Study of Cyclic Sorption–Desorption into Poly(methyl methacrylate) Rods Using NMR Imaging

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Received July 11, 1991; Revised Manuscript Received October 10, 1991

ABSTRACT: A proton NMR imaging study has been conducted on the diffusion of methanol into poly(methyl methacrylate) (PMMA) after the cyclic absorption and desorption of water and methanol into PMMA. It was found that the diffusion of methanol into PMMA increases with the number of cycles and the diffusion process changes from Case II to Fickian. This may be attributed to the formation of voids caused by the removal of unreacted monomers and oligomers during the desorption of water and methanol between cycles. These voids increase the porosity within the PMMA and allow for increased diffusion. It was also found that, as the water content in PMMA increased, the rate of diffusion of methanol into the PMMA also increased. At the higher water contents, the diffusion of methanol also changed from Case II to Fickian. This may be due to the plasticizing effect of water on the PMMA which increases the polymer chain mobility to allow increased solvent penetration. Finally, the diffusion coefficients were determined for the PMMA samples in which Fickian diffusion occurred, and diffusion front velocities were calculated for the samples in which Case II diffusion was identified.

Introduction

Polymers in many different applications are exposed to a variety of chemical environments during their lifetime. These environments can subject the polymer to several penetrants at any given time as well as to the cyclic effects of absorption–desorption during its lifetime. This cyclic diffusion can have disasterous effects on the mechanical properties of the polymer. It is therefore important to characterize the diffusion process of these multicomponent systems into polymeric materials so that the physical properties of the polymers can be modified accordingly. Nuclear magnetic resonance imaging (NMRI) has been established as a method which can be used to monitor the diffusion of penetrants into polymers.[1–10] One of the advantages of NMRI that has been elucidated in these studies is its ability to continuously monitor the diffusion process without interruption.[1–10]

Diffusion can be categorized into three general types: Fickian, anomalous, and Case II. Fickian diffusion describes the relationship of the mass flux of a penetrant to the concentration gradient present and can be characterized by an exponential decay in concentration with penetration into a material. The main feature of Case II diffusion is the constant concentration front throughout the imbibed region, while anomalous diffusion falls between these extremes. Fickian diffusion often occurs in polymers which are at temperatures above their glass transition (T_g). This is because the polymer chains are in the rubbery state and possess sufficient mobility in which to allow solvent penetration. Fickian diffusion also commonly occurs when the activity of the solvent is sufficiently low and the diffusion therefore occurs only in the free volume of the polymer. Case II and anomalous diffusion are found primarily in polymers which are below their glass transition temperatures. At these lower temperatures the polymer chains are not sufficiently mobile to immediately accommodate the solvent. Therefore the polymer dynamics become important for the transport of small molecules through the matrix.[11]

Alfrey et al.[12] classified the various types of diffusion according to their relative rates of diffusion and polymer relaxation. For Fickian diffusion, the diffusion rate is much slower than the polymer relaxation processes. However, with Case II diffusion the diffusion rate is much faster than the polymer relaxation processes Contrastingly, anomalous or non-Fickian diffusion is said to occur when the diffusion and polymer relaxation rates are comparable.

One of the most common applications of poly(methyl methacrylate) (PMMA) is its use in the manufacture of aircraft windows. In this application the polymer experiences a variety of environmental conditions under which it must perform. One such condition is its exposure to a wide range of relative humidities and various organic solvents. It has been shown[13] that the craze resistance of PMMA significantly decreases after exposure to water. This decrease in the craze resistance is attributed to the fact that water has a plasticizing effect on PMMA. This plasticizing effect lowers the T_g of PMMA and therefore increases the mobility of the polymer chains. This increase in mobility permits an increase in the diffusion rate.

The diffusion of methanol into PMMA has been characterized as Case II[5–8,14–18] at ambient temperatures. Thomas and Windle made an extensive study of this system[14–18] and used it to predict the characteristics of Case II diffusion. They described the following four basic characteristics of Case II diffusion in polymers. The first characteristic is a rapid increase in solvent concentration between the inner glassy core region and the swollen region of the polymer that is also known as the sharp front. The second characteristic is that the solvent concentration is nearly constant in the swollen region behind the advancing solvent front. The third characteristic is that the sharp front between the glassy core and the swollen region advances at a constant velocity. Finally, the fourth characteristic is the existence of an induction time of Fickian concentration profile which precedes the sharp front into the glassy core. The first three characteristics were presented by Alfrey[19] while the fourth is from recent theories by Thomas and Windle,[14] Hui et al.,[20,21] and Laskey et al.[22]

Although the diffusion of methanol into PMMA has been examined by a number of groups,[5–8,14–18,23] little attention has been given to the effect of the water content within PMMA on the diffusion of methanol. The diffusion of water into PMMA has been the subject of a number of investigations.[24–30] It is generally influenced by plastici-

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zation[31,32] and by the immobilization of water molecules in clusters.[25,26] In this study, the diffusion of methanol will be examined for various water contents within PMMA. The effects of cyclic absorption and desorption on the diffusion process will also be investigated.

