.45	−4.5

[a] Values from ref 11. [b] From $d\chi_{1i}/dT = -\chi_{1i,H}/T$ as given in ref 11.

Experiments have also been carried out with higher molecular weight fractions of PS. Consistent with ref 6, the closed two-phase region increases in size with increase of molecular weight, and in fact the low solvent concentration part of the region could not be observed due to the viscosity of the solution. Evaporation of these solutions left a cloudy film. However, for the systems with PS of 2100 molecular weight, solvent evaporation produced a clear film. This indicates that in the work of Thies and collaborators the cloudy films cast from chloroform were in a nonequilibrium state brought about by the high viscosity.

It seems likely that the $|\Delta\chi|$ effect will be found of general importance in interpreting polymer incompatibility in solution. The effects of temperature and pressure on phase equilibria could be quite different from those expected from a consideration of χ_{23} alone. For polymers to be compatible, χ_{23} must be negative, or if positive extremely small. This virtually requires some specific interaction between the polymers like the donor–acceptor interaction between PS and PVME. As with that pair, an increase of χ_{23} with T would be expected, leading to a decrease of ternary stability with T. For incompatible polymers, $\chi_{23} > 2$, and we expect $d\chi_{23}/dT < 0$, leading to an increase of stability with T. However, $d|\Delta\chi|/dt$ may be of either sign so that, as in the present case, ternary stability could change with T in a manner opposite to that expected from a consideration of χ_{23}. The pressure dependence of phase equilibria data, e.g., spinodals and binodals, may also be quite different when considering $|\Delta\chi|$ rather than χ_{23}. The latter quantity would be expected to be only slightly pressure dependent, whereas the polymer–solvent interaction parameters, and hence $|\Delta\chi|$, may have considerable pressure dependences. Thus pressure has been found[14] to have a large effect on the compatibility of the polystyrene–poly(dimethylsiloxane) pair in various solvents. If the $|\Delta\chi|$ effect is important, phase relationships in ternary systems should show complex effects unpredictable from χ_{23} which has so far dominated the discussion of polymer–polymer incompatibility in solution.

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(2) Here χ_{23} is the quantity defined by Flory,[3] the 2–3 interaction being between all the r_2 segments of component 2 and r_2 of the r_3 segments in the neighboring component 3 molecule. It is thus proportional to the molecular weight of 2, which in the case of a high polymer may make χ_{23} inconveniently large. The Tompa[5] χ_{23} is normalized to the 2–3 contact between a pair of equal-sized 2 and 3 segments. The choice of what constitutes a segment is arbitrary but can be taken to be a repeat unit of one of the polymers. Much ternary work uses an interaction parameter χ_{23}' which is normalized to contacts between r_1 segments of both components 2 and

3, where r_1 is the number of segments in the solvent molecule. From these definitions, it follows that

$$\frac{\chi_{23}(\text{Flory})}{V_2} = \frac{\chi_{23}'}{V_1} = \frac{\chi_{23}(\text{Tompa})}{v}$$

where V_2, V_1, and v are respectively the molar volumes of polymer 2, solvent 1, and the segment.

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Determination by Gas–Liquid Chromatography of the Polystyrene–Poly(vinyl methyl ether) Interaction

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The gas–liquid chromatography (GLC) or molecular probe technique[1–3] uses a vapor phase component (1) to determine the interaction between two nonvolatile components (2 and 3) in the stationary phase. The method involves obtaining the χ parameters characterizing the interactions of the vapor phase probe with each of the two nonvolatile components, χ_{12} and χ_{13}, and with their mixture, $\chi_{1(23)}$. This last parameter is affected by the interaction between the components themselves, corresponding to χ_{23}, so that

$$\chi_{1(23)} = \varphi_2\chi_{12} + \varphi_3\chi_{13} - \frac{V_1}{V_2}\chi_{23}\varphi_2\varphi_3 \qquad (1)$$

Here the φ are the volume fractions of the polymers in the mixture with the V being molar volumes. The χ_{ij} are the traditional Flory interaction parameters defined by

$$\chi_{ij} = r_i z \Delta w_{ij}/kT \qquad (2)$$

with Δw_{ij} being the interchange energy for a pair of segments. In this definition[1] χ_{ij} is normalized to a unit of size equal to r_i segments, i.e., a molecule of component i. In eq 1 therefore the quantities χ_{12}, χ_{13}, and $V_1\chi_{23}/V_2$ are all normalized to the size of the probe molecule (component 1). It is clear that since component 2 is polymeric, χ_{23} would be an inconveniently large quantity, hence the utility of the probe-normalized parameter $V_1\chi_{23}/V_2$. This has been termed $\chi_{23}^{\dagger}$ in ref 2, but prior to this χ_{23}' in ref 4, and we shall adhere to this terminology in our work, i.e.,

$$\chi_{23}' \equiv V_1\chi_{23}/V_2 \qquad (3)$$

Equation 1 is based on the Flory–Huggins solution thermodynamics. The more recent Prigogine–Flory approach may also be used[1] leading to an evaluation of the X_{ij} parameters for the contact interaction between molecules of types i and j. We believe, however, that the simple Flory–Huggins treatment is sufficient for the present discussion.

