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NMR characterization of penetrants in high permeability polymers

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Abstract

Spectra of xenon-129 sorbed into two high permeability polymers are reported. The polymers are the copolymer of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole as well as poly(1-trimethylsilyl-1-propyne). At room temperature, the xenon-129 shifts are smaller than in conventional glassy polymers. The smaller xenon-129 shift indicates the presence of larger sorption sites in high permeability polymers relative to conventional polymers. The temperature dependence of solubility in these polymers is drastically different from the behavior in conventional polymers. There is a rapid exponential increase in solubility in high permeability polymers as temperature decreases corresponding to a large negative enthalpy change on sorption and it is this increase in solubility which leads to a large increase in shift with decreasing temperature. Pulse field gradient (PFG) determinations of the self-diffusion constant are made for xenon, propane, pentane and a decafluoropentane in the copolymer. Rapid diffusion is observed as well as a dependence of the apparent diffusion constant on the time scale of the PFG experiment. The translational mobility of smaller simpler moieties depends less on the time scale or equivalently, the length scale of observation in the PFG NMR experiment. For larger, more complex species, the interconnectedness of high free volume domains plays a role in reducing the apparent diffusion constant as the time of measurement increases. © 2002 Published by Elsevier Science Ltd.

Keywords: NMR; Diffusion; High permeability polymers

1. Introduction

The sorption environment and mobility of low molecular weight compounds in polymers can be determined by a variety of NMR experiments. Mobility can be determined by line shape and relaxation experiments including pulse field gradient (PFG) measurements of translational motion. These could be based on proton or carbon-13 nuclei but xenon-129 NMR [1–4] has an additional advantage since the shift is very sensitive to the local environment. In this report, a combination of these approaches will be applied to two high permeability polymers [5–12]: first, the random copolymer of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (TFE/BDD); and second, poly(1-trimethylsilyl-1-propyne) (PTMSP). PTMSP is one of the most permeable polymers known and has attracted considerable attention for applications in separations of gases and low molecular weight compounds. The permeability of TFE/BDD is close to PTMSP and both polymers have a number of properties in common despite having very different repeat unit structures. The self-diffusion constant of penetrants of differing size can be compared with solubility and permeability data to improve the understanding of these unusual polymers.

^{129}Xe NMR has been used to characterize rubbery and glassy polymers for a number of years so that typical characteristics of xenon spectra can be summarized [1–4]. In polymeric rubbers, the xenon-129 resonance is relatively narrow while in glasses it is commonly broader. Glasses are locally heterogeneous on the size scale of a xenon atom. Thus, there are a variety of environments experienced by xenon which leads to a distribution of shifts. At higher temperatures, xenon diffuses among the various environments which averages the shift leading to a narrower line and at lower temperatures diffusion slows and the line becomes broader. In a rubber, segmental motion of the polymer itself averages the environments which further narrows the line width.

The size of local free volume elements associated with gas sorption can be probed. Qualitatively, the larger the local free volume in a polymer matrix, the smaller the shift of the xenon-129 resonance relative to the free gas line [1–4]. For xenon dissolved in simple fluids, larger xenon-129 shifts are observed for xenon in high refractive index environments. Thus, if xenon is in a hole in a solid, this is a low refractive index environment and produces less of a shift from the free gas resonance. Quantitative calculation of the shift changes is not simple but a dense packing

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environment leads to larger shifts and a pore leads to smaller shifts. This effect is of particular interest in these high free volume polymers which are reported to have larger free volume elements for gas sorption sites relative to conventional polymers.

PFG NMR can be used to directly determine the self-diffusion constant of small molecules in polymers [13]. PFG measurements of self-diffusion are on a longer length scale measurement, typically microns, while the xenon-129 line narrowing is sensitive to heterogeneities on a nanometer length scale and diffusion amongst these heterogeneities. In polymeric rubbers containing a fixed concentration of penetrant, PFG NMR observes simple Fickian diffusion. In conventional polymeric glasses, diffusion is often too slow to be conveniently measured by PFG NMR, but another NMR experiment based on progressive saturation can again be interpreted in a simple manner [14]. In these high permeability polymers, permeability measurements indicate diffusion constants which are two orders of magnitude larger: a range readily accessible by PFG NMR.

