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Effects of Conditioning, Aging, and Copolymer Content on the Diffusion of Propane and Pentane in Amorphous Glassy Perfluorodioxole by Pulse Field Gradient NMR

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ABSTRACT: The diffusion of pentane and propane in TFE/PDD copolymer was studied using pulse field gradient NMR as a function of time after sample preparation. Pentane and propane display tortuous diffusion behavior in TFE/PDD copolymer (65% PDD) which means the apparent diffusion constant of these molecules slows as a function of the time, milliseconds to seconds, over which diffusion is observed in the pulse field gradient NMR experiment. High-permeability polymers are known to have changes in permeability as a result of aging and conditioning. These changes occur over a period of hours, days, and weeks so the determination of apparent diffusion constants was repeated on the same sample over this time scale. Pentane or propane was added to a freshly cast film of the copolymer and then sealed in an NMR tube. The first measurement of apparent diffusion constants was made within 24 h and then repeated a few weeks later and then a year later. Diffusion became more rapid after a few weeks which was ascribed to conditioning by the penetrant. More rapid diffusion at short times or small length scales indicates the introduction of high free volume regions, and the more rapid diffusion at longer lengths scales indicates improved connectivity between these regions. After a year, diffusion at short time scales corresponding to short length scales slowed. This was interpreted as resulting from the densification of smaller high free volume regions. Over longer length scales diffusion remained relatively constant which was interpreted as little change in the connectivity of high free volume regions. Diffusion as seen in the pulse field gradient experiment was compared for two copolymer compositions: 65% PDD and 87% PDD. Diffusion in 87% PDD copolymer is faster and no evidence of tortuosity is observed, both of which are consistent with a larger proportion of high free volume regions.

Introduction

High-permeability polymers display rapid aging which leads to a reduction in permeability adversely affecting potential applications.[1−8] One of the most permeable polymers known, poly(1-trimethylsilyl-1-propyne) (PTMSP), suffers from this problem, and aging in this system has been well characterized from a number of standpoints. High-permeability polymers have high fractional free volumes and large free volume elements which act as sorption sites. In terms of a dual mode description, there is a large Langmuir sorption capacity associated with these elements that decreases with time after a film of the polymer is cast from a solvent. Another way to describe the situation is that there is a nonequilibrium excess free volume upon casting of the polymer that disappears over a period of hours and days leading to a reduction of permeability.

The presence of large free volume sorption elements has been detected by positron annihilation lifetime spectroscopy[9] (PALS) and by xenon-129 NMR.[10] In one study of aging using PALS, the number and size of the largest free volume elements both decreased[9] with time. In wide-angle X-ray diffraction experiments, the *d* spacing decreases.[9] These experimental results are consistent with the interpretation developed from permeability and sorption measurements.

Another polymer with nearly as large free volume elements and about as high a fractional free volume is the random copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (PDD).[11−14] However, this polymer is less permeable and ages less rapidly. Diffusion of small molecules in this polymer has been characterized using pulse field gradient (PFG) NMR[15−17] which determines the self-diffusion constant. In the TFE/PDD copolymer which is 35% TFE, the apparent diffusion constant in the PFG NMR experiment depends on the time over which diffusion is allowed to occur.[18−21] This behavior is indicative of an impediment to the random walk a penetrant would undergo in a homogeneous system. The impediment results from regions which are impenetrable or less penetrable (support slower diffusion and/or lower solubility). Two classes of impeded diffusion are tortuous diffusion[19−21] and restricted diffusion.[18] In tortuous diffusion the material can be considered to have pores which support rapid diffusion surrounded by walls which are impenetrable or allow for only much slower diffusion. In tortuous diffusion there is a pathway for long-range diffusion associated with an interconnected pore space. In restricted diffusion, the pores are isolated so long-range diffusion is absent if the walls are impenetrable or very slow if the barriers support only very slow diffusion. In the 35% TFE copolymer, tortuous diffusion has been observed for low molecular weight penetrants such as propane and pentane.[15−17] Thus, the self-diffusion constant for these penetrants appears larger if one observes diffusion over a short time or length scale in the PFG NMR experiment since diffusion within a pore is being monitored. As time increases, the penetrant encounters the pore wall restricting its path, and the self-diffusion constant apparently decreases. At very long times in an interconnected pore space a plateau value of the self-diffusion constant is reached. Tortuosity is quantitatively described by the ratio, α, of the self-diffusion constant within the pore divided by the plateau value. The presence of tortuous diffusion

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as indicated by PFG NMR is consistent with the reduced permeability of TFE/PDD relative to PTMSP despite similar fractional free volumes. Stated in another way, the connectivity of the high free volume regions in PTMSP may be better than in TFE/PDD.

