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.

Table I
Thermodynamic Parameters for Interactions between Vapor Phase Probes, PS, and PVME

	Probe + PS		Probe + PVME		PS + PVME	
Probe	χ_{12}	$\chi_{12,H}$	χ_{13}	$\chi_{13,H}$	χ_{23}'	
n-C_6	0.97	2.7	1.16	3.7	0.00[a]	−0.10[b]
n-C_7	0.95	2.1	1.15	2.8	0.02	−0.09
n-C_8	0.95	1.9	1.16	2.6	−0.03	
2,2,4-Tetramethylpentane	1.11	3.4	1.53	5.0	−0.01	−0.13
Cyclopentane	0.64	2.4	1.14	4.1	0.08	−0.02
Cyclohexane	0.64	2.5	1.16	4.1	0.01	−0.10
Benzene	0.26	0.8	0.15	0.6	0.12	0.06
Toluene	0.19	0.6	0.14	0.3	0.11	0.07
Isopropyl ether	0.78	2.4	0.76	3.4	0.03	−0.08
p-Dioxane	0.43	0.2	0.20	−0.2	0.11	0.00
Propyl acetate	0.52	1.0	0.25	0.6	0.06	−0.04
Acetone	1.08	2.1	0.75	1.8	0.28	0.25
2-Butanone	0.84	0.8	0.50	0.6	0.18	0.03
Isopropyl alcohol	2.64	7.7	0.90	2.7	1.36	1.47
Carbon tetrachloride	0.29	1.3	0.06	0.4	0.15	0.01
Chloroform	0.13	−0.2	−0.92	−2.6	0.65	0.53
Dichloromethane	0.34	0.8	−0.39	−0.7	0.30	0.14
Tetrachloroethene	0.36	0.7	0.34	0.0	0.10	0.02
Trichloroethene	0.19	0.1	−0.26	−1.3	0.24	0.06
Fluorobenzene	0.37	1.0	0.00	0.2	0.18	0.07

[a] PS:PVME = 0.45:0.55 by weight. [b] PS:PVME = 0.625:0.375 by weight.

The values of χ_{23}' in Table I, obtained through the use of eq 1, depend slightly on the PS/PVME composition of the column, the χ_{23}' being about 0.1 less positive for the lower PVME concentration. However, the values vary considerably more with the probe. (A small dependence is expected since χ_{23}' is normalized to the probe size, eq 3.) A similar variation of the observed χ_{23}' with probe was found for the poly(vinyl chloride) + di-n-octylphthallate system[2] and for the poly(vinyl chloride) + poly(caprolactone) pair.[3] In those cases the variation was attributed to nonrandom mixing of the probe with the mixed stationary phase, i.e., a preferential interaction of the probe with the polymer of lower χ value. This would result[2] in an effective raising of the value of χ_{23}', i.e., more positive. This effect appears clearly where the difference between χ_{12} and χ_{13} is very large, e.g., for isopropyl alcohol and chloroform probes. Furthermore, the effect is more apparent for larger concentration of the preferred polymer,[2] PVME in this case. Giving most weight to the data for the column with lower PVME concentration, and neglecting anomalously large positive values, χ_{23}' lies in the range −0.1 to 0.1, i.e., considerably smaller than the value of −0.4 found in ref 4. The lower critical solution temperatures[5] (LCST) of PVME + PS systems of different polymer molecular weights provide evidence of very small or negative χ_{23}' values. These were calculated using the Flory–Huggins formula

$$\chi_{23}' \text{ (critical)} = \frac{1}{2}\left[\left(\frac{V_1}{V_2}\right)^{1/2} + \left(\frac{V_1}{V_3}\right)^{1/2}\right]^2 \qquad (5)$$