Semi-crystalline polymers and blends have more complex behavior [15]. In a semi-crystalline polymeric solid, diffusion of the penetrant must typically occur by moving around the crystals. If the penetrant cannot enter the crystal, the diffusion is said to be tortuous since the path is not a random walk but rather the penetrant is reflected at the crystal surface. In the PFG NMR experiment for such a system, the apparent self-diffusion constant depends on the time scale over which diffusion is observed [16–19]. At short times, diffusion appears fast as the molecule moves unimpeded through the amorphous domain. As time passes, it will be reflected from the crystalline domain. Consequently diffusion appears to slow. At long times, the penetrant would be reflected many times. After very long times corresponding to length scales larger than the size of crystalline domains, the diffusion constant will again become constant. In a blend where mobility is high in one domain and slow in the other, tortuous diffusion might also be expected.

A simple model for diffusion through randomly packed, impenetrable spheres is available for comparison with experiment [16–19]. It shows a rapid decline in the apparent diffusion constant at short times which levels off to a constant value at long times as is expected for tortuous diffusion.

Tortuous diffusion is observed for pentane [20,21] in TFE/BDD and a combination of tortuous and restricted diffusion is observed for a decafluoropentane [20,22] in this polymer. If molecules are trapped in a volume and can diffuse within this volume but not escape it, the diffusion is referred to as restricted [13]. For this case, the apparent diffusion constant monotonically decreases with time in the PFG NMR experiment. The size of the volume containing the diffusing penetrant can be determined from the PFG NMR data. In this report, the translational diffusion of xenon and propane as determined from PFG NMR will be compared to earlier results on pentane and decafluoropentane. Thus, the effect of molecular size on the complex diffusion observed in TFE/BDD can be ascertained. There are permeability and solubility data available [9] on propane in TFE/BDD which can be compared with the results of the PFG NMR experiment.

The shift of xenon-129 gas in TFE/BDD will be compared to xenon gas in poly(tetrafluoroethylene) (PTFE) to qualitatively probe the size of free volume regions occupied by xenon. For further comparison, the xenon-129 shift in PTMSP will be measured and compared with a typical glassy, hydrocarbon polymer, poly(styrene). The temperature dependence of concentration and shift will also be presented for these systems. Results can be compared with positron annihilation life time spectroscopy [5,7,11,12] which indicates the presence of high free volume elements in TFE/BDD and PTMSP relative to conventional polymers.

2. Experimental

All xenon-129 NMR experiments were performed on a Varian Unity 500 NMR spectrometer interfaced to a Sun IPX workstation running VNMR 4.1A software package. A two-channel 10 mm broadband probe was employed. The one-dimensional ^{129}Xe NMR spectra were acquired at 138.3 MHz typically with a 20 μs $\pi/2$ pulse and a relaxation delay of about 100 s. In some cases, tip angle experiments were used with a shorter 6 μs pulse length and shorter relaxation delays.

The proton PFG measurements were made on a Varian Inova 400 MHz wide bore NMR spectrometer with a ^{1}H(^{15}N–^{31}P) 5 mm PFG indirect detection probe by observing proton signals from the penetrant. The xenon PFG measurements were made in an 8 mm direct detection probe with high gradient capability from Doty Scientific. Samples were prepared by adding the appropriate amount of the penetrant to a cast film of TFE/BDD. The sample was then sealed in a 5 or 8 mm NMR tube. The TFE/BDD films were cast from a perfluoroheptane solution of the copolymer and were dried to constant weight in a vacuum oven at 50 °C. The copolymer was AF1600 (Dupont™) and was provided by Dupont. The penetrant/film system equilibrated for a period of days before measurements were made and no changes in the mobility of the penetrant were observed over a period of the next couple of weeks during which measurements were made. Glass spacers were used in the NMR tube to center the sample of the correct size in the region of the rf and gradient coils. The apparent diffusion constant of the penetrant, D, was measured as a function of the time, Δ, indicated in the stimulated echo pulse sequence shown in Fig. 1. Only the initial decay of echo amplitude was monitored,