According to the NMR data, the "pore" dimensions are about a micron[15−17] in TFE/PDD. The PALS data[22] show two different sizes of free volume elements of about 0.3 and 0.6 nm. What is the relationship between the free volume elements and pore dimensions? The interpretation has been that the large free volume elements cluster into a region to form a domain that acts like a pore.[15−17] Thus, in this high-permeability polymer the pore is a region containing high free volume elements. In truly porous system such as limestone, the pore is empty space surrounded by a truly impermeable wall. In polymers of this type, the pore is a region of high free volume that supports rapid diffusion. This region is surrounded by regions containing the smaller free volume elements, and these regions act as the impediments to diffusion. The regions that have only the smaller free volume elements would support diffusion comparable to that seen in traditional glassy polymers which is orders of magnitude slower than that which is observed in the high-permeability polymers. The fractional free volume in high-permeability polymers[11] is about 0.3 while the fractional free volume associated with the larger free volume elements is considered to be about 0.03. Thus, 10% of the free volume is associated with the large free volume elements. The fraction of the system that is porous is still not defined because the porous domain will contain occupied volume as well as the large free volume elements. It is not a true pore because it is not free space but rather an aggregation of high free volume elements in a polymer matrix. One could assume that if 10% of the free volume is associated with high free volume elements then 10% of the total volume is associated with the porous domain, but this would only be an arbitrary assumption.

Permeability decreases in these high-permeability systems at least partially because diffusion slows as the polymer densifies during aging. PFG NMR can monitor the apparent diffusion constant over different time scales which is associated with different length scales. Does the apparent diffusion constant observed at different times slow down equally as aging occurs? Robertson[23] has proposed that higher free volume regions age first. These would be associated with the fastest diffusion seen at the shortest diffusion times in the pulse field gradient NMR experiment. Therefore, one might expect the apparent diffusion constant observed at short times to change more rapidly than the apparent diffusion constant at long times.

There is another aspect to aging in the presence of penetrants. The high-permeability polymers are often conditioned or "freshened" by treating them with a nonsolvent, frequently methanol.[6,24] This increases permeability. After conditioning or freshening, permeability decreases with time during application or study of the membrane. In the PFG NMR experiment, a dry, annealed membrane was combined with a fixed amount of pentane or propane, and then self-diffusion of the penetrant is monitored over a period of days and months. This situation is different from the freshened membrane subsequently being used in an application or actual permeability measurement which is the usual basis for studying the aging of these materials. The propane or pentane may itself freshen the membrane, but there may be further changes as a function of time after the freshening process. In any case PFG NMR offers the possibility of following the aging process in a different manner with the concomitant possibility of generating new insights.

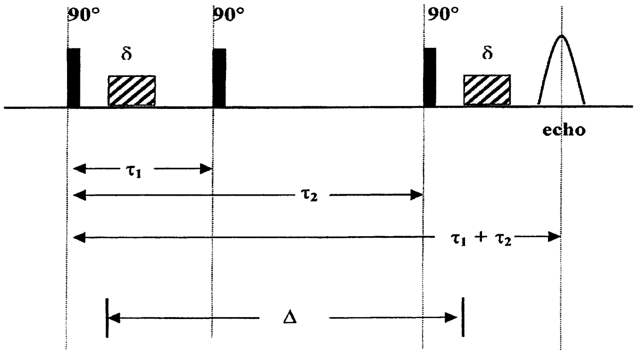

Figure 1. Stimulated echo sequence for the measurement of the apparent diffusion constant.

Increasing the fraction of PDD in the TFE/PDD copolymer from 65% to 87% is also known to increase permeability by increasing the number of high free volume elements. This might be expected to improve connectivity and reduce tortuosity. To check this expectation, the apparent diffusion constant of pentane in TFE/PDD copolymers with two different monomer ratios will be compared.

