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Nuclear Spin Diffusion between Polyurethane Microphases

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ABSTRACT: The rate at which nuclear spin energy diffuses from one spin population to another in a polyurethane was measured by a technique based on the Goldman–Shen experiment. Determination of the spin diffusion constant permitted the diffusion path length to be calculated. The agreement between these results and the interdomain spacing determined by small-angle X-ray diffraction gives strong support to the hypothesis that the two components of a polyurethane's free induction decay correspond to the material's two microphases. Variation of the soft-phase spin–spin relaxation time with pulse spacing showed that the mobility of soft-phase segments depends on their proximity to the interface region.

I. Introduction

Recent studies[1,2] have shown that several polyurethanes exhibit a two-component NMR free-induction decay (FID). In the past such behavior by a polymer was associated with the presence of both crystalline and amorphous phases.[3,4] These systems, however, show no evidence of a crystalline phase by wide-angle X-ray diffraction. The two components were interpreted to correspond to the hard and soft domains of a system which had undergone microphase separation. The rigid segments comprising the hard domains give rise to a fast decay while the flexible segments comprising the soft domains give rise to a slow exponential decay. Before confidence can be placed in this interpretation, other explanations for a two-component decay must be carefully considered.

The most probable alternative explanation for a two-component decay is that proposed by Resing in his studies of molecules adsorbed on surfaces.[5] He discusses how a very broad distribution of correlation times can give rise to a two-component decay without the system existing in two distinct phases. Another explanation is that cross correlation effects in a segment moving anisotropically can cause a nonexponential decay.[6,7] To eliminate these two alternatives we have performed a Goldman–Shen[8] experiment first suggested for this purpose by Resing.

If two distinct spin populations have different spin temperatures, they will tend to approach a common spin temperature by the mechanism of spin diffusion. The Goldman–Shen experiment is a technique to put the separate spin systems at different temperatures and then sample them as a function of time so that their approach to equilibrium can be followed. By measuring the diffusion time and calculating the diffusion constant from relaxation data, the diffusion path length can be determined. Of course, for a system with a broad distribution of correlation times or one exhibiting cross-correlation effects, there is only one spin population so the equilibration time is much faster. Experiments reported in this study show that the spin populations having different relaxation rates are separated in space by a distance compatible with previous measurements of interdomain spacing made by the small-angle X-ray scattering technique (SAXS).

The effects of spin diffusion have been seen before in polymeric systems by measurements of the spin–lattice relaxation time in the rotating frame[9] and in biological and polymeric systems by spin–lattice relaxation time (T_1) measurements.[10-13] The time scale for diffusion in each of these experiments was fixed by the corresponding relaxation parameter. The advantage of the Goldman–Shen experiment is that the time for spin diffusion can be arbitrarily varied, and if this time is much less than T_1, the analysis is straightforward.

II. Experimental Section

a. Instrumentation and Signal Analysis. The FID measurements were made on a Bruker SXP broad-band spectrometer operating at 90 MHz in the phase-sensitive detection mode. The external field was that imposed by a Varian V-3800-1 high-resolution magnet equipped with a flux stabilizer. The FID signals were captured by a Biomation 610 transient recorder and stored by a Digital Equipment Corp. PDP-11/10 computer. Several decays, each containing 256 data points, were averaged and then decomposed by means of nonlinear least-squares regression into a fast Gaussian or exponential component and a slow exponential component associated with the rigid and mobile phases, respectively. Care was taken to minimize the effects of field inhomogeneities and field drift. All measurements were performed at 25 °C.

b. Materials. EN-4, EN-7, and EN-8 are cross-linked polyurethanes manufactured by Conap Co. Each has polybutadiene soft segments, 2,4-toluene diisocyanate based hard segments with 2-ethyl-1,3-hexanediol, and bis(2-hydroxypropyl)aniline curing agents. EN-4 uses a mercury oleate catalyst while EN-7 and EN-8 use varying amounts of ferric acetylacetonate as a catalyst. The formulation of these compounds has been discussed in the literature.[14] The other type of polyurethane investigated is designated Adiprene L-100/MOCA. It is made from a 2,4-toluene diisocyanate end-capped ether (polyoxy-1,4-butylene) with methylenebis(*o*-chloroaniline) (MOCA) as a curing agent. Samples of Adiprene L-100/MOCA cured at 298 and 347 K were investigated.