and are plotted in Figure 1 against the critical temperatures to form a $\chi_{23}'(T)$ plot. (In using eq 1 with hexane as probe, the molar volumes were taken independent of the temperature, i.e., V_2 and V_3 reflect only the different molecular weights. The introduction of a temperature dependence would not change the results greatly and would probably be contrary to the spirit of the Flory–Huggins lattice theory.) Figure 1 indicates that the χ_{23}' are all less than 0.015, i.e., extremely small, and they extrapolate to be slightly negative at 40 °C. Nishi and Kwei[5] present evidence for an upper critical solution temperature occurring in the system at low temperature. If this is the case, χ_{23}' would remain slightly positive. The GLC estimate is consistent with a very small negative or positive χ_{23}'. However, the method is not capable of accurately measuring such small values as are apparently found in this system. Recent work[12a] on phase equilibria in polymer mixtures modifies the Flory–Huggins approach by essentially allowing for a concentration dependence of χ_{23}'. Nevertheless, eq 5 should still give a reasonable approximate value of this interaction parameter, and it appears to be extremely small.

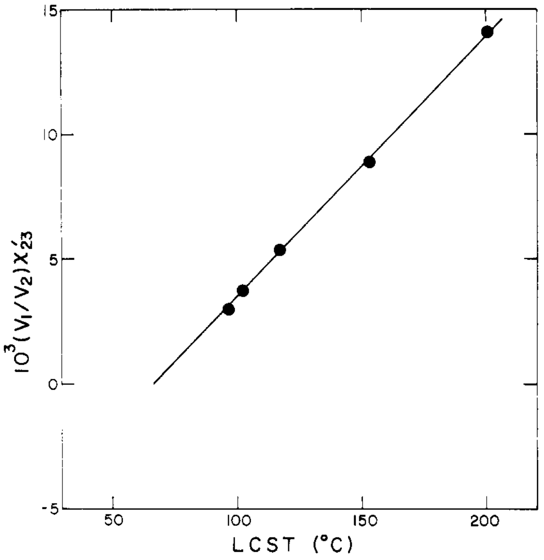

Figure 1. Plot of χ_{23}' for PS–PVME against T using critical values of χ_{23}' from eq 5 and values of the LCST for this system from ref 5; the probe is n-hexane.

The temperature dependence shown in Figure 1 is also of interest in considering the mechanism of the LCST in the PS + PVME system. McMaster[12b] has stressed that any difference in thermal expansion coefficients, i.e., free volume, between the two polymers in a compatible mixture gives a positive contribution to χ_{23}' which increases with temperature, tending toward an LCST. On the other hand, the compatibility of the polymer pair requires a negative or very small positive value of χ_{23}'. Since the usual dispersion force between unlike polymers gives a sizable positive contribution to χ_{23}', compatibility requires a special attractive interaction between the polymers. This in turn would almost certainly be accompanied by a negative enthalpy of interaction, i.e., $\chi_H < 0$, and therefore, following eq 4, χ_{23}' would increase with T. Thus, an LCST in a compatible system would be favored both by the free volume difference between the polymers and by the specific interaction between them. In the present case, the specific interaction presumably occurs between the ether and phenyl groups of the polymer pair, and indeed χ_H for the interaction of benzene and toluene with PVME is small in Table I. Solution calorimetry shows it becomes negative for lower PVME concentration. The thermal expansion coefficients of PS[13] and PVME[14] are respectively 5.72 and 6.45×10^{-4} K^{-1} at 25 °C. Using the Prigogine–Flory theory, the free volume contribution to $d\chi_{23}'/dT$ is found to be less than 1×10^{-5} deg^{-1}. This is small compared with the experimental value of $\sim 10 \times 10^{-5}$ deg^{-1}, found from Figure 1. The LCST in the PS–PVME system seems due to the breaking-up with increasing temperature of the specific interaction between the PS and PVME chains rather than to the free-volume difference between PS and PVME.

