The average separation between the two manifolds is found to be 104 cm$^{-1}$ if the barrier splitting for the proton exchange of the parent compound is taken as the reported 69 cm$^{-1}$. This value is in good agreement with the experimentally assigned value of 92 cm$^{-1}$.

More interesting is that in this system the exchange between the minimum energy tautomers is not given by the splitting between the two manifolds. Also, in this case the proton oscillates anharmonically between the structures of minimum energy. The time evolution of the system is calculated by expanding the initial state in terms of the stationary states and using the coefficients of this expansion to calculate the expectation value of the proton's position as a function of time. When this value is calculated, one finds that only the transition moments between the $A_{1g}$ and $A_{2u}$

levels contribute to the time dependent part. However, only the coefficients of the states belonging to the same manifold contribute significantly to the amplitude of the oscillation, whose frequency corresponds to a separation of 23 cm$^{-1}$. This amounts to a reduction by more than one half compared to the rate of exchange in the parent compound, 9-HPLN, in line with previous claims that the proton exchange is controlled by the rotation of the methyl group.

This effect may also explain the at least tenfold increase in the rate of vibrational relaxation when the methyl group is attached in the symmetric position of the parent compound. This increase may be due to an increase in the density of states in the manifold, which would favor the transfer of energy to the phonons in the cryogenic matrix.

# Transport of Small Molecules in Swollen Polymer Beads[†]

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*Contribution from the Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104, and the Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078. Received December 11, 1985*

**Abstract:** Pulsed-field-gradient spin-echo (PGSE) NMR experiments have been used to determine self-diffusion coefficients of toluene in swollen cross-linked polystyrene beads with 5.7–40% cross-linking. Self-diffusion coefficients were also determined for toluene in linear polystyrene solutions over a concentration range of 0.1–0.7 weight fraction of polymer. The swelling ratios of the cross-linked beads were used to determine the concentration of toluene in the beads by assuming that the increase in volume is due only to solvent uptake. A comparison of solvent diffusion in the cross-linked and the non-cross-linked systems at similar concentrations shows remarkably close agreement. These results suggest that the diffusion rate in the cross-linked polymer beads is not significantly affected by the presence of cross-links and is mainly determined by the concentration of solvent in the bead.

The use of cross-linked polymer beads is widespread in the chemical industry. They are used as supports for catalysts, ion exchange resins, solid-phase peptide syntheses, and packings for chromatography columns. In all of these applications, efficiency may be limited by the rate of transport of low molecular weight species through the polymer matrix. Previous studies have investigated reaction rates of a number of heterogeneous reactions involving polymer-bound catalysts.[1-3] By varying polymer bead size and mixing rate it was shown that in many cases the reaction rate was limited by the rate of transport of reactants in the polymer matrix.

Although there have been a significant number of studies of the dynamics of the polymer chain in these systems, very little is known about the motions of small molecules embedded in the polymer matrix. In some cases the state of the solvent can be probed with NMR since separate resonances for solvent species inside and outside of a bead may be observed in high-resolution proton[4,5] and carbon-13 NMR spectra.[6,7] Carbon-13 spin–lattice relaxation time measurements have been used to probe differences in the rotational mobility of the solvent, and, in favorable cases, these differences can be used to estimate the exchange rate in and out of the beads.[8]

In the present study, we report direct measurement of the self-diffusion coefficients of solvent molecules inside swollen cross-linked polymer beads. This is the first time that such measurements inside cross-linked polymer beads have been reported, although diffusion measurements of solvents in other microporous media, particularly zeolites, have been published

previously.[9-12] The method used to probe the self-diffusion behavior of the solvent is the pulsed-field-gradient spin-echo (PGSE) NMR method. The advantage of this method is that the distance scale over which the experiment is sensitive is much less than the size of the polymer beads used. Therefore exchange between adsorbed and interstitial solvent makes a minimal contribution to the experimental results. A detailed theoretical treatment of signal attenuation in the PGSE NMR experiment as a function of diffusion, relaxation, exchange rates, and particle size in heterogeneous systems has been reported.[9-11] A general solution of it is not possible, but solutions for some limiting conditions are available. A comparison of the results of NMR studies with diffusion coefficients determined by sorption techniques[11-12] and neutron scattering[13] indicates that diffusion in the zeolite crystals can be readily determined with the PGSE technique.

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The system of interest in this study is polystyrene (PS) cross-linked with divinylbenzene and saturated with toluene. We chose PS because it is often used as a catalyst support and in the Merrifield synthesis of polypeptides. Considerable work has been performed in the characterization of cross-linked PS systems. Toluene was chosen as a solvent because it is a good solvent for polystyrene and swells the polymer extensively. In addition, we compare our results with self-diffusion measurements on non-cross-linked polystyrene/toluene solutions of similar concentration to examine the possible effects of the solvent self-diffusion.