The EN series gives the cleanest decomposition into fast and slow components of any polyurethane we have investigated while Adiprene L-100/MOCA gives a FID which, as measured by the square root of the mean squared deviation, is the most difficult to fit accurately. It is interesting to note that the SAXS maximum is more distinct for the EN series than for the Adiprene L-100/MOCA. The ease of the FID decomposition and the sharpness of the SAXS maximum both suggest that the domains of the EN series are more sharply defined. A Gaussian/exponential fit is superior to an exponential/exponential fit for the EN series while an exponential/exponential fit is slightly better

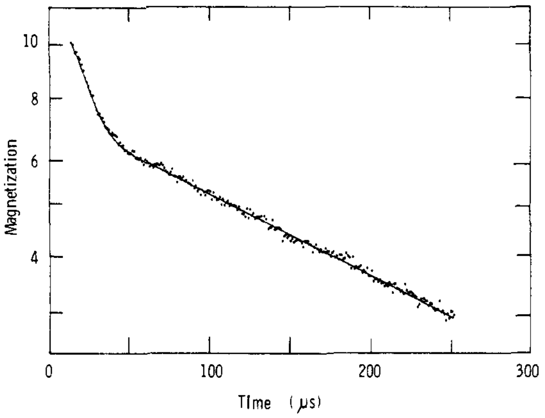

Figure 1. The FID of EN-7 averaged eight times. The solid line is a nonlinear least-squares fit of the points using a fast Gaussian component and a flow exponential component.

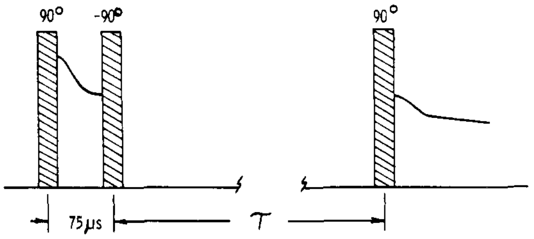

Figure 2. The pulse sequence used for the Goldman-Shen experiment. The time during which the spin energy diffuses to reach an internal equilibrium is τ.

than a Gaussian/exponential for the Adiprene L-100/MOCA material.

III. Results and Discussion

a. The Goldman-Shen Experiment. The FID of EN-7 is shown in Figure 1. The decay was fit by a fast Gaussian component corresponding to the rigid phase and a slow exponential component corresponding to the mobile phase. The Goldman-Shen experiment requires that the decay rates be sufficiently different so that at some point in the FID the spins in the rigid phase are completely random while the mobile phase spins have retained a significant portion of their magnetization. Figure 1 demonstrates that this condition is satisfied in the region from 50 to 100 μs. The FID's of the other EN materials and the Adiprene L-100/MOCA materials are very similar in appearance to Figure 1.

Figure 2 shows how the Goldman-Shen experiment is performed. First, a 90° pulse is used to tip the magnetization along the y axis. By waiting 75 μs the rigid phase spins are randomized while the mobile phase spins retain most of their magnetization. The magnetization is then returned to the z axis by means of a -90° pulse. The rigid phase spins are now randomized in the xz plane so their spin temperature is infinite while the mobile phase spins are still close to their original room temperature distribution. Obviously the system is not at equilibrium with itself or its surroundings.

Two approaches to equilibrium are followed. First the two spin populations approach an internal equilibrium. To do this they exchange energy by means of mutual spin flips. This is an energy conserving or spin-spin relaxation time (T_2) type of process and is termed spin diffusion.[15] Note that the spins of the different populations do not physically change places, only energy is transferred between them. Once the two spin systems reach an internal equilibrium, the system will not be in equilibrium with its surroundings because the total magnetization will be less than that at the start of the experiment. The buildup to an equilibrium amount of magnetization involves the exchange of energy between the spin and lattice systems and is a T_1 or spin-lattice process.[15] The polyurethanes of this study exhibited spin-lattice relaxation times of several hundred milliseconds at room temperature. These times are an order of magnitude longer than the time for magnetization equilibration. For the sake of mathematical simplicity, we shall assume that the contribution from T_1 effects is negligible during the equilibration process. A T_1 long compared to the spin-diffusion time is consistent with the observation of only one T_1 for these materials.

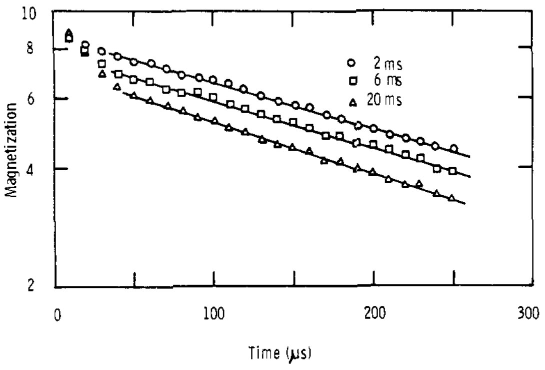

Figure 3. The FID's of EN-7 for various times τ of the Goldman-Shen experiment.

