# Diffusion of Decafluoropentane in Amorphous Glassy Perfluorodioxole Copolymer by Pulse Field Gradient NMR Spectroscopy

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ABSTRACT: Pulse field gradient diffusion measurements were made on the decafluoropentane molecule, $CF_3CHFCHFCF_2CF_3$, in the copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (BDD). The proton spectrum consisted of two overlapping line shapes, and the decay of the echo amplitude with increasing gradient required the use of two apparent diffusion constants. The two apparent diffusion constants differed by 1.5−3 orders of magnitude depending on the length of time over which diffusion occurred. Both apparent diffusion constants were also functions of the diffusion time, indicating the presence of structure in this system that obstructs the translational motion of the penetrant molecules. The slower diffusion process ranged from $10^{-8}$ to $10^{-10}$ cm$^2$ s$^{-1}$, while the faster diffusion process ranged from $10^{-6}$ to $10^{-8}$ cm$^2$ s$^{-1}$. The product of the slower diffusion constant and the diffusion time was constant within experimental error, which is typical of restricted diffusion. Assuming a spherical geometry, the length scale was 0.7 $\mu$m. The fast diffusion constant appeared to decrease toward a plateau at large diffusion times, which is typical of tortuous diffusion in a porous medium. The slower diffusion process was considered to involve molecules in low-free-volume regions as this process was associated with the broader proton resonance and a longer spin−lattice relaxation time. The faster diffusion process was considered to involve penetrant molecules in high-free-volume regions that were interconnected. A narrower resonance with a shorter spin−lattice relaxation time was associated with this process.

## Introduction

Perfluorodioxole copolymer is a random copolymer of tetrafluoroethylene (TFE) and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (BDD) with a high glass transition temperature and very high permeability.[1−5] Among glassy polymers, only poly(1-trimethylsilyl-1-propyne) (PTMSP) is more permeable. Both of these polymers have high fractional free volumes, greater than 0.3, and contain large free volume elements according to positron annihilation lifetime spectroscopy. It has been suggested[4,6] that these free volume elements are grouped into interconnected regions in PTMSP, which leads to very high permeability. As permeability is lower in the TFE/BDD copolymer, these regions might not be as well interconnected, leading to a lower permeability even though the two polymers have comparable fractional free volumes and comparable free volume elements.

As for traditional glassy polymers, the dual-mode model has been used to characterize the solubility and permeability of penetrants in TFE/BDD copolymer.[3,5] Measurements have been made on permanent gases, hydrocarbons, and fluorocarbons. High solubility in this copolymer is mainly due to the Henry's law component, and fluorocarbons are more soluble than comparable hydrocarbons. The latter plasticize TFE/BDD copolymer so that diffusivity increases with increasing concentration. Activation energies increase with the size of the penetrant but are low relative to those of conventional glassy polymers.

Pulse field gradient NMR (PFG NMR) spectroscopy allows for the direct determination of self-diffusion constants that can be compared with the indirect diffusion information deduced from permeability and solubility experiments. PFG NMR spectroscopy is also sensitive to changes in the diffusion process as a function of length scale controlled by the experimental time scale if diffusion is obstructed by impermeable or less permeable walls.[7,8] Typically, the apparent diffusion constant (as obtained from the initial echo decay in the PFG experiment) decreases as the time scale and length scale increase. The reduction in the apparent diffusion constant results from the penetrant encountering barriers restricting the pathways for diffusion. Such behavior is observed for pentane and decafluoropentane in TFE/BDD copolymer and indicates the presence of structural features influencing diffusion on a micron length scale.[9,10] The apparent diffusion constant for pentane in this polymer decreases to a constant value as the time scale of the experiment increases, which is characteristic of diffusion in a porous material. For decafluoropentane, more complex behavior was noted. The apparent diffusion constant decreased by 2 or 3 orders of magnitude as the time scale of the experiment was increased. Superficially, this corresponded to a decreasing length scale with increasing time, which is physically unreasonable. However, the line shape consisted of two components with different widths and a slight offset in resonance frequency. The apparent diffusion constant is a combination of the whole line shape, and if the two components have different diffusion constants and different spin−lattice relaxation times, then the overall apparent diffusion constant could appear to change in an unreasonable manner as a function of the time scale of the experiment.

