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Topology of High Free Volume Regions from Pulsed Field Gradient Diffusion Studies of Penetrant Motion in Perfluorodioxole Copolymer

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Recently a new class of glassy polymers has drawn interest as potential membrane materials. These polymers have bulky backbone units and constrained backbone reorientation which leads to high free volume regions in the glassy state. One of these, perfluorodioxole (TFE/PDD) is a random copolymer of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole with very high permeability[1−4] especially for a high glass transition polymer. In fact, the permeability of TFE/PDD is second only to the permeability of another polymer of this general type, poly(1-trimethylsilyl-1-propyne) (PTMSP), which is considered to have statically interconnected regions of high free volume.[5] TFE/PDD has a high fractional free volume, around 0.3 or twice the value for conventional glassy polymer membrane material like polysulfone.[2] The value of 0.3 is about an order of magnitude larger than that associated with typical glassy polymers. The highest free volume is considered to be located in disordered regions of this polymer containing free volume elements of 0.59−0.64 nm as determined by positron annihilation lifetime spectroscopy.[1] The fraction of free volume in these disordered regions is 0.03−0.04 when the fraction of PDD in the copolymer is 0.87. For PTMSP, the corresponding fraction is 0.1 while it is 0.001−0.003 in conventional glassy polymers; the latter also have smaller pores. Note that these fractional free volumes are not the total fractional free volume but only that associated with the disordered regions containing the largest free volume elements. TFE/PDD has lower permeability than PTMSP which is attributed to the smaller fraction of high free volume regions and the likelihood that they are not as well interconnected.

While the information summarized above rationalizes some of the properties of TFE/PDD compared to PTMSP and conventional polymers, there are still unanswered questions. Can the presence or absence of interconnected regions containing high free volume due to the existence of nanometer sized high free volume elements be experimentally verified? If there are interconnected regions, what is the topology? If there are isolated regions, what is the domain size? Pulse field gradient (PFG) NMR can address these questions by examining the behavior of the translational motion of penetrants as a function of length scale or equivalently time scale.[6−9] For interconnected regions that allow for rapid transport, porosity and tortuosity are applicable concepts and have a signature in the PFG NMR experiment. Similarly, if regions of rapid transport are not interconnected and diffusion is restricted by a surrounding region with slower transport, PFG NMR experiments yield a distinctly different yet characteristic result. PFG NMR experiments of this type have recently been applied to the diffusion of xenon in a semicrystalline copolymer.[10]

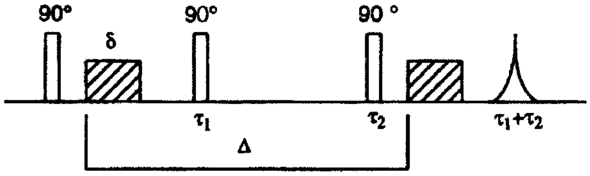

Figure 1. Stimulated echo pulse gradient sequence used to determine *D* as a function of diffusion time (Δ).

One experimental approach for distinguishing between a system undergoing restricted diffusion (diffusion confined by a physical boundary) and a porous system subject to tortuosity is to measure the apparent diffusion constant as a function of the time over which diffusion is allowed to occur in the PFG NMR experiment.[6−9] Figure 1 displays the stimulated echo pulse gradient sequence which can probe diffusion over a wide range of time scales by variation of the time Δ. Actually in this approach only an initial fraction of the decay of the spin echo is monitored by keeping the quantity $q = \gamma\delta g/2\pi$ small where δ is the length of the gradient pulse and g is the gradient strength. Thus, for a given choice of Δ, *D* (an apparent diffusion constant) is determined by variation of the quantity δg.

To apply this strategy to TFE/PDD, pentane and a partially fluorinated pentane with the structure $CF_3CHFCHFCF_2CF_3$ were used as the penetrants. An 8 wt % pentane and both an 8 and a 20 wt % sample of the decafluoropentane were prepared and sealed in a 5 mm glass NMR tube by adding the appropriate amount of penetrant to a cast film of TFE/PDD. The copolymer was AF1600 (Dupont Trademark) 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 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. For measurements on this system, Δ was varied from 10 ms to 1 s. A fixed value of δ of 8 ms was used for a given determination of the apparent diffusion constant. The gradient strength was varied to obtain the apparent diffusion constant from a plot of the logarithm of the echo amplitude vs g^2. The maximum value of g in each determination ranged from 60 to 100 G/cm. The measurements were made at 60 °C on a Varian Inova 400 MHz wide bore NMR spectrometer with a $^1H(^{15}N-^{31}P)$ 5 mm PFG indirect detection probe by observing proton signals from the penetrant.