Experimental Section

PFG measurements were made on a Varian Inova 400 MHz wide bore NMR spectrometer either in a ^{1}H(^{15}N−^{31}P) 5 mm PFG indirect detection probe by observing proton signals from the penetrant or in an 8 mm direct detection probe with high gradient capability (1000 G/cm) from Doty Scientific. Samples were prepared by adding the appropriate amount of the penetrant to a cast film of TFE/PDD. The first sample studied was 8 wt % pentane in AF 1600 (DuPont Trademark), and the second sample was propane at a pressure of 5 atm. Each sample was then sealed in a 5 or 8 mm NMR tube. AF 1600 is 65% PDD, and a second sample of pentane in AF 2400 was also prepared. AF 2400 is 87% PDD. The TFE/PDD films were cast from a perfluoroheptane solution of the copolymer and were dried to constant weight in a vacuum oven at 50 °C. The TFE/PDD copolymers were provided by DuPont. Measurements of the 65% PDD copolymer were made as soon as possible after sample preparation and then repeated periodically over the next 12 months. To compare the effect of copolymer composition, measurements of 8% pentane in the two copolymers were measured at a comparable time after preparation (a few weeks). Glass spacers were used in the NMR tube to center the sample of the correct size in the region of the radio frequency and gradient coils. The apparent diffusion constant of the penetrant, D, was measured as a function of the time Δ over which self-diffusion occurs in the stimulated echo pulse sequence shown in Figure 1. Only the initial decay of echo amplitude was monitored, 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 for the indirect probe and 0 to 800 G/cm 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 vs g^2. Uncertainty in a given value of the apparent diffusion constant is about ±10%.

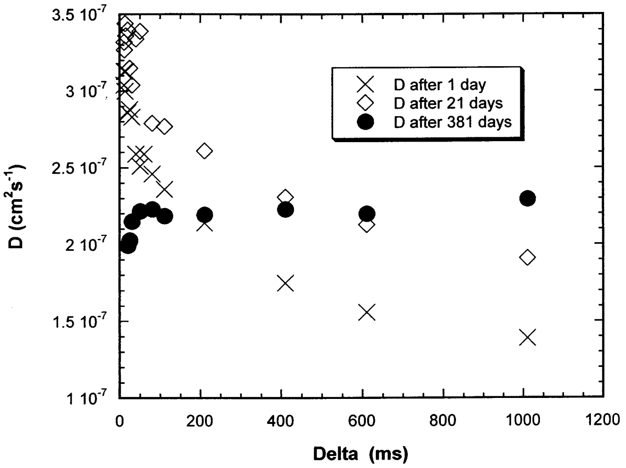

Figure 2. Apparent diffusion constant of pentane in TFE/PDD copolymer (65% PDD) as a function of the time over which diffusion occurs, Δ. Measurements are reported for three different times to study the effect of time after sample preparation.

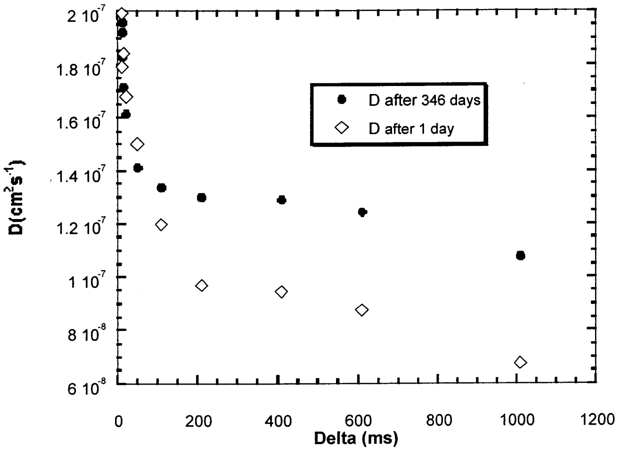

Figure 3. Apparent diffusion constant of propane in TFE/PDD copolymer (65% PDD) as a function of the time over which diffusion occurs, Δ. Measurements are reported for two different times to study the effect of time after sample preparation.

Results

The apparent diffusion constant for pentane in TFE/PDD is presented in Figure 2 as a function of the time over which diffusion occurs Δ. Three sets of data are given. The first is within 24 h of sample preparation, the second is about 3 weeks later, and the third is about 1 year later. A second data set is shown in Figure 3 for propane in TFE/PDD. The first set of data is again within 24 h of sample preparation, and the second set is about 1 year later. Figure 4 compares pentane diffusion in the 65 and 87% copolymers at a similar stage of aging, a few weeks after sample preparation.

Discussion

Each set of apparent diffusion constants taken in the 65% PDD on a given date is qualitatively similar in that the apparent diffusion constant decreases as Δ increases. The exception is the pentane data taken after 1 year in 65% PDD and the pentane data taken in 87% PDD. In both these cases the apparent diffusion constants are constant within experimental error, which is about 10%. The slight downturn at short times in the data taken after 1 year is less than experimental error and therefore of no concern. These results are similar to those reported earlier[15−17] for pentane and propane in TFE/PDD which were taken a few weeks after sample preparation. The diffusion constants reported here for propane are close to those determined from solubility and permeability,[25] which is discussed elsewhere.[10]