To monitor the spin diffusion process, another 90° pulse is applied at various times, τ, after the -90° pulse. The resultant FID's are shown in Figure 3. For very short τ the spin energy has diffused very little, and the FID is nearly all contributed by the soft phase which results in a slow exponential decay. After 20 ms a significant amount of energy exchange has taken place and the fast decay from the rigid phase is evident. This contribution is not from T_1 processes because the magnitude of the total magnetization has not grown significantly. It is obvious that the fast component has increased at the expense of the slow component.

If the two-component decay were due to a broad distribution of correlation times in a one-phase material or due to cross-correlation effects of an anisotropically moving segment, we would expect the recovery of the fast decaying component to be comparable to the system's longest correlation time. On the basis of the second moment of the fast-decaying component (1) this is calculated to be approximately 2×10^{-5} s. The fact that it takes three orders of magnitude longer for the fast-decaying magnetization to recover is strong evidence that the spins corresponding to the two components are distinct and separated in space by some distance over which the spin energy must diffuse. In the following section we will show that the buildup of hard-phase magnetization can be accurately described by a diffusional model and that the path length of diffusion is consistent with SAXS studies.

b. Diffusion Model. Figure 4 shows the buildup of rigid-phase magnetization as a function of the square root of the diffusion time, τ. To fit the experimental points a lamellar configuration of rigid and mobile phases was chosen. Since spin diffusion is a T_2 process, it is expected to occur much faster in the rigid phase than in the mobile phase. This comparison will be made quantitative in the next section. In the following calculations we will assume that the rate of diffusion is controlled by the mobile phase and that equilibrium within the rigid phase is instantaneous. Thus, the geometry of the rigid phase is irrelevant and a coplanar model is equivalent to a rigid sphere surrounded by a uniform layer of mobile material in the

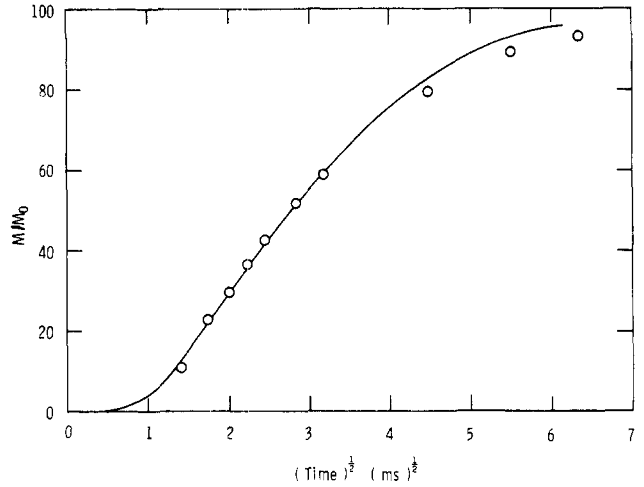

Figure 4. Recovery of the rigid-phase magnetization as a function of diffusion time. The solid line is a theoretical fit of the data using a planar model.

limit that the rigid sphere becomes infinitely large compared to the layer thickness.

We make the assumption that the spin energy diffuses isotropically within the mobile phase. This contrasts to an earlier study when diffusion was assumed to be limited to flips along the chain axis.[13] We believe that isotropic diffusion is reasonable because the inter- and intramolecular contributions to the line width of typical polymers are comparable[16] and these same interactions are responsible for spin diffusion.

The diffusion of spin from one phase to the other with the condition that initially all the spin energy be contained in the mobile phase was calculated by a finite difference method using 100 divisions.[17] The quantity $(l^2/D)^{1/2}$ was considered an adjustable parameter where l is the diffusion distance and D is the diffusion constant. The results of the calculation are shown in Figure 4. We believe that the excellent fit supports the spin diffusion model. Note that the recovery does not naturally pass through the origin. This is due to the preparation procedure lasting 75 μs. During this time some spin energy was diffusing from the mobile to the partially depleted rigid phase. This creates a depletion layer modeled by curves, a, b, and c of Figure 5. It was found that the shape of the magnetization recovery curve was not sensitive to the exact model so curve (a) was chosen for the remaining calculations.