The nonvolatile components of the system may interact unfavorably, i.e., χ_{23}' may be positive as in ref 1. In that case the components must be of sufficiently low molecular weight so that the mixture does not phase separate. In other systems, χ_{23}' may be negative as in a high polymer plus plasticizer, e.g., poly(vinyl chloride) + di-n-ocyylphthallate,[2] or as in a pair of compatible high polymers, e.g., polystyrene + (poly(caprolactone).[3] The best-known compatible pair is probably polystyrene + poly(vinyl methyl ether) which forms clear films at ordinary temperatures but which phase separates[5] on raising the temperature. The PS–PVME interaction has already been studied[4] at 30 and 50 °C using essentially the probe method but with a Cahn electrobalance instead of a gas chromatograph to determine the uptake of vapor by the polymer. Large negative values were obtained for $\chi_{23}' \sim -0.4$, consistent with the compatibility of the two polymers. However, while both the PVME and the PS–PVME mixture were in the liquid state, the high molecular weight PS was a glass. There is evidence[6] that a polymer in the glassy state shows a greater affinity for a diluent than it would as a liquid, i.e., the χ_{12} value would be anomalously low. According to eq 1 this would result in a negative displacement of the calculated χ_{23}' value, *suggesting that the value of ref 4 may be too negative.* In the present GLC study of the PS–PVME system we used a PS sample of low molecular weight ($\overline{M}_n \simeq 600$) for which we found $T_g \simeq -30$ °C. Braun and Guillet[7] have given, as a rough guide, the recommendation that GLC thermodynamic measurements should be carried out at temperatures at least 50 °C above T_g. In the present case, a temperature range of 25–55 °C was used. A very small effect associated with a low rate of probe diffusion into the PS was observed near 25 °C, but this disappeared at higher temperature.

Experimental Section

The PS sample was obtained from the Pressure Chemical Co., Pittsburgh, Pa., who give $\overline{M}_n \simeq 600$ and $\overline{M}_w/\overline{M}_n < 1.1$, and the PVME sample (Gantrez M 093) from the GAF Corp., New York, N.Y. An intrinsic viscosity determination in 2-butanone gave[8] $\overline{M}_v = 10\,000$. The gas chromatographic technique and the preparation of the columns are as in ref 1. Two PS + PVME columns were used, corresponding to 0.45:0.55 and 0.625:0.375 proportions by weight. The experimentally measured quantity is the specific retention volume corrected to 0 °C, $V_g°$. This may be converted to an activity coefficient or, as here, directly to the χ_{12}, χ_{13}, and $\chi_{1(23)}$ parameters through eq 5 of ref 1.

Results and Discussion

Values of χ_{12}, χ_{13}, and χ_{23} were obtained at 25, 40, and 55 °C and for certain probes at temperatures up to 100 °C. However, only the results at 40 °C are presented in Table I. The temperature dependence of these parameters yields the enthalpic part of the χ parameter, i.e., χ_H, through the relation

$$\chi_H = -T(\partial\chi/\partial T)_P \qquad (4)$$

Values of χ_H are listed in Table I. At 25 °C, where probe diffusion into the PS was slow, apparently reasonable values of χ_{12} were obtained but values of $\chi_{12,H}$ were clearly too positive. Thus, as T increased so did the fraction of the PS sensed by the probe, resulting in a decrease of the effective value of χ_{12} and an anomalously large $\chi_{12,H}$ value. For the usual dispersion force interaction between probe and polymer, both χ and χ_H would be expected to be positive, particularly when, as here, the probe enters the polymer at effectively infinite dilution. It is noteworthy that the aromatic probes + PVME give unusually small positive values of χ and χ_H. For halogenated hydrocarbon probes (except tetrachloroethene) χ and χ_H are still smaller, or even strongly negative. These values reflect the formation of weak charge transfer complexes in the ether-aromatic[9] and ether-halogenated hydrocarbon[10] systems. Among the polystyrene systems the interaction with chloroform gives a particularly small value of χ and a negative value for χ_H, corresponding to the known formation of a weak hydrogen bond[11] between $CHCl_3$ and an aromatic ring.