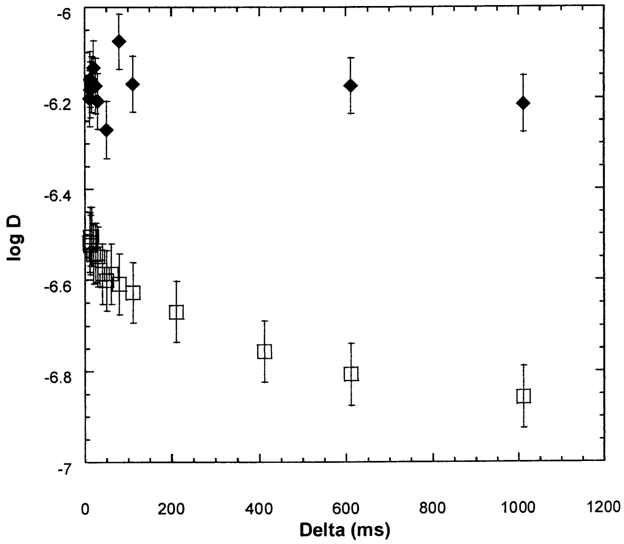

Figure 4. Apparent diffusion constant of pentane in TFE/PDD copolymer of different PDD compositions. The squares are for 65% PDD, and the diamonds are for 87% PDD.

The point of this study is to compare how the diffusion constants change when time is allowed for aging. For pentane, the apparent diffusion constant increases at all values of Δ as the sample is aged from 1 day to 3 weeks. This would correspond to faster diffusion at all length scales where length is given by

$$r = \sqrt{6D\Delta} \tag{1}$$

In terms of earlier results, this increase in diffusion constants may correspond to sample freshening upon the addition of a nonsolvent, in this case pentane.

If the results of the data after 3 weeks of aging are compared to the data after 1 year of aging, a different picture emerges. At short length scales corresponding to short diffusion times, diffusion has slowed. The fast diffusion seen at short times in the 3 week old data would be viewed as diffusion occurring in high free volume or low-density regions which are smaller in size. These regions appear to densify, leading to slower diffusion in qualitative agreement with the views of Robertson.[23] At long times or long length scales diffusion is not slowing but is about constant or possibly increasing slightly at the longest times observed.

The results for propane between freshly prepared and after 1 year of aging are similar to the pentane data. At short times diffusion has slowed and at long times has increased.

Another way to present this result is to divide the diffusion data after little aging by the data after 1 year of aging. The latter data are presumed to be relatively stable or at least only changing slowly after 1 year. Figures 5 and 6 show the pentane and propane data after only a little aging divided by the data taken after 1 year. The apparent diffusion constant at each value of Δ is divided by the corresponding value taken 1 year later. This allows a comparison of aging at different length scales. If the diffusion constant normalized in

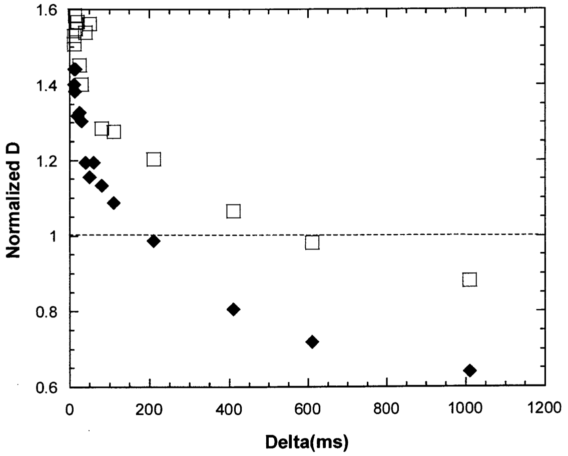

Figure 5. Normalized apparent diffusion constant for pentane in TFE/PDD (65% PDD) as a function of the time over which diffusion occurs, Δ. The apparent diffusion constant at each value of Δ at an earlier date of observation is divided by the value observed 1 year after sample preparation.

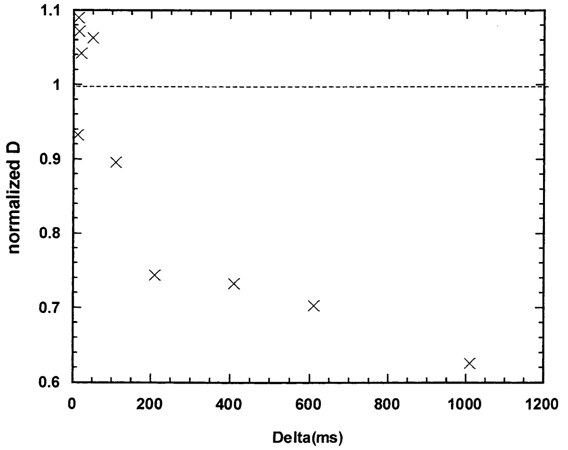

Figure 6. Normalized apparent diffusion constant for propane in TFE/PDD (65% PDD) as a function of the time over which diffusion occurs, Δ. The apparent diffusion constant at each value of Δ at an earlier date of observation is divided by the value observed 1 year after sample preparation.