C. Domain Spacing. In the previous section the recovery of the magnetization was shown to be accurately described by a diffusional process. The experimental results were fit by using the adjustable parameter $(l^2/D)^{1/2}$. In this section we derive an expression for D in terms of relaxation parameter and thus obtain the diffusion path length l which can be related to the interdomain spacing.

The three-dimensional diffusion constant $D(r_{ij})$ for a system of spins separated by a distance r_{ij} can be written[18]

$$D(r_{ij}) = W(r_{ij})r_{ij}^2/6 \tag{1}$$

where $W(r_{ij})$ is the probability of a spin flip for two adjacent spins. If $\omega_0\tau_c \gg 1$, where ω_0 is the Larmor precession velocity and τ_c is the molecular correlation time, then Kalk and Brendson[11] have shown that

$$W(r_{ij}) = 2/9T_2(r_{ij}) \tag{2}$$

The r dependence of T_2 can be explicitly displayed as

$$1/T_2(r_{ij}) = C/r_{ij}^6 \tag{3}$$

where C is a constant depending on the spin quantum numbers and gyromagnetic ratios of the nuclei. Combining eq 1, 2, and 3 we get

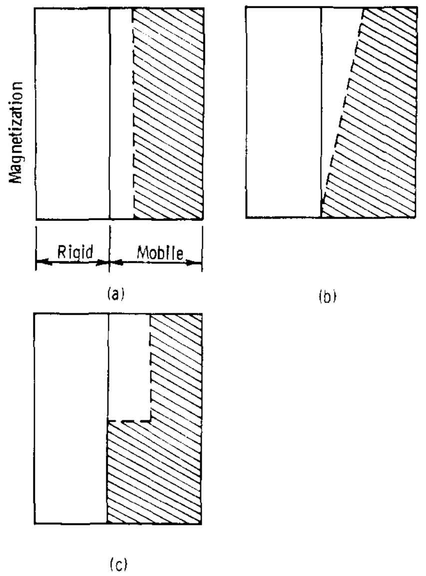

Figure 5. Several models of the depletion layer which were tested to fit the initial portion of the magnetization recovery. Model (a) was used to fit the data shown in Figure 4.

$$D(r_{ij}) = C/6r_{ij}^4 \tag{4}$$

which can now be integrated over space. The integration is performed from $2r_0$, where r_0 is the radius of the hydrogen atom, to infinity. The result is

$$D = \pi\rho C/3r_0 \tag{5}$$

where ρ is the density of spins which was assumed to be uniform and isotropic.

To evaluate the parameter ρ and C the same integration is performed on eq 3 to obtain

$$1/T_2 = \pi\rho C/6r_0^3 \tag{6}$$

This allows D to be expressed as

$$D = 2r_0^2/T_2 \tag{7}$$

This result supports our assumption made in the previous section that spin diffusion in the mobile phase with a long T_2 is much slower than spin diffusion in the rigid phase with its short T_2.

One can now use eq 7 to calculate the spin-diffusion constant of the polyurethanes. The hydrogen van der Waals radius of 1.17 Å was used for r_0[19] while T_2 is the decay time of the slowly decaying components. Once D is known the magnetization recovery rate shown in Figure 4 can be used to calculate a path length for diffusion. The diffusion constants and path lengths are shown in Table I for the several polyurethanes of this study.

SAXS gives an average periodicity of the microphase structure, that is, the average distance between the centers of adjacent hard domains. To compare our results with SAXS we must convert the spin-diffusion path length into an interdomain spacing. The hard spheres are assumed to be covered with a uniform layer of soft material of thickness l as shown in Figure 6. To obtain the hard-shell diameter, one sets the ratio of the number of hard- and soft-phase hydrogens equal to the ratio of their corresponding FID components. Knowing the molecular formula of each phase and estimating each phase's density,

Table I
Diffusion Lengths and Domain Spacings for Several Polymers

	cure, K	diffusion length, Å	domain spacing by NMR, Å	domain spacing by SAXS, Å
EN-4		11.2	83	
EN-7		11.4	84	93 ± 1[a]
EN-8		12.3	91	
Adiprene L-100/MOCA	298	9.7	98	135 ± 15[b]
Adiprene L-100/MOCA	347	10.9	96	

[a] R. R. Lagasse, *J. Appl. Polym. Sci.*, **21**, 2489 (1977). [b] R. R. Lagasse, Sandia Laboratories Report SAND77-0822, October 1977.