Figure 2 contains a plot of the logarithm of the apparent diffusion constant, *D*, for pentane in TFE/PDD vs the time Δ. The apparent diffusion constant is a strong function of the experimental time Δ indicative of complex translational motion rather than simple Fickian diffusion. If this system were to display classical tortuous diffusion in a porous medium,[7−9] *D* would become constant at large Δ and be linear at small Δ when plotted vs $\Delta^{1/2}$ approaching the value of the pure penetrant at $\Delta = 0$. The limiting behavior is realized at

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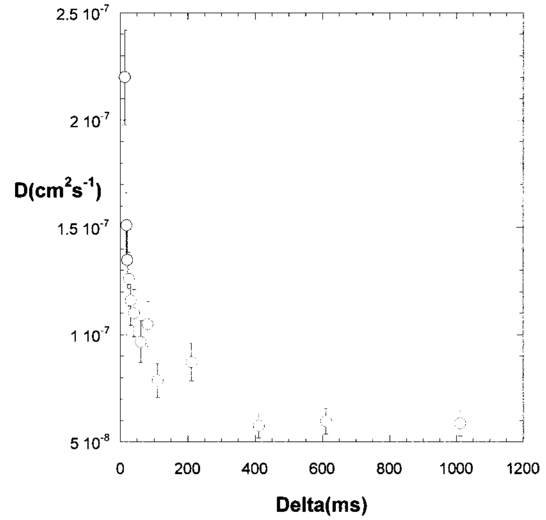

Figure 2. Apparent diffusion constant, D (cm^2/s), of pentane in the polymer TFE/PDD, vs the time Δ (s) at 26 °C.

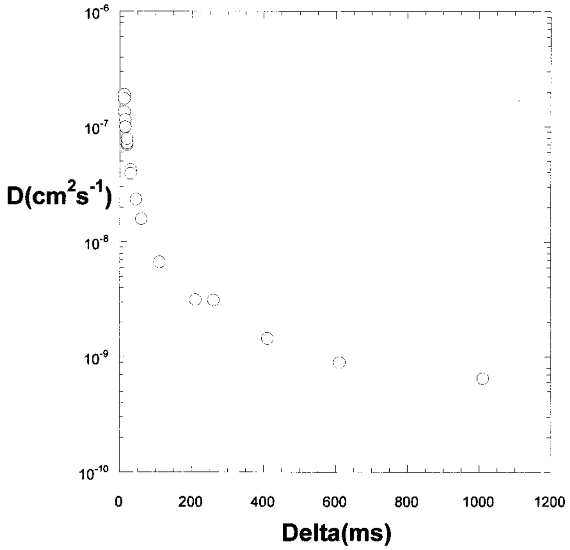

Figure 3. Apparent diffusion constant, D (cm^2/s), of decafluoropentane in the polymer TFE/PDD, vs the time Δ (s) at 60 °C.

large Δ but not at small Δ. Figure 3 shows the same type of information for the decafluoropentane in TFE/PDD, and the changes in the apparent diffusion constant are even greater. At the shortest times measured, D approaches 1×10^{-7} cm^2/s and decreases by more than 2 orders of magnitude to 6.5×10^{-10} cm^2/s. D does not become constant at large values of Δ so the system does not appear to undergo tortuous diffusion in a porous medium.