Experimental Section

Poly(methyl methacrylate) (PMMA) rods with diameters of 0.25 in. (6.25 mm) were purchased from Commercial Plastics and Supply Corp., Cleveland, OH. These PMMA rods were cut into lengths of approximately 51 mm, resulting in a length to a diameter ratio (*L:D*) of 8:1. With L:D = 8:1, the diffusion can be characterized as occurring in a semi-infinite cylinder (i.e., diffusion from the ends can be considered negligible).

The penetrants used were distilled and deionized water, methanol (MeOH), and hydroxy-deuterated methanol (MeOD) which was 99.5 atom % deuterated. The methanol and hydroxy-deuterated methanol were purchased from Aldrich Chemical Co.

The PMMA rods were placed under vacuum at 60 °C in order to eliminate any water or unreacted monomer present in the material. This was accomplished by monitoring the weight loss until no further measurable weight change was apparent (approximately 2 weeks). This final weight was then considered to be the zero weight point for all diffusion experiments. The weight loss was approximately 0.55 wt % and depended on the processing conditions of the PMMA and the humidity.

The dried PMMA rods were placed in water and allowed to absorb various amounts of water. The water-swollen PMMA rods were then placed in methanol (MeOH). The subsequent experiments were performed in two different ways.

The first method involved varying the water content of the PMMA rods and then allowing the continuous diffusion of MeOH into the PMMA rods until the MeOH reached a saturation point. This therefore allowed the effect of the water content of PMMA on the diffusion of methanol to be monitored.

The second method involved varying the water content of the PMMA samples and then allowing only an equal molar quantity of MeOH to be absorbed. The PMMA rod was then placed in a vacuum oven at 60 °C to dry out the rod until no further weight loss was apparent. The absorption of water and MeOH was then repeated for a second cycle.

All weight gain measurements were repeated using MeOD in place of MeOH and gave corresponding weight gain results when adjusted for the difference in weight between the deuterated and protonated species. In the imaging experiments, MeOD was used so that only the proton signal from the methyl resonance would be observed. The proton signal from the water imbibed in the PMMA could not be resolved; therefore, only the methyl resonance of the MeOD appears in the proton NMR images.

All experiments were made at 298 ± 1 K. The imaging experiments were controlled with a thermocouple in the sample chamber and a Bruker variable-temperature unit. The weight gain measurements were maintained in a constant-temperature bath.

The NMRI experiments were performed on a Bruker MSL-300 spectrometer with a superwide bore (150 mm), 7.0-T superconducting magnet and a microimaging accessory. A 25-mm radio-frequency coil insert was used, and the samples were placed in three 10-mm NMR tubes contained within a 25-mm NMR tube. In this way, PMMA rods with the three different initial water contents or degrees of cycling could be imaged simultaneously. The PMMA rods lay along the direction of the magnetic field (*z*-direction) so that radial diffusion into the rods (*xy*-plane) could be imaged.

The images were acquired using the FLASH pulse sequence, as shown in Figure 1.[33] FLASH is an acronym for Fast Low-Angle SHot, which indicates the use of pulses that give short tip angles (15° in our case) instead of the usual 90° and 180° angles.[33] With the use of short tip angles, less time is required for the magnetization to relax back to equilibrium between acquisitions. The time needed to acquire an image using the FLASH pulse sequence is less than the time needed to acquire a spin-echo image which requires waiting 5 times T_1 between acquisitions. The FLASH pulse sequence generates a gradient field echo by gradient reversal in the read direction (*x*-direction). In contrast, the more common spin-echo technique utilizes a 90°–τ–180° pulse pair to generate the necessary spin echo.

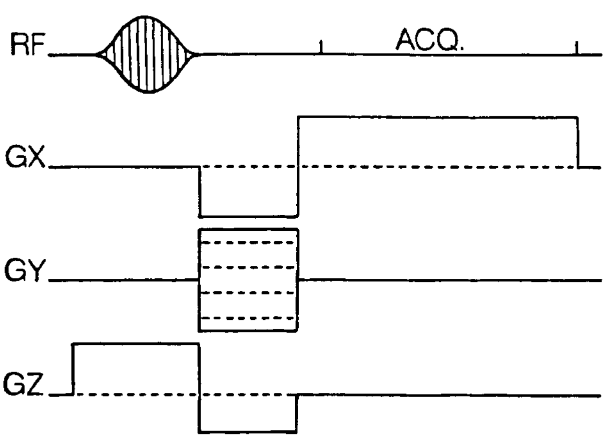

Figure 1. Timing diagram for the FLASH pulse sequence.