## Experimental Section

The cross-linked polymer beads were suspension polymerized with varying ratios of styrene/divinylbenzene (DVB). The details of their syntheses are described elsewhere.[2] The percent cross-linking is taken as the percent DVB used in the feed. The beads used were all –60+100 mesh before swelling, corresponding to diameters between 150 and 250 μm. The swell ratio is the ratio of the volume of the fully swollen beads to that of the dry bead. Swell ratios were determined by placing the beads in a graduated cylinder with excess solvent and noting the initial and final volumes of the beads. Some of the swell ratios were also determined by measuring the diameter of the beads before and after swelling under an optical microscope equipped with a micrometer. The results of the two methods were in close agreement. Reagent-grade toluene was used as received from Aldrich. The samples for NMR analysis were prepared in 10-mm tubes by adding the cross-linked beads to the tube followed by excess solvent, about twice the volume of the beads. The samples were allowed to equilibrate for at least 2 days to achieve uniform solvent uptake. Air bubbles were removed from the samples by shaking and most of the interstitial solvent was squeezed out of the samples with a vortex plug. Some excess solvent was allowed to remain in the tube above the plug, ensuring that the beads remained saturated during the long-term experiments. Linear polystyrene (viscosity average molecular weight of 280 000) was used as received from the DOW Chemical Co. These samples were prepared by adding weighed amounts of PS and solvent to 5-mm NMR tubes. The tubes were then sealed and placed in a heating block for several days until homogeneity was achieved.

All diffusion measurements were made at ambient temperature (23 °C) with a JEOL-FX90Q NMR spectrometer operating at 90 MHz for protons. Typical spectra were taken with a 2000-Hz window, 4096 points, and a pulse delay of 8 s. The number of scans ranged from 24 to 500 depending on the concentration and gradient pulse length. The pulsed-gradient spin-echo sequence has been previously described[14,15] and is similar to the Stilbs modification[16] of the Stejskal–Tanner method.[17] With this modification, the NMR signal intensity is given by[14–17]

$$A = A_0 \exp[-\gamma^2 G^2 D \delta^2 (\Delta - \delta/3)] \qquad (1)$$

where $A_0$ is the signal intensity with $\delta = 0$, $\gamma$ is the gyromagnetic ratio of the proton, $G$ is the field gradient strength (typically 0.05 T/m), $D$ is the self-diffusion coefficient, $\delta$ is the length of the field gradient pulse, and $\Delta$ is the fixed time between the preparation and refocusing pulses. A plot of log intensity vs. $\beta$ $\{\beta = \delta^2(\Delta - \delta/3)\}$ yields a straight line for molecules in isotropic solution with a slope of $-\gamma^2 G^2 D$. This simple exponential behavior was observed for neat cyclohexane, which was used for gradient calibration, and for toluene in polystyrene solutions.

In the case of the polystyrene beads, the resonance broadening due to the gradient pulses caused overlap of the two resonances corresponding to the solvent inside and outside the polymer bead. The intensity of the single peak is therefore a function of the diffusion coefficients in the two regions and of the exchange rate between these regions. The functional dependence of the signal intensity on $\delta$ has been determined for the limiting conditions of $p_a \gg p_b$ and $D_a \ll D_b$,[10,11] where the subscripts a and b refer to solvent inside and outside of the polymer bead, respectively, $p$ is the fraction of solvent in a given region, and $D$ is its self-diffusion coefficient. When one assumes that these conditions apply to the system of interest, the signal intensity is governed by an apparent diffusion coefficient ($D_{app}$), given by

$$D_{app} = D_a + p_b D_b / (1 + \gamma^2 \delta^2 G^2 \tau_a p_b D_b) \qquad (2)$$

here $\tau_b$ refers to the mean lifetime of the free solvent. This dependence
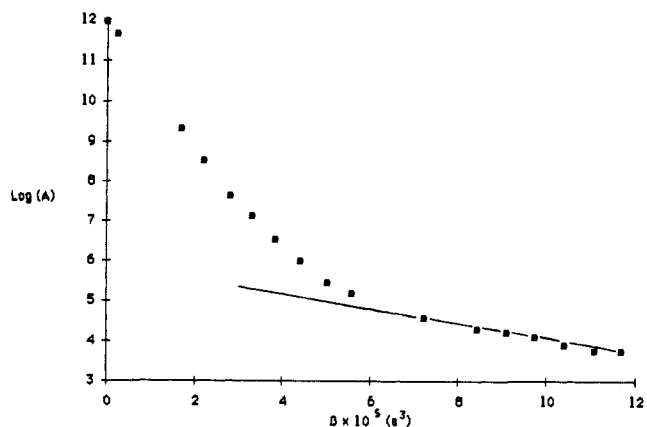


**Figure 1.** Signal intensity ($A$) from the PGSE experiment as a function of $\beta$ for toluene in a 20% cross-linked polymer bead. The diffusion coefficient inside the polymer bead is calculated from the points at large $\beta$ values (shown by dashed line).