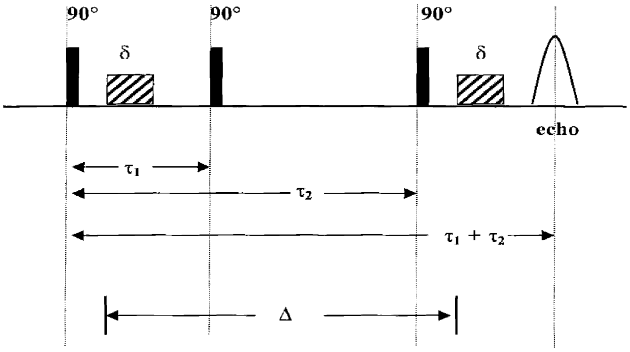

Fig. 1. Pulse sequence for the PFG experiment.

typically to a level of about 50% of the original amplitude. At a given time, Δ, the quantity $q = \gamma\delta g/2\pi$ was varied by changing the gradient amplitude, g, from 0 to 60 G cm^{-1} for the indirect probe and 0–800 G cm^{-1} for the Doty Probe. The time, Δ, ranged from 2 ms to 1 s. A fixed value of δ, the length of the gradient pulses, of 1–8 ms was used for a given determination of the apparent diffusion constant. The apparent diffusion constant at a given value of Δ is calculated from the slope of a plot of the logarithm of the echo amplitude versus g^2.

3. Results

Fig. 2 displays ^{129}Xe spectra as a function of temperature for a 3 atm sample of xenon over PTFE. For comparison, Fig. 3 shows ^{129}Xe spectra for 2 atm of xenon gas over the TFE/BDD copolymer. Fig. 4 contains ^{129}Xe spectra for 2 atm of xenon over PTMSP. Fig. 5 compares the apparent diffusion constant of xenon, propane, pentane and decafluoropentane in TFE/BDD. The xenon pressure in the diffusion experiment is 8 atm and the propane pressure is 5 atm. The pentane sample is 8 wt% and the decafluoropentane is 20 wt%.

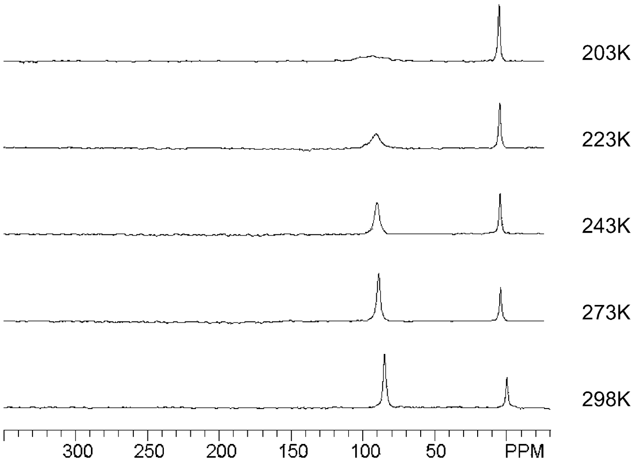

Fig. 2. Xenon-129 spectra as a function of temperature for 3 atm of xenon over PTFE.

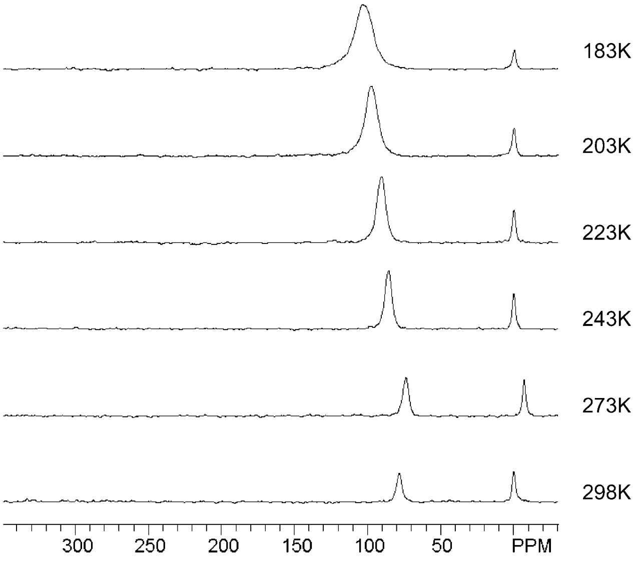

Fig. 3. Xenon-129 spectra as a function of temperature for 2 atm of xenon over TFE/BDD copolymer.

