specific volume of the polymer, and $\rho_e$ 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 $\chi$ plotted as a function of the volume fraction $\phi_2$. 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 $\chi$.

**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($\gamma$-benzyl L-glutamate) Liquid Crystal As Studied by $^1$H NMR under High Pressure

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Poly($\gamma$-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 $\alpha$-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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