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3), relative ESCA intensity of PMMA blend films containing various amounts of GM-411 (Suppl. Figure 4), contact angle changes for water droplets at 20 °C on the air-side surface of various siloxane polymer-PMMA blends treated with *n*-hexane (Suppl. Figure 5), observation by SEM of air-side surfaces of blend films containing 1% siloxane polymers GM-411 and MTS-45 before and after *n*-hexane treatement (Suppl. Figure 6), and ESCA of the air-side surface of PMMA blend film containing 1% GM-411 (Suppl. Figure 7) (8 pages). Ordering information is given on any current masthead page.

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Thermodynamic Interaction Parameter χ Determined by Small-Angle X-ray Scattering

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The thermodynamic interaction parameter χ is an important measure for solubility of polymers in solvents[1] and compatibility between different polymers. While osmometry has successfully been employed to determine this parameter in solution, experimental difficulties are encountered in its application to polymer–polymer systems. For such systems a few attempts have been made to apply scattering methods such as light scattering,[2] small-angle X-ray scattering (SAXS),[3] and neutron scattering.[4] In this study we measure χ for polymer–solvent systems by SAXS and compare it with results obtained by other methods, in order to examine the reliability of this technique as a means for determining χ.

According to the Flory–Huggins theory[1] the excess chemical potential $\Delta\mu_1$ per mole of solvent is given by the equation

$$\Delta\mu_1 = RT\{\ln(1-\phi_2) + (1 - V_1/V_2)\phi_2 + \chi\phi_2^2\} \quad (1)$$

where ϕ_2 is the volume fraction of the polymer and V_1 and V_2 are the molar volumes of the solvent and the polymer, respectively. Although originally eq 1 was not meant to apply to dilute solutions, we can reinterpret it as a definition of χ applicable to all concentrations.

A general thermodynamic theorem[5] relates $\Delta\mu_1$ with the scattering law $S_m(0)$ per monomeric unit of the polymer observed at zero scattering angle by the equation

$$S_m^{-1}(0) = -(M_u/RTV_1)\partial\Delta\mu_1/\partial c \quad (2)$$

where M_u is the molar mass of the monomeric unit and c is the mass concentration of the polymer. Therefore integration of $S_m^{-1}(0)$ with respect to c yields $\Delta\mu_1$, which in turn determines χ through eq 1.

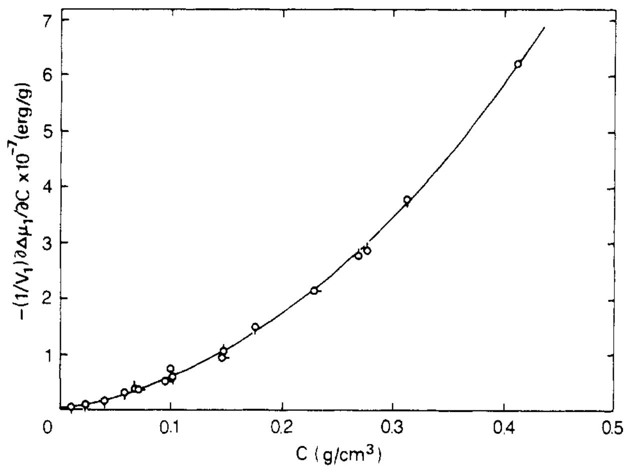

Figure 1. Value of $-(1/V_1)\partial\Delta\mu_1/\partial c$ plotted as a function of concentration c of polystyrene in toluene for molar masses M = 1.75×10^4 (O), 3.7×10^4 (ó), 5.0×10^4 (O-), and 1.1×10^5 (ϙ). The solid curve is used for the calculation of $\Delta\mu_1$.

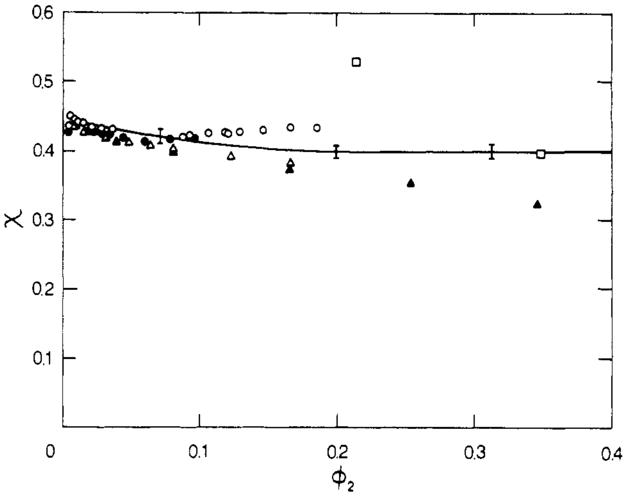

Figure 2. Thermodynamic interaction parameter χ plotted vs. volume fraction ϕ_2 of polystyrene in toluene. The solid curve represents the result by SAXS obtained in this work. The vertical bars indicate the errors in graphical integration. Other symbols show the results observed by other methods: (●) calculated from osmotic pressure measured by Schick et al.[7] for $M = 5.4 \times 10^5$ at 27 °C; (O) data from osmotic pressure measured by Kuwahara et al.[6] for $M = 1.33 \times 10^5$ at 30 °C; (△) obtained from light scattering by Scholte[2] for $M = 1.63 \times 10^5$ at 25 °C; (□) obtained from vapor pressure measured by Bawn et al.[8] for $M = 2.9 \times 10^5$ at 25 °C; (▲) calculated from sedimentation equilibrium measured by Scholte[9] for $M = 1.54 \times 10^5$ at 25 °C.

