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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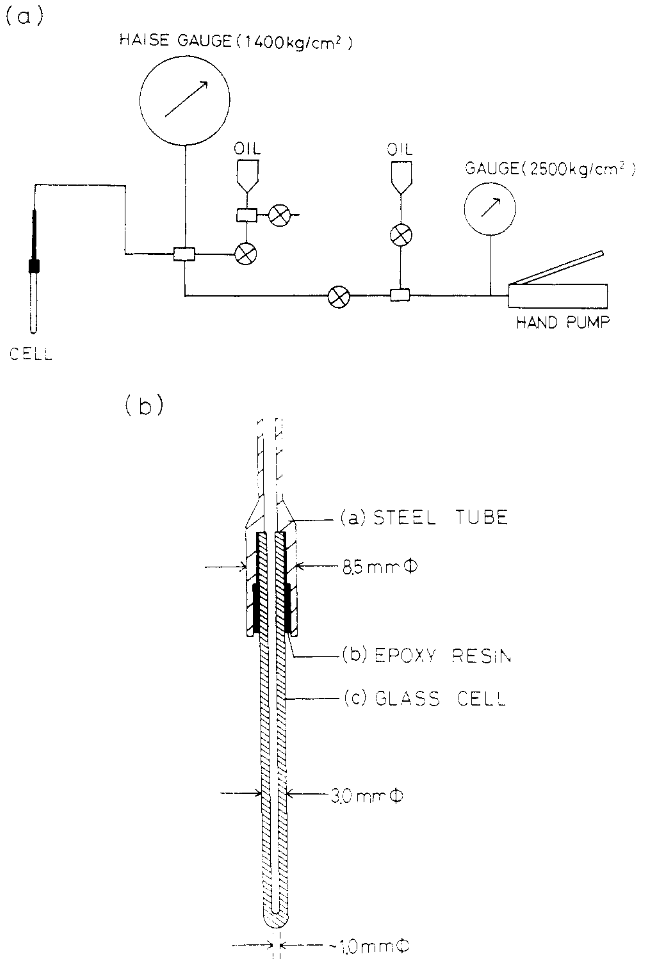

Figure 1. Schematic drawings of the pressure-generating system (a) and the cell (b).

expected to provide another dimension in the investigation of the PBLG liquid crystal because volume changes under pressure have a major effect on molecular motions in the system. In the present note, in order to obtain new information about the magnetic orientation of the PBLG liquid crystal, which is closely related to molecular motion, ^{1}H NMR and volume changes were measured under pressures up to 500 kg/cm^2.

PBLG was prepared from the *N*-carboxyanhydride of γ-benzyl L-glutamate. Its average molecular weight was 3.3×10^4 as determined by intrinsic viscosity.[14] The solvent CH_2Cl_2 was purified by ordinary distillation. The concentration of the polymer was 15 wt % (PBLG/CH_2Cl_2).

The high-pressure apparatus used in this work is schematically illustrated in Figure 1.[15,16] The sample cell was made from a Pyrex capillary tube with 9-mm o.d., 3-mm i.d., and 180-mm length. The outside and inside walls of the capillary were etched with 5% aqueous hydrogen fluoride for 1 h and rinsed to remove dissolved glass. After etching, the capillary was drawn out to form a capillary of 3-mm o.d., 1.0-mm i.d., and 100-mm length. This was etched with 5% aqueous hydrogen fluoride for 3 h and rinsed once again. One edge of the capillary was closed. The capillary was glued to a nonmagnetic stainless steel tube. The glue was made by mixing epoxy resin and hardener in a 1:1 ratio. The pressure in the cell could be changed continuously during the NMR measurement. The sample in the cell was isolated from the pressure-transmitting fluid by placing perfluorodecalin fluid between them. Perfluorodecalin is insoluble in both CH_2Cl_2 and the pressure-transmitting fluid. The sample cell was placed in a tube made of Teflon which prevented the bursting of the glass cell during the NMR measurement. The NMR spectra were taken at 25 °C by using a JEOL PS-100 spectrometer (operating at 100 MHz) equipped with a Fourier transform accessory. Deuterated chloroform was employed as a ^{2}H lock. The number of accumulations was from 10 to 20. The Fourier-transformed spectra contained 8192 data points for a 2000-Hz spectral width and this results in a limit on resolution of 0.25 Hz. The NMR capillary cell was also used for the volume-change experiment. The cell was placed in constant-temperature water bath (25 ± 0.5 °C). The volume change was measured by means of a cathetometer.