The gradient echo time (TE) is 6 ms, and the repetition time (TR) is 50 ms. Slice selection (*z*-direction) is used to generate a 1-mm-thick *x*–*y* slice. With 256 phase encoding steps in the *y*-direction, CYCLOPS phase cycling is used to yield a 256 × 256 pixel image within 1 min. Signal averaging is performed 10 times resulting in a total experimental time of 10 min. This total time is shorter than the time necessary for the diffusion to proceed by a single pixel length. All front movement takes place within a pixel dimension which is less than 100 μm so there is no distortion of the images due to the movement of the solvent fronts.

The FLASH pulse sequence was used instead of some form of the chemical shift imaging (CSI). This was due to the overlap of the chemical shifts of water and methanol and the difficulty in sufficiently eliminating the signal from one component in order to observe the other. In addition, the time frame of the CSI experiment which is similar to that of the spin-echo experiment requires 5 times T_1 between acquisitions. If 5 times T_1 is used (T_1 of methanol is approximately 5–9 s[34]), each experiment would take from 7 to 13 h in order to acquire a 256 × 256 image. For diffusion experiments, this would cause distortions in the image due to the solvent movement. The FLASH experiment in our case takes 1 min per image and can be signal averaged in less time than it would take for the diffusion front to proceed by a single pixel dimension. This would yield an image with a greater signal to noise ratio than a corresponding chemical shift image and would not contain distortions due to the solvent front movement during the imaging experiment.

Results and Discussion

Initial experiments involved the analysis of weight gain measurements for a variety of water contents in PMMA. Weight gain versus time plots of methanol diffusion into PMMA samples with various weight percents of water (0.6–1.25 wt %) are shown in Figure 2. It can be seen that, with an increase in the water content of PMMA, the methanol diffuses at a faster rate. The plasticizing effect of imbibed water in PMMA increases the mobility of the polymer chains. This increased mobility allows the PMMA to more easily accommodate the diffusion of methanol and therefore increases the diffusion rate.

There is an initial lag time in the mass uptake followed by a region of linear dependent with time. This indicates that the methanol is following Case II behavior after an initial time period of anomalous diffusion. For small percentages of the total mass uptake at infinite time, a linear dependence with time would be expected for Case II diffusion into a cylinder.

As the water content of the PMMA samples reaches 1.0 and 1.25 wt %, the methanol diffusion becomes more anomalous. This is evident in the slight downward curvature developing at these higher water contents. The PMMA may be sufficiently plasticized by the water to

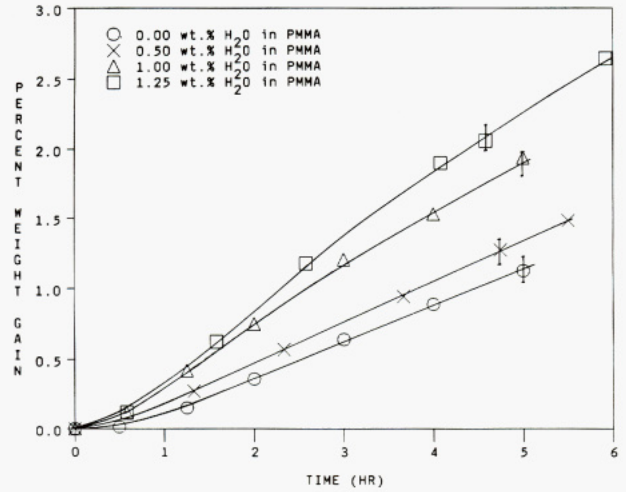

Figure 2. Weight uptake of methanol into water-soaked PMMA rods for various weight contents of water plotted versus time.

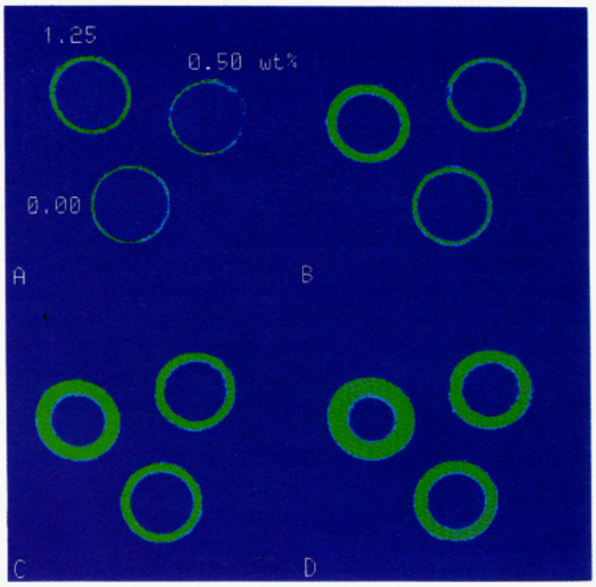

Figure 3. Proton NMR images of the diffusion of MeOD into PMMA rods which contain various water contents: (A) 2.93 h, (B) 8.25 h, (C) 18.08 h, (d) 28.42 h.

alter its relaxation behavior to the diffusion of methanol. This would therefore allow more anomalous type diffusion to occur. The increased plasticization increases the mobility of the polymer chains to permit a traditionally Case II solvent–polymer pair to act anomalous.