4. Interpretation

The shift of the xenon-129 resonance in fluorocarbons is lower than hydrocarbons because of the low polarizability of fluorine. In general, the higher the refractive index or the dielectric constant, the larger the shift from the free gas line [23,24]. At room temperature, the shift

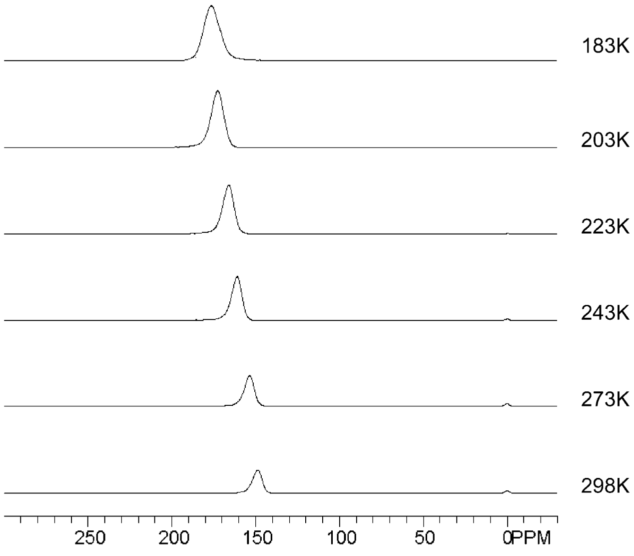

Fig. 4. Xenon-129 spectra as a function of temperature for 2 atm of xenon over PTMSP.

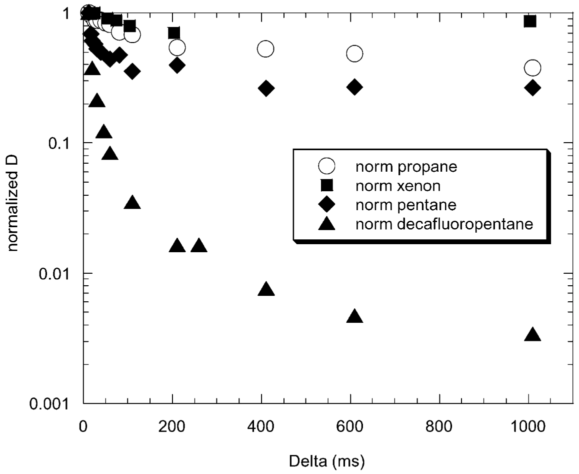

Fig. 5. Normalized apparent diffusion constant versus Δ, the time scale of the diffusion measurement. The diffusion constants were normalized to by dividing by the value of D at the shortest time observed for a given penetrant.

of the xenon-129 resonance in TFE/BDD copolymer is lesser than in PTFE. This is expected since the copolymer is considered to have larger free volume elements. However, the TFE/BDD copolymer is glassy and the amorphous part of PTFE is rubbery so the shift difference between the two polymers is smaller than it would be if the high permeability TFE/BDD were compared with a conventional glassy fluoropolymer. The shift of xenon-129 of about 150 ppm in PTMSP is also much smaller than in a traditional hydrocarbon polymer like poly(styrene) [16] where it is 200–225 ppm. This again reflects the larger volume of the sorption sites which positron annihilation lifetime spectroscopy has identified in these systems.

What is even more striking than the low shift values is the temperature dependence of the shift shown in Fig. 6. The shift increases dramatically as temperature is lowered because there is increased xenon–xenon contact in the TFE/BDD copolymer. Xenon itself has a high polarizability especially relative to the fluorocarbon environment so there is a dramatic increase in the shift as more xenon is sorbed. In pure PTFE, the increase in solubility with decreasing temperature is smaller so there is no such large change in the shift. The differences in the temperature dependence can be easily identified qualitatively from the spectra in Figs. 2 and 3.

A large temperature dependence of the shift is also seen in PTMSP as shown in Fig. 7 relative to a more typical hydrocarbon-based polymer like poly(styrene) [16]. The reason for the large increase in shift with decreasing temperature is the same but the effect appears less dramatic because of the larger shift in a hydrocarbon-based material to begin with. Fig. 8 shows the intensity of the xenon resonance in PTMSP normalized by dividing by the intensity of the free gas resonance as a function of temperature. The rapid increase is striking, as is the apparent disappearance of the free gas line at low temperatures in the spectra. Both the shift dependence and the intensity dependence as a function of temperature are characteristics of xenon-129 resonances in high permeability polymers. The high solubility