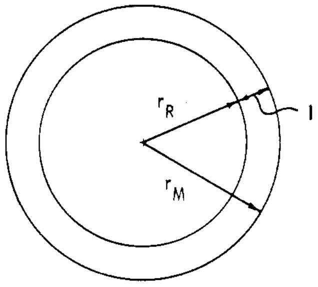

Figure 6. The three-dimensional domain model used to calculate the interdomain spacing from the spin-diffusion distance.

one can convert the hydrogen ratio into a volume ratio and hence solve for the ratio of sphere radii. From the ratio of the radii and their difference, *l*, one can solve for each radius. Twice the outer radius of the soft sphere is taken to be equal to the interdomain spacings shown in Table I. We believe that agreement between NMR and SAXS is excellent considering the nature of the experiment and calculations.

The weakest point in the calculation of an interdomain spacing from the Goldman–Shen experiment is the assumption that diffusion is uniformly isotropic. It is obvious that the hydrogen nuclei are not distributed uniformly throughout space. We should consider a sum of inter- and intramolecular distribution functions. The intermolecular distribution function may be liquid-like, that is, have a maximum at twice the van der Waals radius and a minimum at three times the van der Waals radius. The intramolecular distribution would vary sharply with distance as the path length to nearest and next nearest neighbors would be identical for similar chain conformations. In the absence of detailed information for such a complex material as a polyurethane, however, the assumption of a uniform distribution appears to be reasonable.

In the course of the experiment, it was noticed that the decay rate or $1/T_2$ of the soft phase varied with τ. The results for EN-7 are shown in Figure 7. We believe that this difference is real and may be related to domain inhomogeneity or interface effects. Consider the relative spin population vs. position during the course of an experiment as shown in Figure 8. For small τ the aligned spins are part of the mobile phase and because of the depletion layer effect reside predominantly in the center of the domain. As τ increases the spin population begins to equilibrate until for very long times the spin population is uniform across the domain. Thus, for short τ we see spins predominantly in the center of the domain while for long τ the spins are distributed uniformly across the domain. The variation of T_2 with τ shows that the motion of segments in the center of the soft domain is less restricted than the motion of the average soft-phase segment. This effect may be due to the mixing of segments at the interface or due to the hard phase acting as a tie-down point for soft segments close to the interface.

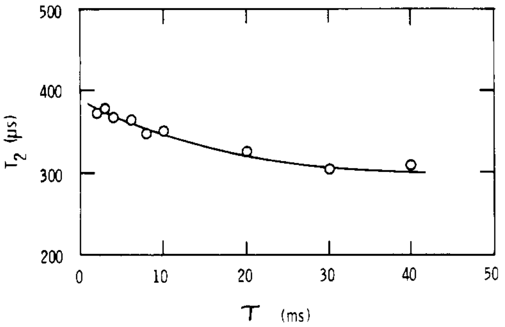

Figure 7. Variation of the mobile phase spin–spin relaxation time with the spin-diffusion time.

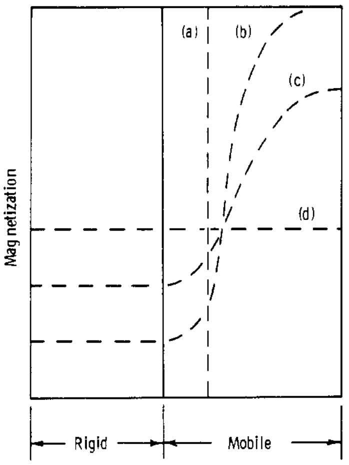

Figure 8. Diagram of the magnetization intensity vs. position for various times τ: (a) $\tau = 0$; (d) $\tau = \infty$. As τ increases the spin magnetization near the interface region increases.

IV. Conclusion

Although the agreement between the interdomain spacing calculated from the Goldman–Shen experiment and SAXS is quite good, the complexity of the experimental procedure and interpretation of the results mean that the technique probably cannot compete with SAXS in the determination of interdomain spacings on a routine basis. The results of this study strongly support the claim that the fast and slow components correspond to two physically distinct spin systems in a phase-separated polyurethane.

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Concentration Dependence of Coil Dimensions by Means of Exclusion Chromatography

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ABSTRACT: Decrease of the effective coil dimensions $\langle r^2 \rangle$ with increasing polymer volume fraction ϕ_2 has been measured by gel permeation chromatography for polystyrene standards ($2 < M \times 10^{-3} < 2500$) in toluene. Good correlation is found with the limiting equation $\langle r^2(\phi_2) \rangle / \langle r^2(0) \rangle \sim 1 - 0.043 N^{0.72} \phi_2$ ($N >> 1$, $\phi_2 << 1$) based on computer simulation recently performed by De Vos and Bellemans.