A final point concerns the compatibility of PS and PVME in solution. Thies and collaborators[15] found that the mixture of the two polymers with each of the three solvents, benzene, toluene, and tetrachlorethene, gave a one-phase ternary solution, and a clear film is left on evaporating the solvents. On the other hand, when any of three other solvents, chloroform, dichloromethane, or trichloroethene, is used, the solution is phase separated. The turbidity remains on solvent evaporation giving a cloudy film. Recent work[16] has predicted that the compatibility of polymers in solution should reflect not only the interaction between the polymers themselves, i.e., χ_{23}', but also any difference between the interaction of the polymers with the solvent,

$$\Delta\chi = |\chi_{12} - \chi_{13}| \qquad (6)$$

In the present case, the interaction between the polymers is negligible or attractive, indicating that the stable state of the film should be clear. From Table I, $\Delta\chi$ for benzene, toluene, and tetrachloroethene is respectively 0.1, 0.1, and 0.0. However, for chloroform, dichloromethane, and trichloroethene $\Delta\chi$ is respectively 1.2, 0.7, and 0.5, i.e., substantial. These results suggest that the incompatibility of PS and PVME in the second set of solvents is due to the "$\Delta\chi$ effect" which overcomes the normal PS–PVME compatibility. Further work[17] has confirmed this in the chloroform/(PS + PVME) case.

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Aromatic Polyamides by a Direct Polycondensation Reaction

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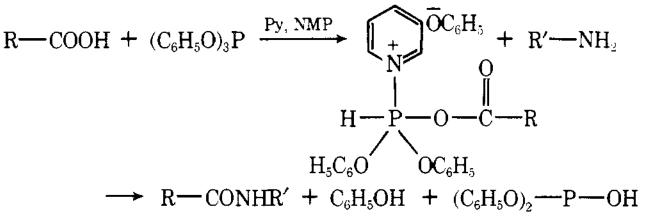
The solution polycondensation of terephthaloyl chloride with *p*-phenylenediamine or the homopolymerization of *p*-thionylaminobenzoyl chloride affords high-modulus, temperature-resistant polyamides.[2] Aromatic polyamides also have been obtained by the direct polycondensation reaction of aromatic dicarboxylic acids with aromatic diamines catalyzed by triphenyl phosphite in NMP–pyridine solution containing lithium chloride at 100 °C.[3] Trimellitic anhydride reacts with 4,4′-diaminodiphenylmethane in the presence of triphenyl phosphite at 200–210 °C in NMP to afford a polyamide–imide.[4] In this work a polyamidation reaction catalyzed by triphenyl phosphite prepared in situ from phenol and phosphorus trichloride in the presence of a large excess of pyridine is described. The proposed mechanism[3] for this polycondensation reaction involves a mixed anhydride.

$$C_6H_5OH + PCl_3 \xrightarrow[25\text{-}30\,^\circ C]{Py} (C_6H_5O)_3P + Py{\cdot}HCl$$



Results and Discussion

Since pyridine is not a good solvent for polyaramides but is necessary for catalyst formation, the polycondensation of *p*-aminobenzoic acid (*p*-ABA) depends both on the concentration of monomer and the amount of pyridine. For a 0.4 M concentration of monomer, the necessary minimum amount of pyridine is 20% (1:4 v/v, pyridine/NMP Table I). Table II shows the effect of monomer concentration in this polycondensation reaction; the highest viscosity being obtained at 0.40 M (11%). Optimum conditions for the polycondensation reaction between isophthalic acid and aromatic diamines were obtained under the same conditions but with 50% pyridine (Table III). In each case the temperature of the reaction was increased slowly from 80–90 (2 h) to 100–105 °C, where it was held for 4 h. Temperatures higher than 100-105 °C did not improve the viscosity.

The positive influence of 3–4% lithium chloride in polycondensation reactions of aromatic polyamides is well-known.[2,3,5,6] In these reactions, low viscosities were obtained without lithium chloride, since early precipitation of the polymer occurred. Polymers 4–7 (Table IV) are lower in molecular weight, since they precipitated from the reaction solution as a result of their rigid structure.

Thus, polyamidation can be carried out simply by forming triphenylphosphite in situ. It is not necessary to isolate this