**Table I.** Self-Diffusion Coefficients of Toluene in Linear Polystyrene Solutions

| wt % PS | $10^{10}D$, m²/s | wt % PS | $10^{10}D$, m²/s |
|---------|------------------|---------|------------------|
| 0.000 | 31.2 | 0.431 | 7.81 |
| 0.138 | 23.2 | 0.521 | 5.36 |
| 0.249 | 17.4 | 0.629 | 2.07 |
| 0.336 | 12.9 | 0.691 | 1.25 |

of $D_{app}$ on $\delta$ suggests that in the limit of large $\delta$, a plot of log intensity vs. $\beta$ will asymptotically approach a line with slope $-\gamma^2 G^2 D_a$ (Figure 1), from which one can determine the diffusion coefficient of the solvent in the bead. In all cases more accurate measurements of the solvent self-diffusion coefficients were made by collecting data at large $\beta$ values rather than using the whole curve, as in Figure 1. Since at high $\beta$ values, the large interstitial solvent resonance intensity is no longer significant, a better signal-to-noise ratio can be obtained by adjusting the receiver gain to the amplitude of the solvent signal within the beads only.

## Results and Discussion

The measured self-diffusion coefficients of toluene in linear polystyrene solutions are shown in Table I as a function of the weight fraction of polymer. The solvent diffusion coefficients are independent of the molecular weight of the polymer. The self-diffusion data from solution can be interpreted with free volume theory,[18] obstruction and solvation effects,[19] or the Vrentas–Duda theory.[20] The detailed interpretation of the solution data is beyond the scope of the present work as these measurements are only made for comparison with diffusion of solvent within the beads. However, recent work[21] has suggested that over a wide range of concentrations solvent self-diffusion in polymer solutions is dominated by obstruction and nonspecific kinetic effects rather than any chemical binding (e.g., hydrogen bonding). The evidence for this is that many polymer–solvent systems show normalized solvent self-diffusion coefficients that fit on a "master" curve regardless of the thermodynamic quality of the solvent.[21,22]

The PGSE data for the solvent in the cross-linked samples show a nonexponential decay. An example of this is shown in Figure 1 for the 20% cross-linked sample. In the initial part of the curve in Figure 1, the decay is seen to be intermediate between that of the pure solvent and the solvent within the bead as suggested by eq 2, although in this case $p_a$ is not necessarily much greater than

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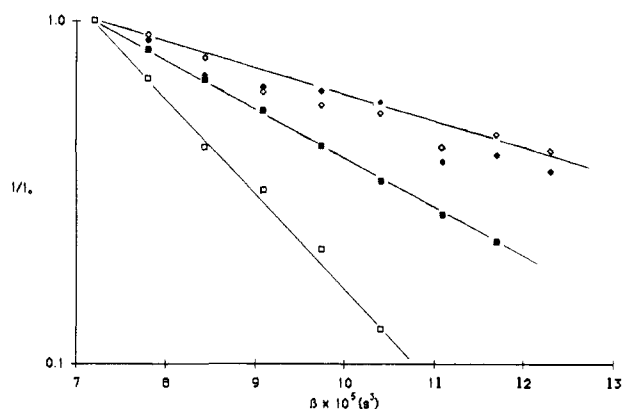(17) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.

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**Figure 2.** Normalized signal intensity (semilog scale) as a function of $\beta$ in the region of large $\beta$ values for systems with (□) 5.7%, (■) 10%, (◊) 20%, and (♦) 40% cross-linking.

**Table II.** Measured and Calculated Self-Diffusion Data for Toluene in Swollen Polymer Beads

| sample % DVB | swell ratio | wt. % PS[a] | $10^{10}D_{calcd}$,[b] m²/s | $10^{10}D_{measd}$, m²/s |
|---|---|---|---|---|
| 5.7 | 2.1 | 0.514 | 5.2 | 4.57 |
| 10 | 1.8 | 0.593 | 2.8 | 2.47 |
| 20 | 1.4 | 0.686 | 1.4 | 1.35 |
| 40 | 1.2 | 0.835 | <1.3 | 1.45 |

[a]Calculated from swell ratio. [b]Estimated from weight percent polymer and polystyrene solution data.