It is the purpose of this report to resolve the overall diffusion process into two components to determine whether a physically reasonable interpretation can be developed. This requires better signal-to-noise ratios than the original experiment, which are approached through a combination of signal averaging and a more sophisticated pulse sequence.[7] Then, a separation of the two components is undertaken through deconvolution of the two contributing signals and/or through allowance for two diffusion constants. Proton spin−lattice relax-

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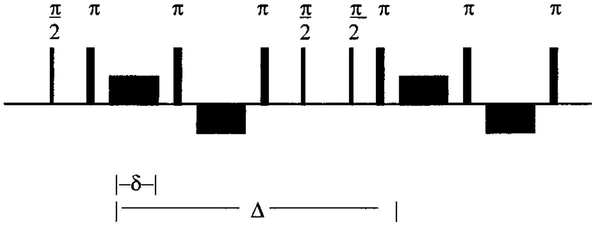

**Figure 1.** Pulse sequence used for the measurement of diffusion. The gradient pulse width, $\delta$, was 4 ms, and the direction of the gradient was reversed every other pulse as indicated in the figure. The time over which diffusion occurs, $\Delta$, was varied from 16 to 1000 ms.

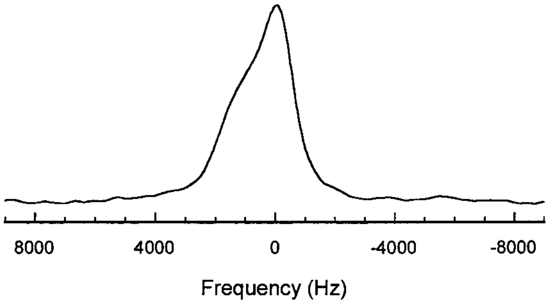

**Figure 2.** Proton line shape obtained from the echo at a low value of the gradient.

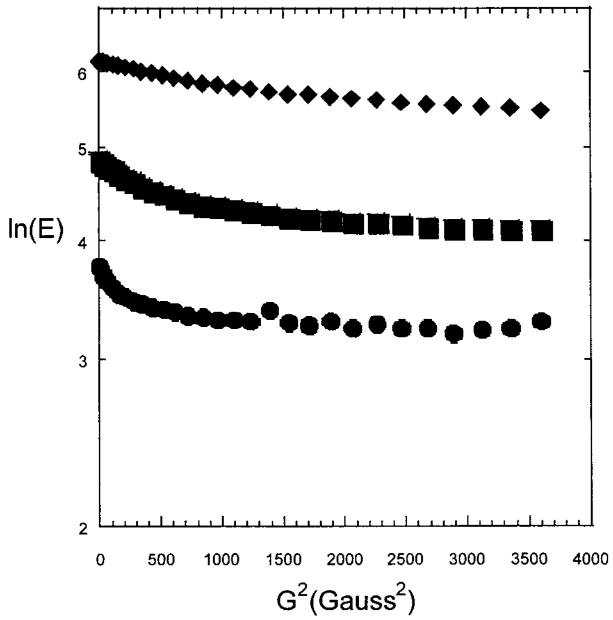

**Figure 3.** Echo amplitude as a function of the square of the gradient for three different values of $\Delta$. The top set of points is for $\Delta = 21$ ms, the middle set is for $\Delta = 111$ ms, and the lowest set is for $\Delta = 1011$ ms.

ation times of the penetrant are also measured to assist in developing an understanding of the state of the penetrant molecules in this system.

## Experimental Section

A 20 wt % decafluoropentane sample was prepared by adding the appropriate amount of this penetrant to a cast film of TFE/BDD. The sample was then sealed in a 5-mm NMR tube. The decafluoropentane has the structure $CF_3CHFCHFCF_2CF_3$. The film was cast from a perfluoroheptane solution of the copolymer and was dried to constant weight in a vacuum oven at 50 °C. 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 the next few 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 $\Delta$ indicated in the modified stimulated echo pulse sequence[7] shown in Figure 1. Only the initial decay of the echo amplitude was monitored typically to a level of less than 50% of the original amplitude. At a given time $\Delta$, the quantity $q = \gamma\delta g/2\pi$ was varied by changing the gradient amplitude, $g$, from 0 to 60 G/cm. The time, $\Delta$, ranged from 16 ms to 1 s. A fixed value of $\delta$, the length of the gradient pulses, of 4 ms was used for a given determination of the apparent diffusion constant. The apparent diffusion constant was calculated from the slope of a plot of the logarithm of the echo amplitude versus $g^2$. 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. Proton spin−lattice relaxation times were also measured on the penetrant in the TFE/BDD film using a $180-\tau-90$ pulse sequence.

## Results

Figure 2 displays a proton spectrum of decafluoropentane in the TFE/BDD film. The line shape consists of two components, one broad and one narrow, with a spectral offset of about 1 kHz between the two. Figure 3 shows three representative plots of echo amplitude versus $g^2$. If diffusion is characterized by a single apparent diffusion constant, these plots should be exponential decays, but they are not. At values of $\Delta$ larger than about 50 ms, the plots indicate the presence of two diffusion constants, which is reasonable given the presence of two components in the line shape.