this fashion is greater than one, diffusion is faster in the less aged sample, and if it is less than one, diffusion is slower in the less aged sample. A dashed line is inserted in the diagram at a value of 1 to emphasize the change from faster to slower as a function of the time scale for diffusion Δ. For both pentane and propane, the data viewed in this manner show diffusion has slowed at short diffusion times or short length scales and has increased at long diffusion times or long length scales. As mentioned, the short time behavior corresponding to a slowing of diffusion at short length scales presumably as a result of densification of smaller high free volume regions is consistent with the view of Robertson.[23]

How is one to understand the speeding up of diffusion on longer length scales as the sample ages? For pentane in TFE/PDD, the speeding up at longer times or larger length scales occurs mostly between the first 24 h and 3 weeks after the sample is prepared. The values changed rather little at larger values of Δ from 3 weeks to 1 year. In the PFG experiment, the diffusion values at long times are a reflection of the connectivity.[15−17,19−21] If free volume elements are well interconnected, diffusion is faster. Thus, the level of interconnection improves in the first 3 weeks in the presence of pentane. As already mentioned at a short length scale free volume appears to increase. At long length scales free volume cannot be increasing uniformly since only a small fraction of the total volume is associated with the highest free volume elements. Thus, the interconnected character is considered to improve. This implies that during the first 3 weeks the highest free volume elements improve their connectivity. The high free volume elements are poorly packed regions and are a minority of the sample which might be considered as defects in packing. From this point of view, the defects are clustering to improve connectivity. The defect regions are not growing larger as larger spheres since this would not lead to better connectivity if they still only constitute a few percent of all volume. They must grow as strings in a one-dimensional sense to improve connectivity. This would lead to better long-range diffusion and better permeability. Such string defect structures have been seen in computer simulations.[26]

What might be the mechanism for the production of a string of defects? The addition of the penetrant might allow for repacking of the polymer chains as some free volume regions are increased on a short length scale. Repacking of the polymer chains might lead to growth of better packed regions with the defect regions (low density, disordered, high free volume regions) pushed to the edges of the better packed regions. If the defects are forced together at the edges of better packed regions, a stringlike structure could be produced. This would give the improved long-range diffusion seen after 1 month.

The propane data taken at 1 day after sample preparation and then 1 year later are similar to the two comparable sets on pentane. Short time or short length scale diffusion slows as time passes and long time-long length scale diffusion speeds up as time passes. The effects at short times or short length scales are smaller for propane as compared to pentane. Propane could be less effective as a conditioning agent so that there is not as large an increase in high free volume regions upon the addition of penetrant, and subsequently there is less densification of the high free volume regions as time passes.

The comparison of diffusion of pentane in 65% PDD to that in 87% PDD copolymer shows an increase in diffusion and a loss of tortuousity in the 87% PDD. The 87% PDD copolymer has more high free volume regions and better connectivity between the high free volume regions—a view which is consistent with the apparent diffusion constant behavior.

Conclusions

The aging and conditioning experiments performed in these NMR studies are different from that observed in permeability studies. In the NMR experiments, exposure to the penetrant is continuous, but the level of contaminants does not increase. Loss of permeability is frequently attributed to the presence of contaminants, particularly pump oil, in the permeability experiment.[4] The penetrant in the NMR experiment can act as a “conditioning” agent, but it is different than the situation where the membrane is conditioned; the conditioning agent is then removed, and permeability is measured. Also, aging in the presence of the penetrant is not the same as aging of a dry membrane followed by the measurement of permeability. This makes comparisons between earlier studies and the NMR data difficult.

Nevertheless, two main conclusions can be made. There is an increase in diffusion at both short and long length scales when diffusion measurements made immediately after sample preparation are compared with diffusion observed 1 month later. Second, diffusion on the short length scale slows from the initial situation relative to diffusion observed 1 year later. Changes at short length scales are attributed to densification of local high free volume−low density regions. Changes over longer length scales are discussed in terms of changes in connectivity. Using eq 1 with D near 10^{-7} cm^2 s^{-1} and $\Delta = 10^{-3}-1$ s, the shortest length scales are about 0.1 μm and the longest length scales are about 10 μm. Last, increasing the amount of PDD in the copolymer reduces tortuousity and increases diffusion.

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