Monodisperse polystyrenes of four different molar masses were obtained from Pressure Chemical Co. Spectral grade toluene (E. Merk Co.) was dried over calcium hydride and fractionally distilled. SAXS measurements were made at 25.0 °C with a Kratky camera using Cu Kα radiation. The scattering law $S_m(h)$ per monomeric unit ($h = 4\pi(\sin\theta)/\lambda$) was determined by the excess scattered intensity $I(h)$ of the polymer through the relation

$$S_m(h) = (1/KcM_u)(a^2/Pd)I(h)$$

where a is the sample-to-detector distance, d is the sample thickness, and P is the intensity of the primary beam, which was determined by using a secondary standard sample, a Lupolen platelet. The contrast factor K is given by

$$K = i_e(z - \bar{v}_2\rho_e)^2N_A$$

where i_e is the Thomson constant, z is the number of moles of electrons per unit weight of the polymer, $\bar{v}_2$ is the partial

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specific volume of the polymer, and ρ_e is the mole electron density of the solvent. The value of $S_m(0)$ was determined by extrapolation of the plot of $S_m^{-1}(h)$ vs h^2. The value $\bar{v}_2$ of polystyrene ($M = 5.0 \times 10^4$) in toluene at infinite dilution was determined to be 0.919 cm^3/g at 25.0 °C.

Figure 1 shows the plot of $-(1/V_1)\partial\Delta\mu_1/\partial c$ vs. polymer concentration c. Since a slight molar mass dependence was observed at low concentrations ($c \lesssim 0.05$ g/cm^3), the results for the highest molar mass alone are shown within this range. The smooth and unambiguous plot allows graphical integration with respect to c to yield the values of $\Delta\mu_1$ at given concentrations.

Figure 2 shows the interaction parameter χ plotted as a function of the volume fraction ϕ_2. The values determined from osmotic pressure,[6,7] light scattering,[2] vapor pressure,[8] and sedimentation equilibrium[9] are also plotted by circles, open triangles, open squares, and filled triangles, respectively, for purposes of comparison. The SAXS result is in good agreement with those obtained by other methods over a wide concentration range. Therefore we conclude that SAXS can provide reliable estimates of the interaction parameter χ.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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Interaction of Water with Poly(acrylonitrile): Correlation between Clustering, Phase Separation, and the Melting Point

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In studies of the sorption kinetics and equilibria of water in poly(acrylonitrile)[1,2] Stannett et al. found evidence for clustering of water at intermediate levels of water activity through the application of Zimm and Lundberg's clustering criteria[3] to the sorption isotherms of water in glassy poly(acrylonitrile).

Following another approach to the analysis of clustering,[4] an indication of clustering of water molecules in poly(acrylonitrile) was obtained also by observations of decreases of Flory–Huggins interaction parameter values as the activities of the water molecules increase.[2]

In addition, transport studies[4] revealed a diffusion coefficient which decreases with increasing the activity of the water. This is typical for clustering and has been discussed elsewhere.[5,6]

These studies give three indications of clustering of water in glassy poly(acrylonitrile).

In a recent study of the effect of water on the melting point of acrylic polymers[7] Frushour found an initial decrease of the melting point as the water weight fraction increases up to 25% where the melting point stays constant at 185 °C at higher water weight fractions.

In the high water weight fraction range a distinct phase separation was observed, which can predict the constant melting point by the phase rule, since the additional phase reduces the number of degrees of freedom available to the system to zero. A similar behavior has been observed in polymer–diluent systems,[8] where the polymer–diluent interactions become repulsive, with higher Flory–Huggins interaction parameter values.

The weight fraction of 25% water in poly(acrylonitrile)–water mixture corresponds to 1 mol of water per 1 mol of nitrile group.

Additional water will have favorable water–water interactions, will cluster into the new phase, and will not affect the melting point.

Hereby, the effect of water on the melting point of poly(acrylonitrile) gives evidence of phase separation of water in poly(acrylonitrile) above its glass transition, which is correlated with the clustering of water in the glassy poly(acrylonitrile) that has been suggested by Stannet et al. This indicates also that clustering of water in poly(acrylonitrile) originates in the water–polymer intermolecular interactions, is not related uniquely to the glassy state, and cannot serve as evidence for a specific glassy state structure (i.e., existence of microvoids).

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Effect of Pressure on the Magnetic Orientation of the Poly(γ-benzyl L-glutamate) Liquid Crystal As Studied by ^{1}H NMR under High Pressure

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Poly(γ-benzyl L-glutamate) (PBLG), which has long side chains, forms liquid crystals in concentrated solutions in methylene chloride (CH_2Cl_2), where it assumes an α-helical conformation[1-6]. The molecular motion of the CH_2Cl_2 solvent is considerably restricted in the liquid crystal, and consequently its ^{1}H signal splits into a doublet. This splitting provides useful information about the PBLG nematic liquid crystal, and a number of ^{1}H NMR studies have been reported.[7-13] Some of these studies have used temperature as the only experimental variable while pressure was left constant, usually at 1 atm. Such studies sometimes provide a limited interpretation of the results obtained for the liquid crystal. The use of pressure is

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