To analyze the echo decay with the square of gradient amplitude, two approaches were taken. First, a deconvolution of the line shape into two components, each with a different diffusion constant, was attempted. Reasonable fits were obtained if the line widths and peak position were allowed to float. The narrower line has a width of about 900 Hz, and the broader line has a width of about 1500 Hz. However, the line widths obtained from deconvolution sometimes changed systematically as the square of the gradient increased. They could be held constant during the deconvolution process, but frequently, the deconvolved plots of the logarithm of the echo amplitude versus the square of the gradient displayed considerable scatter. In all cases, though, the narrower line was associated with faster diffusion, and the broader line was associated with slower diffusion.

At long times, the plots are obviously bimodal, and fits could be obtained by simply allowing for two diffusion constants and fitting to a double exponential. In this second approach, the general form of the fitting equation used is

$$E(q) = P_{\mathrm{fast}} \exp(-4\pi^2 q^2 D_{\mathrm{fast}}\Delta) + P_{\mathrm{slow}} \exp(-4\pi^2 q^2 D_{\mathrm{slow}}\Delta) \quad (1)$$

Because the two diffusion constants differed by 1.5−3 orders of magnitude, a reliable separation of the two components was obtained, especially at large values of $\Delta$ where the two diffusion constants differed by 2−3 orders of magnitude. It was noticed that the product of the slower diffusion constant and $\Delta$ was constant for large values of $\Delta$. Estimates of the slower diffusion constant could also be obtained by simply fitting the last part of the decay curves at large $\Delta$,[9] and values similar

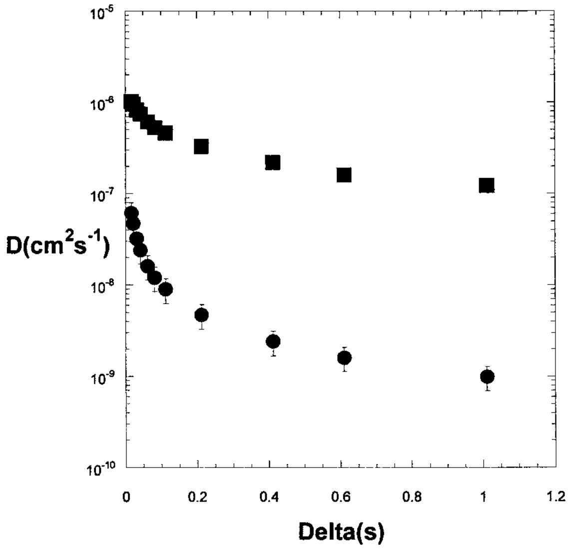

**Figure 4.** Apparent diffusion constants for the two components as a function of diffusion time Δ.

**Table 1. Apparent Diffusion Constants for Decafluoropentane in TFE/BDD Copolymer**

| Δ (s) | $D_{\text{fast}}$ $10^6$ (cm$^2$ s$^{-1}$) | $P_{\text{fast}}$ | $D_{\text{slow}} \times 10^8$ (cm$^2$ s$^{-1}$) | $D_{\text{fast}}\Delta \times 10^8$ (cm$^2$) | $D_{\text{slow}}\Delta \times 10^{10}$ (cm$^2$) |
|---|---|---|---|---|---|
| 0.0162 | 1.03 | 0.39 | 6.1 | 1.7 | 10 |
| 0.0212 | 0.96 | 0.40 | 4.7 | 2.0 | 10 |
| 0.0312 | 0.83 | 0.41 | 3.2 | 2.6 | 10 |
| 0.0412 | 0.75 | 0.43 | 2.4 | 3.1 | 10 |
| 0.0612 | 0.61 | 0.44 | 1.6 | 3.8 | 10 |
| 0.0812 | 0.53 | 0.44 | 1.2 | 4.3 | 10 |
| 0.111 | 0.46 | 0.44 | 0.90 | 5.2 | 10 |
| 0.211 | 0.33 | 0.41 | 0.47 | 6.9 | 10 |
| 0.411 | 0.22 | 0.36 | 0.24 | 9.0 | 10 |
| 0.611 | 0.16 | 0.36 | 0.16 | 9.8 | 10 |
| 1.011 | 0.12 | 0.32 | 0.099 | 12.3 | 10 |