If the system were to display restricted diffusion,[6] the value of the product of the apparent diffusion constant and the time Δ should be constant at large Δ. This behavior is expected if the quantity $qa < 1$ where a is the size of the domain in which diffusion is unrestricted. Figure 4 contains a plot of the logarithm of the product $D\Delta$ vs Δ which indeed is constant for Δ greater than about 100 ms. Thus, decafluoropentane in TFE/PDD displays translational motion in the PFG NMR experiment indicative of restricted diffusion. Although the signature of restricted diffusion is observed, there is no impenetrable barrier present in this system. There must be however a dramatic difference in translational mobility between the disordered high free volume regions and the surrounding lower free volume regions, leading to high free volume regions which are effectively isolated. It should be noted that the initial decrease in the product $D\Delta$ in Figure 4 vs Δ is unphysical since $D\Delta$ is a measure of the mean-square displacement which should increase with time. Thus, the early time behavior cannot be explained by simple restricted diffusion alone. This is a consequence of the fact that D_{app} as measured by the PFG experiment in this case results from composite behavior involving two components having modestly different spin−lattice relaxation times and considerably different diffusion constants. Indeed, the proton line shape for decafluoropentane consists of two components with somewhat different line widths and a slight shift offset of one from the other. A separation of the two components in a spin−lattice relaxation experiment is possible using line shape deconvolution. In the diffusion experiment, application of a more sophisticated pulse sequence[11] to improve signal-to-noise allows for the determination of the two diffusion constants. A more detailed analysis of this behavior based on these additional experiments will be presented in a future publication and shows that the individual $D\Delta$ product for each of the two diffusion constants increases with Δ at short times as is physically reasonable. However, the behavior at large Δ remains as reported here with the product of $D\Delta$ becoming constant because the slower diffusing component dominates the apparent D at large Δ.

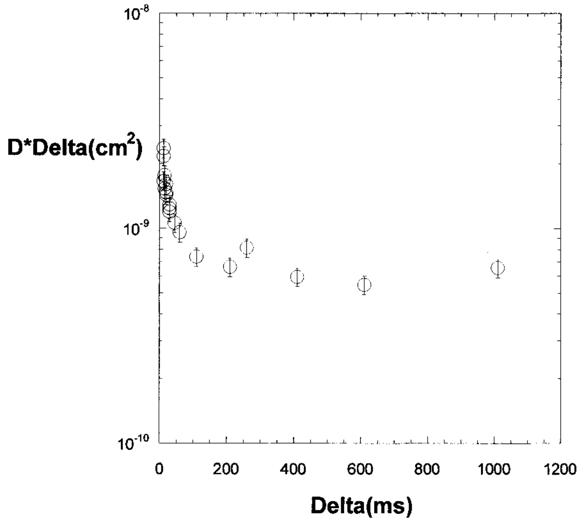

Figure 4. Product $D\Delta$ plotted vs Δ showing that $D\Delta$ is a constant at long times for decafluoropentane in the polymer TFE/PDD at 60 °C.

An estimate of the size of the disordered, high free volume region can be made based on the constant value of the $D\Delta$ product by assuming a geometry for this region and by considering the surrounding region to be impenetrable. It should be emphasized that this estimate is not an estimate of the high free volume elements themselves but rather an estimate of the size of the domain containing the high free volume elements. This size would be associated with the fractional free volume of 0.03 for the disordered regions containing the large free volume elements. If the disordered domain is considered to be spherical, the appropriate relationship[6] is

$$D\Delta = a^2/5$$

where a is the radius of the sphere. The average value of the product $D\Delta$ over the range where it is constant as a function of Δ is $(6.9 \pm 1.0) \times 10^{-10}$ cm^2, leading to a value of a of 0.6 μm. Note that for the conditions employed the requirement $qa < 1$ is met.

PFG NMR has confirmed the view that TFE/PDD has high free volume regions. For the smaller molecule pentane they appear interconnected though the pathway is quite tortuous. For the larger decafluoropentane the high free volume regions are not interconnected as well. For the first time, an estimate of the size of regions containing high free volume regions has been obtained, indicating they are in the micron range and thus are much larger than the high free volume sites occupied by an individual penetrant.

While qualitatively pentane displays tortuous behavior and decafluoropentane displays restricted diffusion at long times, these simplistic models are not the complete picture. In both cases, the change in D in going from $\Delta = 10$ ms to 1 s is quite large, especially in the case of decafluoropentane. A model based on tortuosity comes close to quantitatively matching the pentane results. However, simple restricted diffusion cannot account for the strong dependence of D on Δ at small Δ for decafluoropentane as pointed out above. The reported D's are the composite behavior integrated over the two components. It is this composite behavior which can give rise to the unusual early time drop in the apparent D seen in Figure 3. The more detailed interpretation still results in a description in terms of restricted diffusion with the data at large Δ, yielding an estimate of 0.6 μm for the slowly diffusing component.

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