$p_b$. At larger $\beta$ values the slowly diffusing component is seen to dominate the NMR intensity. This slow decay can be assigned to the diffusion of the solvent inside the polymer bead and can be used to calculate the self-diffusion coefficient of the solvent in the polymer bead. A plot of log intensity as a function of $\beta$ in the region of larger values is shown for each of the cross-linked systems in Figure 2. A normalized intensity (intensity divided by a reference intensity) is used to give the plots the same intercept. In these plots it is clear that the measurements are less precise for the highly cross-linked samples than for the slightly cross-linked ones. The diffusion coefficients calculated from these plots are listed in Table II.

From the measured self-diffusion coefficients we can estimate the root-mean-square diffusion distance that a solvent molecule will travel over the duration of the experiment. This distance is given by

$$X_{rms} = (2Dt)^{1/2} \tag{3}$$

where $D$ is the self-diffusion coefficient and $t$ is the time between the preparation pulse and the echo ($2\Delta$). Using values around $5 \times 10^{-10}$ m²/s for $D$ (which is near the largest measured for solvent in the beads) and $t = 0.15$ s, we calculate that the distance traveled by a toluene molecule is about 12 $\mu$m. This distance is much smaller than the diameter of the beads, which is on the order of 200 $\mu$m. It can be concluded that over the time of the experiment much of the toluene does not escape from the bead. Thus the measurement truly reflects the translational diffusion within the bead.

Comparison of the measured diffusion coefficients for toluene in polystyrene solutions (Table I) and polystyrene beads (Table II) show similarities. As expected, the self-diffusion coefficients of the toluene in the beads show a decrease with an increase in the amount of cross-linking. However, it is not known whether this effect is due to the increase in rigidity of the beads due to increased cross-linking or simply due to the reduced uptake of toluene in the highly cross-linked beads. To answer this question we examined the swell ratios of the polymer beads. These are also shown in Table II along with the calculated weight fractions of polystyrene in the fully swollen beads. The weight fractions were calculated by assuming that the increase in volume is due only to solvent uptake, using densities of 1.01 and 0.862 g/mL for polystyrene and toluene, respectively. Using these calculated

weight fractions, it is possible to estimate the self-diffusion coefficient that the toluene would have if it were in a non-cross-linked polystyrene solution of the same concentration by interpolation of the linear polymer solution data.[21] The calculated results shown in Table II may be compared with the measured value in the same table. The agreement between the two is striking. At low cross-linking, the toluene in the bead is about 15% lower than the solution value, and at higher amounts of cross-linking the two results agree within experimental error.

It has recently been suggested that the diffusion of probes in dilute cellulose gels is indistinguishable from their diffusion in polymer solutions of the same concentration.[23] Similar results have been found for water diffusion in several aqueous gels.[24] It is also found that the normalized self-diffusion coefficients of the solvent ($D_{measd}/D_{pure}$) in a variety of polymer solutions behave similarly as a function of volume fraction of polymer.[21,22] Quasi-elastic light scattering studies of styrene/divinylbenzene polymerizations[25] suggest that the mutual diffusion coefficient in the monomer/polymer system is independent of whether a homopolymer of styrene or copolymer, leading to a gel, is formed. Even though our gels are far from dilute, a comparison of the normalized self-diffusion coefficients as a function of the apparent concentration for the non-cross-linked and cross-linked systems (Table I and II) is appropriate. The apparent concentration is the actual concentration for the solutions, and it is the calculated concentration (based on the swelling ratio) for the beads. The two tables show the excellent agreement between the two sets of data.

The similarity of solvent diffusion coefficients in cross-linked and non-cross-linked systems deserves further consideration. Recent work in concentrated solutions has shown that the solvent self-diffusion and segmental reorientation (as probed by NMR transverse relaxation time, $T_2$) are intimately related.[26] In fact both concentration and temperature changes for $D$(solvent) and $T_2$(polymer) in the poly(isopropyl acrylate)/chloroform system can be described in concentrated solutions with numerically similar parameters with the free volume theory of Ferry.[18] Consequently, studies of the mobility of the polymeric species in swollen beads or gels are relavent to the present study.