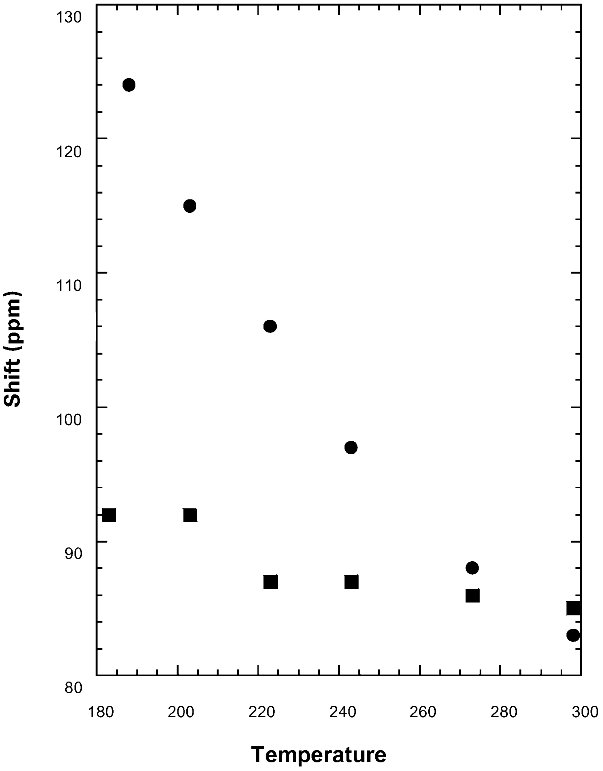

Fig. 6. Shift of the xenon-129 resonance in the polymer versus temperature. Circles are for 5 atm of xenon over TFE/BDD and squares are for 2 atm of xenon over PTFE.

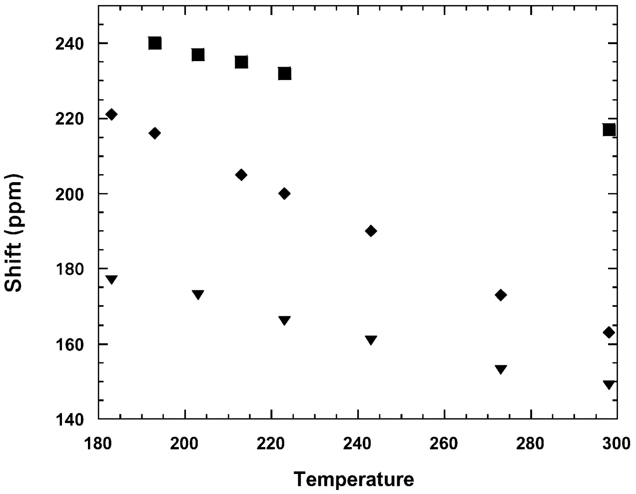

Fig. 7. Shift of the xenon-129 resonance in the polymer versus temperature. Squares are for xenon in polystyrene, circles are for xenon at a pressure of 5 atm in PTMSP, and diamonds are for xenon at a pressure of 2 atm in PTMSP.

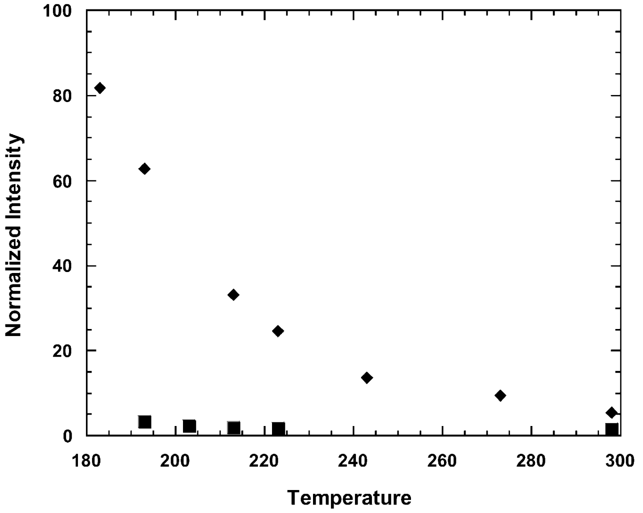

Fig. 8. The normalized intensity of the sorbed xenon resonance as a function of temperature. Dividing by the free gas intensity at that temperature normalizes the sorbed xenon intensity. Circles are PTMSP and squares are for poly(styrene).

of penetrants in this type of system relative to conventional polymers accounts for the behavior. The temperature dependence of solubility [9] can be analyzed based on the usual dual mode equation

$$S = C/P = k_D + \frac{C'_H b}{1 + bP} \tag{1a}$$

and the assumption of the form:

$$S = S_0 \exp\left(\frac{-\Delta H_S}{RT}\right) \tag{1b}$$

The ratio of the intensity of the resonance from sorbed xenon to free gaseous xenon is proportional to S and Fig. 9 contains a fit to this form which yields a value of -106 kJ/mol for ΔH_S. This large negative value is typical of results for the high permeability polymers.