to those from in the double exponential fits were obtained. Again, for values of Δ between 100 and 1000 ms, the product of the slower diffusion constant and Δ was constant. The two procedures yielded values of the slower diffusion constant that were within about 30% of each other. At smaller values of Δ, the values of the slower diffusion constant were less reliably obtained, but the product of the slow diffusion constant and Δ remained constant within the uncertainty of the determination. Given that the slow diffusion constant times Δ was a constant within our ability to determine it, the value of the product was fixed based on the fits of the long-time tails of the decay curves from 100 to 1000 ms. A value of the product $D_{\text{slow}}\Delta$ determined in this fashion is $(10 \pm 3) \times 10^{-10}$ cm$^2$. Then, double exponential fits were repeated with the slow diffusion constant fixed based on the value of the product set by fitting the long-time tails. Table 1 contains the values of $D_{\text{fast}}$ and $D_{\text{slow}}$ as functions of Δ, as well as the product of the diffusion constants times Δ obtained in this manner. Figures 4 and 5 display the diffusion constants as functions of Δ and the product of the diffusion constants and Δ. The fractional population of the fast component, $P_{\text{fast}}$, is also listed. The values of $D_{\text{fast}}$ determined by the fits are stable and only vary modestly, by about 10%, depending on the assumptions made concerning the slow component. The slow component is less well defined by the data and depends somewhat on the analysis approach as just discussed. The uncertainty of 30% for the slow component includes the dependence on the analysis approach. The values of $D_{\text{slow}}$ at short times have an even greater uncertainty, but the assumption of constant value of the product of $D_{\text{slow}}$ and Δ is valid at all times within experimental error.

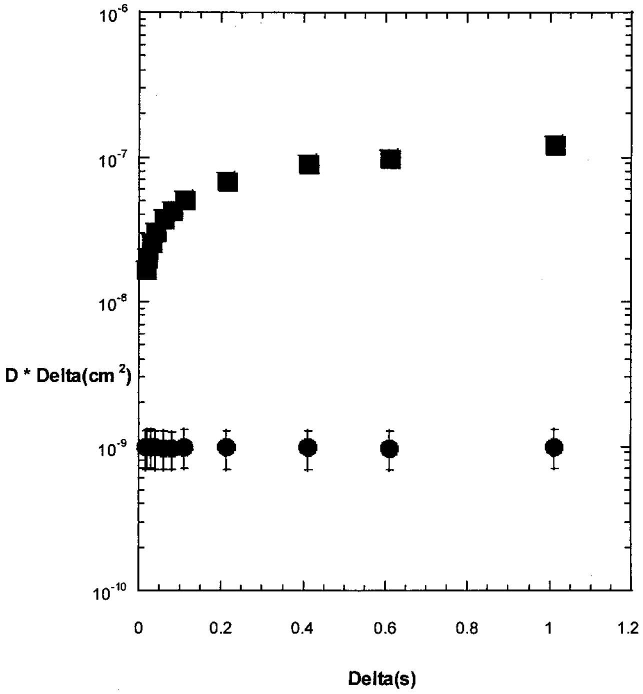

**Figure 5.** Product of the diffusion constants and the diffusion time versus the diffusion time Δ.

The spin−lattice relaxation times of the proton resonance were measured. The narrow component of the line shape had a value 0.66 s, and the broad component of the line shape had a value of 1.6 s. The line shape was deconvolved to obtain spin−lattice relaxation times for each of the two components. The effects of the differences in $T_1$ are also apparent in the dependence of $P_{\text{fast}}$ on Δ in Table 1.

## Interpretation

The separation of the diffusion process for decafluoropentane into two components resolves the apparent unphysical behavior that the product of the apparent diffusion constant from a fit using a single diffusion constant and the diffusion time, Δ, decreased. Figure 5 shows a plot of the product of the $D_{\text{fast}}$ and $D_{\text{slow}}$ with Δ individually, and now the length scale associated with $D_{\text{fast}}$ increases, and the distance associated with $D_{\text{slow}}$ is a constant. Both of these results are reasonable.

However, the question remains whether any physical sense can be attributed to the presence of two components relative to the properties of the copolymer. It has been suggested[1−6] that there are high-free-volume regions and low-free-volume regions in this type of high-permeability, high-glass-transition-temperature polymer. The high-free-volume regions are disordered regions containing the large, approximately 0.6-nm, sorption sites. The low-free-volume regions are considered to have smaller free volume elements more like those of traditional glassy polymers. The slow diffusion component would be associated with a lower-free-volume region. The spin−lattice relaxation time of the broad component in the proton line shape is longer, indicating less rotational mobility, assuming rotational motion is on the slow side of the $T_1$ minimum. Also, in as much as deconvolution was successful in the diffusion experiment, the broad component was the slow-diffusing component. The breadth of this component is also consistent with slower rotational motion. Thus, the line width, the spin−lattice relaxation experiment, and the diffusion experiment are consistent with the view that one type of penetrant molecule is in a lower-free-volume region that reduces both rotational and translational mobility.