Several carbon-13 studies have shown that line widths in swollen gels are only slightly broader than those in solutions of linear polymers.[27-30] These line widths are also found to correlate with swell ratios. Carbon-13 studies in similar swollen poly(styrene-co-divinyl benzene) beads have shown decreases in $T_1$ and NOE values and increases in the line width of the polymer with increased cross-linking.[31,32] In most cases, differences in $T_1$ are not large while the line width increases are significant. Analysis of proton NMR line shapes of spectra with and without magic-angle spinning (MAS) reveals that the polymer resonance has at least two components.[33-35] A sharp component, which can be attributed to the polymer segments that are far from cross-links, is superimposed on a dipolar broadened resonance for the protons at or near the cross-links. The fact that the broadening of the resonance can be removed by MAS suggests that the motions of segments

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near the cross-links are slow and/or anisotropic.[36] The other component behaves much like a linear polymer in a solution of similar concentration. Deuterium NMR studies of backbone reorientation in poly(isopropyl acrylate)-$d_1$/chloroform (1% cross-linked) gels[37] yielded results for $T_1$ and $T_2$ that are virtually the same as the solution results.[38] The deuterium NMR results are perhaps the most straightforward to interpret since the deuteron was shown not to be affected by dipolar (or quadrupolar) coupling as the proton and perhaps carbon-13 results are.[36]

Our current diffusion data are basically in agreement with the above results, showing that translational as well as rotational motions in the polymer beads are determined by the degree of swelling. In addition, for the majority of polymer segments, the polymer mobility in solutions and gels is similar. Since solvent diffusion is related to the segmental motions of the polymer,[26] the diffusion results for both solutions and cross-linked beads are also similar. This would not necessarily be true in very highly cross-linked systems.

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## Conclusions

It has been shown that it is possible to measure the translational self-diffusion coefficients for solvents inside a swollen polymer bead. To the best of our knowledge this is the first direct measurement of this kind in this type of system. Such an experiment is possible because the PGSE NMR experiment is sensitive over a distance scale that is small compared to the size of the bead. In contrast, other techniques, such as radioisotope labeling, are often complicated by contributions from bulk solvent in equilibrium with the swollen gel phase. It was also demonstrated that the self-diffusion coefficients of solvent within the bead could be predicted with accuracy with the swell ratio and diffusion data from polymer solutions. These results will be useful in areas of research where swollen polymer beads are used.

**Registry No.** Polystyrene, 9003-53-6; Poly(styrene co-vinyl benzene), 9003-70-7; Toluene, 108-88-3.

# Structural Studies of Carbohydrates by Deuterium NMR: Sucrose

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**Abstract:** Sucrose has been catalytically deuterated at several positions in the fructose and glucose rings. Deuterium NMR spectra of the labeled molecule in an ordered potassium laurate liquid crystal have been assigned on the basis of spectroscopic properties and differential rates of deuterium incorporation. Quadrupole splittings measured for various sites have been used to deduce orientational and conformational preferences for the molecule.

Carbohydrates play important structural and functional roles at the surface of biological membranes.[1-3] They function as receptors for a variety of hormones and seem to play critical roles in cell recognition and differentiation. Prerequisite to understanding their function is a molecular level description of the conformational and associational properties of these molecules when at or near membrane–water interfaces. The association of carbohydrates with membrane surfaces has received some recent attention,[4] but there is very little information relating to preferred orientation and conformation when near membrane interfaces.[5]

Recently we applied deuterium NMR to the analysis of orientational preferences of a simple deuterium-labeled monosaccharide in a liquid-crystal medium consisting of an aqueous dispersion of potassium laurate micelles.[6] While the micelle surfaces bear only a distant relationship to surfaces of biological membranes and a monosaccharide is structurally very simple compared to the oligosaccharide moieties found at membrane

surfaces, the methodology appeared to offer substantial promise for the structural investigation of more complex systems. It was clear from the initial work, however, that extension to more complex systems would require both an improved method for obtaining deuterium-labeled molecules and a stepwise exploration of the spectral properties of larger saccharides. We present here an application of deuterium NMR to an orientational analysis of the simple disaccharide, sucrose, dissolved in a potassium laurate liquid crystal. The introduction of a general means of deuterium-labeling oligosaccharide moieties, and the utilization of labeling rates as a spectral assignment tool greatly enhance the potential of the methodology for application to more complex systems.

The use of deuterium NMR as a probe of orientational properties is based on the extraction and analysis of quadrupole splittings for deuteriums located in a number of specific carbon–deuterium bonds. The methods stem from the successful application of deuterium NMR to the analysis of conformational and dynamical properties of lipids in biological membranes.[7,9] They differ from most previous studies in that magnetic field ordered liquid crystals are employed to improve spectral resolution and orientational definition.[8,10,11]

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