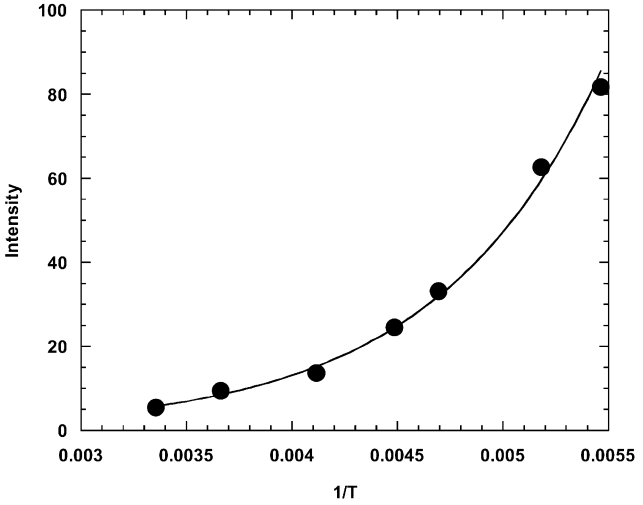

Fig. 9. Intensity of the xenon resonance in PTMSP versus reciprocal temperature. The line is a fit of the data using Eqs. (1a) and (1b).

In Fig. 5, the dependence of the apparent diffusion constant on the time scale over which diffusion is observed is revealing. For the simplest penetrant, xenon, there is almost no dependence on Δ while for propane there is a modest dependence. The apparent diffusion constant of pentane changes by a factor of four over the time scale of observation and the behavior can be matched by a description of tortuous diffusion. The decafluoropentane changes by orders of magnitude over the same time scale and the interpretation here involves the presence of two components one of which behaves as if it is undergoing restricted diffusion while the other appears tortuous. Decafluoropentane has a larger molecular weight relative to pentane and is also closer to being a solvent for the polymer.

Interestingly, the apparent diffusion constants of all four molecules are quite close at small values of Δ. At $\Delta = 10$–15 ms, the diffusion constants are 2.2×10^{-7} cm^2 s^{-1} for propane, 2.0×10^{-7} cm^2 s^{-1} for pentane, 1.9×10^{-7} cm^2 s^{-1} for decafluoropentane and 1.2×10^{-7} cm^2 s^{-1} for xenon. This time scale corresponds to a length scale of about 1 μm for all four penetrants which is the size of the regions containing the larger free volume elements identified from the restricted diffusion of the decafluoropentane. Thus, it is the connections between these disordered regions of high free volume which produces the differences in the diffusion constants of the four molecules at long times. The smaller, simpler molecules can transit the interconnections better than larger entities with internal conformational degrees of freedom.

At large values of the time Δ and at a pressure of 5 atm, the self-diffusion constant for propane is 1.0×10^{-7} cm^2 s^{-1} from PFG NMR while the values for diffusivity from permeability range from 1.0×10^{-7} to 2.0×10^{-7} cm^2 s^{-1} for pressures in the range of 1–3 atm [9]. The comparison is quite reasonable given the differences in technique and the exact quantity measured. The value of the diffusion constant also depends on film preparation and aging of the film.

5. Conclusions

The smaller xenon-129 shift indicates the presence of larger sorption sites in high permeability polymers relative to conventional polymers. The temperature dependence of solubility in these polymers is drastically different from the behavior in conventional polymers. There is an exponential increase in solubility in high permeability polymers as temperature decreases corresponding to a large negative enthalpy change and it is this increase in solubility which leads to the larger change in shift with temperature. The translational mobility of smaller simpler moieties depends little on the time scale or equivalently, the length scale of observation in the PFG NMR experiment. For larger, more complex species, the interconnectedness of high free volume domains plays a role in reducing the apparent diffusion constant.

Acknowledgements

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