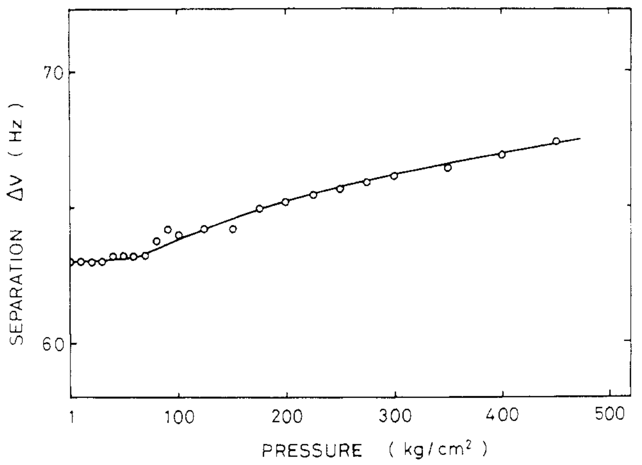

Figure 2. Pressure dependence of doublet separations for CH_2Cl_2 signal in PBLG/CH_2Cl_2 liquid crystalline solution.

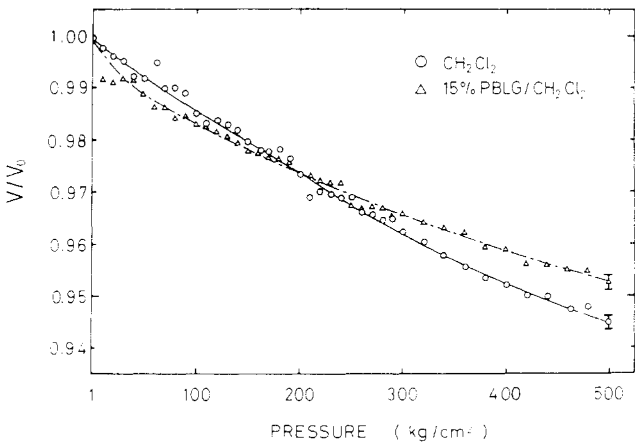

Figure 3. Pressure dependence of volume ratio V/V_0 of PBLG/CH_2Cl_2 liquid crystalline solution and pure CH_2Cl_2 liquid. V_0 is the volume at atmospheric pressure, and V is the volume at a given pressure. The bar indicates experimental error.

Magnetic orientation of the PBLG liquid crystal was achieved in the field of the NMR magnet. The dipolar coupling of the proton pair on each CH_2Cl_2 produces a doublet whose separation ($\Delta\nu$) varies with the orientation of the surrounding PBLGs. Solvent ordering is proportional to liquid crystal order. Thus, the separation is a function of the order parameter of the liquid crystal.[13] The observed $\Delta\nu$ is shown as a function of pressure in Figure 2. It is observed that $\Delta\nu$ increases with increasing pressure. In other words, the order parameter increases with pressure. If we look at this figure in detail, we see that $\Delta\nu$ increases slowly and linearly with pressure up to about 70 kg/cm^2 and increases rapidly above 70 kg/cm^2. Let us consider the origin of such behavior. It is assumed that the slow change of $\Delta\nu$ up to 70 kg/cm^2 arises from the balance between the disturbance to the orientation of CH_2Cl_2 due to the conformational change of the PBLG side chains and the increasing orientation of the CH_2Cl_2 due to the decrease of the intermolecular distance between the α-helical PBLGs.