The translational mobility of decafluoropentane in the lower-free-volume regions appears to be restricted diffusion as the product of $D_{\mathrm{slow}}$ with $\Delta$ is a constant.[8] Thus, the free volume in this region does not appear to be interconnected, but rather, it appears to be isolated. The size of the domain over which restricted diffusion occurs can be estimated from the formula

$$D\Delta = a^2/5 \qquad (2)$$

This leads to a value of $a = 0.7\ \mu$m, which differs only slightly from the estimate of 0.6 $\mu$m made from the value of the diffusion constants at large $\Delta$ in the initial report.[9] Equation 2 assumes a spherical geometry.

The fast component would be identified with penetrant molecules in the high-free-volume regions. This component is associated with the narrower component of the line shape with the shorter spin−lattice relaxation and the larger diffusion constant. All of these aspects are consistent. One might also note that fluorocarbons plasticize the TFE/BDD copolymer,[3] so this component might also have increased rotational and translational mobility because of localized plasticization. The plot of $D_{\mathrm{fast}}$ versus $\Delta$ in Figure 4 appears to be decreasing toward a plateau value of around $1 \times 10^{-7}$ cm$^2$ s$^{-1}$. This behavior is similar to that of the apparent diffusion constant in a porous system[11−13] undergoing tortuous diffusion. Similar results were obtained with pentane in the TFE/BDD copolymer,[10] but the results for pentane could be explained by the presence of only one component. The decay of the logarithm of the echo amplitude with the square of the gradient was linear for pentane, and the line shape did not appear to consist of two components. Possibly all of the pentane was in interconnected free volume regions as the smaller size of pentane might allow ready movement between all regions. Also, pentane is not a solvent for the TFE/BDD copolymer, whereas decafluoropentane is more apt to dissolve into low-free-volume regions in addition to sorbing into the high-free-volume regions.

If one assumes that the fast component is undergoing tortuous diffusion, an estimate of tortuosity can be made. At 60 °C, the diffusion constant of pure decafluoropentane is $4 \times 10^{-5}$ cm$^2$ s$^{-1}$, and a rough estimate of the apparent plateau of $D_{\mathrm{fast}}$ in Figure 4 is $1 \times 10^{-7}$ cm$^2$ s$^{-1}$. The tortuosity,[10−13] $\alpha$, is defined as

$$\alpha = D/D_0 \qquad (3)$$

where $D$ is the plateau value of the diffusion constant at large $\Delta$ and $D_0$ is the diffusion constant of the pure penetrant. This leads to a value of $\alpha = 4 \times 10^2$. This is smaller than the value estimated from the pentane data, which was $1 \times 10^3$, but as mentioned, there was only a single component present in that analysis. Pentane might have moved among more of the free volume regions, leading to a single component, but this process could lead to a more tortuous path.

## Discussion

A reasonable interpretation of the translational diffusion of decafluoropentane in TFE/BDD copolymer can be developed by assuming there are two dynamic states of the penetrant molecule. The decay of the echo amplitude with increasing square of the gradient amplitude has two distinct components at large values of the diffusion time $\Delta$, and the proton line shape consists of two components. The more mobile state is associated with faster translational diffusion, and faster rotational diffusion is associated with a narrower proton line shape. Given the expectation that there are high-free-volume regions in the TFE/BDD copolymer, the more mobile penetrant is assumed to reside in these regions. The decafluoropentane might also plasticize the copolymer in this region, further enhancing mobility. The less mobile penetrant is assumed to reside in lower-free-volume regions of this polymer.

The presence of two components might also be related to the use of the dual-mode model to describe sorption and permeability in this system, although measurements of this type have not been performed on the decafluoropentane used in this study. The view that there are two domains in the copolymer with significantly different translational mobilities is consistent with the use of the description of tortuous diffusion for the more mobile component. The low-free-volume regions have sufficiently slower diffusion, 1.5−3 orders of magnitude, that they might reasonably be regarded as isolated by a wall. Diffusion over macroscopic distances would likely be dominated by penetrant diffusion through the high-free-volume regions. If exchange is slow between the two regions, as appears likely since the line shape consists of two components, tortuous diffusion for the mobile component would be plausible. Modeling of the diffusion process with a variety of topologies and exchange rates might also be informative.

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