The mode of the gel permeation chromatogram (PEV) is known to be shifted toward a larger elution volume when the concentration of injected solution is increased; the effect is more pronounced, the better the solvent, the higher the molecular weight of the sample or the narrower its molecular weight distribution.[1-7]

Many attempts have been made to isolate the various contributions to such a retardation behavior. Column overloading (secondary exclusion) and adsorption on the support may safely be ruled out. A viscosity effect, such as the so-called viscous fingering, cannot explain alone the mode dependency on concentration.[8] However, the observed trend might well be a consequence of the enhanced penetrability within the internal volume of the gel for the macromolecules whose effective dimensions in solution are a decreasing function of concentration.[9,10]

Recently, Janča et al.[11] made a thorough examination of the problem but failed to reconcile theory and experimental data on a quantitative basis. They assumed for the elution curves a Gaussian analytical form in conjunction with a linear calibration curve. However, the latter appears to be nonlinear in the interval considered by these authors, moreover, departure from a Gaussian profile, either symmetrical or asymmetrical, might also be a cause of the observed discrepancy.

The problem of the effective dimensions of the polymer molecule will be considered below in conjunction with some theoretical values computed by De Vos and Bellemans[12] for statistical coils in athermal solution.

Experimental Section

Procedure. A Waters Associates Chromatograph Model 200 has been equipped with five 4-ft Styragel columns (10^5, 10^5, 4×10^4, 10^4, 10^3) and operated at room temperature with toluene as eluent. Flow rate was kept at 1 mL/min; injection time interval was 120 s.

A water-jacketted syphon (volume = 2.41 mL) has been built to ensure better temperature control and to prevent solvent evaporation. Data were obtained in numercial form, by means of an analog/digital converter and of a serializer coupled to a chronoscope unit (Viscomatic, Fica), for further processing on a Hewlett-Packard 9830 A calculator. Fourier transform analysis has been applied to the elution curve to determine the mode position with a reliability of ±0.02 mL between two successive injections of the same elution. Solution concentration range was kept between 0.2 and 2.0 mg/g.

Average molecular weights of polystyrene standards purchased by Waters Associates (W) or Pressure Chemicals Inc. (PC) or synthetized in the laboratory (L) are given in Table I.

The calibration curve has been established at infinite dilution by appropriate extrapolation of the mode of the chromatograms, as discussed below. No corrections have been made for dispersion, assuming negligible influence of the latter on the concentration dependence of the mode.

Data given in Table I display the good fit of the results when a linear dependence is assumed for the mode of the elution curve vs. concentration of the injected solution. The error on the extrapolation eventually arising from this assumption amounts to less than 0.15 count for the PS2300 sample and becomes vanishingly small with decreasing molecular weight. The PEV increments refer to the situation prevailing at the top of the column set and will therefore be termed $[\Delta\mathrm{PEV}/\Delta C]_{\mathrm{IN}}$.

But on passage through the columns, the solution is continuously diluted. This will in turn cause the PEV values to be less shifted than expected solely on a molecular weight basis at equal injected concentration. The ratio of the peak height to the zeroth order moment of the chromatogram could be used as a rough estimate to calculate a relative dilution factor Q (Table I). In this way, one obtains the elution volume increments $[\Delta\mathrm{PEV}/\Delta C]_{\mathrm{OUT}}$ more appropriate to the conditions prevailing at the end of the column set. Accordingly, the proper average value should be comprised somewhere between the two limiting increments, i.e., $[\Delta\mathrm{PEV}/\Delta C]_{\mathrm{IN}}$ and $[\Delta\mathrm{PEV}/\Delta C]_{\mathrm{OUT}}$.

A linear relationship has also been assumed for the logarithm of the hydrodynamic volume V_{h} vs. concentration; this dependence has been calculated on a semiempirical basis proposed by Rudin,[9] using the eq

$$V_{\mathrm{h}} = [\eta]M = 11.6 \times 10^{-3}\ \mathrm{M}^{1.72} \qquad (1)$$

for the magnitude of V_{h} at infinite dilution.

Correlation of V_{h} with both PEV increments discussed above is given in Figure 1 and appears satisfactory in either case. Recently, the contraction of a N segment coil with increasing volume fraction of the polymer in an athermal solution has been evaluated by De Vos and Bellemans[12] in terms of the ratio of the

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