In addition, in order to better understand this behavior from the macroscopic viewpoint, we measured the volume change of the PBLG liquid crystal and pure CH_2Cl_2 liquid as a function of pressure. The volume ratio V/V_0 (V_0 is the volume at atmospheric pressure, and V is the volume at any given pressure) of PBLG/CH_2Cl_2 liquid crystal and of pure CH_2Cl_2 liquid is shown as a function of pressure in Figure 3. It is shown that the volume ratio of pure CH_2Cl_2 liquid decreases monotonically with an increase in pressure, while the volume ratio of PBLG/CH_2Cl_2 liquid crystal varies abruptly at about 70 kg/cm^2. These ratios clearly change in different ways. From this, it is concluded that the side-chain conformation changes from "extended"[17] to "compact" with increasing pressure up to about 70 kg/cm^2 and that the large change of V/V_0 arises thereby, while above 70 kg/cm^2 the small observed volume change comes from the decrease of the intermolecular distance between the PBLG α-helices. This interpretation parallels that of the change in $\Delta\nu$.

Finally, we suggest that the conformational change of the PBLG side chains and the intermolecular distance are important factors in understanding the pressure effect.

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Communications to the Editor

Sub-Θ Noncollapse of Poly(α-methylstyrene)

Continuing and lively interest in the study of sub-Θ shrinkage and particularly of the "collapse transition" or the "coil–globule transition" of linear, flexible polymers in solution has resulted in a considerable literature from theoretical[1-22] as well as experimental[23-27] work since that interest was sparked more than 30 years ago.[1] To date, the most extensively investigated system of this kind has been that of polystyrene in cyclohexane for temperatures more or less in the range 1–10 °C below the Θ temperature.[29,30,32-34,37] In certain of these studies,[30,32,33,36,37] the transition itself is reported to have been observed. A noteworthy feature common to these sub-Θ studies has been the restrictive requirement that only extremely dilute solutions be employed.

During a recent photon correlation spectroscopy (PCS) study[38] of the size dependence on temperature and molecular weight of four sharp fractions of linear, atactic, high molecular weight samples of poly(α-methylstyrene) in cyclohexane (see Table I here and in ref 39 for additional sample information), it was observed that even though samples were of "normal" dilute solution concentration (Table I and Figure 1) and had been prepared at 50–55 °C, all four maximum concentration solutions remained clear upon cooling to room temperature, exhibiting no evidence of cloudiness, aggregation, or separation. Since room temperature varied between about 25 and 27 °C and the PαMS/cyclohexane Θ temperature is Θ = 34.5 ± 0.5 °C,[40] it was quickly appreciated that PαMS in cyclohexane would lend itself to the study of polymer behavior at sub-Θ temperatures. This communication presents the results of a study of PαMS/cyclohexane sub-Θ behavior.

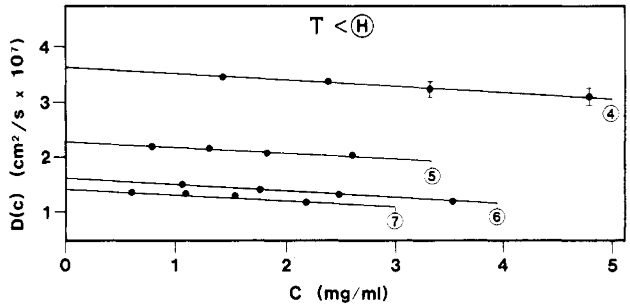

Figure 1. $D(c)$ vs. c.

The focus of the present work was the nature of PαMS coil shrinkage in cyclohexane for solution temperatures 10 °C below Θ. A comparison between PαMS behavior and comparable polystyrene behavior was also of interest. The dependence of coil shrinkage on polymer molecular weight and sample temperature was monitored by PCS measurement of the coil hydrodynamic radius, R_H. The measurement of R_H using PCS is now routine:[41,42] Briefly, polymer z-averaged mutual diffusion coefficients, $D(c)$, were determined from PCS measurements of dilute solutions for temperatures in the range 24.6–27.5 °C and molecular weights in the range 10^5–10^6 using the method of cumulants.[43] Coil self-diffusion coefficients, D_0, were then extracted from least-squares fits to concentration-dependent $D(c)$ data (Figure 1) using the virial expansion

$$D(c) = D_0(1 + k_D c) \qquad (1)$$

with c the polymer concentration and k_D the virial coefficient. Though k_D is not of particular interest here, it is certainly of interest in the more general study, ref 38. R_H

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