In addition to weight gain measurements which describe the uptake of solvent, NMRI was used to observe the solvent diffusion front movement into PMMA. When the solvent diffusion front movement is monitored, the determination of the corresponding diffusion coefficients and diffusion front velocities could be made.

In Figure 3, proton NMR images of the diffusion of MeOD in PMMA containing various water contents are shown. The FLASH images show the movement of the MeOD diffusion front within the water-soaked (0.0, 0.5, and 1.25 wt % water) PMMA rods after 2.93, 8.25, 18.08, and 28.42 h. The images include only the imbibed portion of the PMMA rods (shown in Green) and the unexposed glassy core (shown in blue). The free solvent mixtures surrounding the PMMA rods in the images were removed by computer processing. This was done to reduce the problems that occur when observing the diffusion fronts caused by the differences in the dynamic range of intensities between the free solvent and the imbibed solvent. As can be seen in these images, the MeOD diffuses into the PMMA rod containing 1.25 wt % water most rapidly while diffusions into the non-water-soaked PMMA rod and the PMMA rod containing 0.5 wt % water are the slowest. This result was anticipated from the previous weight gain measurements.

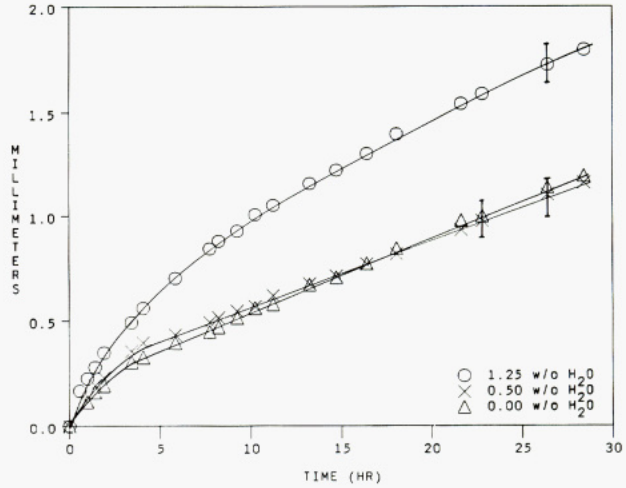

Figure 4. Diffusion front movement of MeOD into PMMA versus time for PMMA with water contents of 0.0, 0.5, and 1.25 wt %.

From this set of images we can now monitor the solvent front movement of MeOD into the PMMA rods for varying degress of initial water content. The movement of the solvent front of MeOD into PMMA versus time is shown in Figure 4 of the 0.0, 0.5, and 1.25 wt % water content PMMA rods. As expected from Figure 2, the methanol diffusion into PMMA increases as the water content of the PMMA increases. In addition, after an initial period of anomalous diffusion there is a linear dependence between the solvent front movement and the time of diffusion for the PMMA rods containing 0.0 and 0.5 wt % water. This indicates that the diffusion of MeOD into PMMA in this linear region is Case II.[12,14] This result was anticipated since the diffusion of methanol has been previously determined in the literature to be Case II.[5-8,14-18]

The slopes of the curves in Figure 4 for the 0.0 and 0.5 wt % water in PMMA yield solvent front velocities of 10.0 and 8.9 nm/s, respectively. These values are higher than those found by Thomas and Windle[15] and Weisenberger and Koenig[5,7] because the drying treatment and water content of PMMA was not taken into account in these previous experiments. The removal of water and unreacted monomer leads to a greater level of porosity within the PMMA and therefore increases the diffusion rate.[24]

Case II diffusion is most often encountered for solvent diffusion into a polymer that is below its glass transition temperature. Since the diffusion of methanol into PMMA with water contents of 0.0 and 0.5 wt % is Case II, the water content within PMMA has not sufficiently plasticized the polymer to affect the type of diffusion process which is taking place. In these cases, the polymer relaxation rate due to the solvent penetration remains much slower than the solvent diffusion rate.[11]

As shown in Figure 4, when the water content of PMMA is increased to 1.25 wt %, the MeOD diffusion front movement no longer advances linearly with time. The diffusion front movement of MeOD is plotted against the square root of time in Figure 5. After an initial lag of anomalous diffusion there exists a linear dependence which indicates Fickian diffusion. Thus as the water content of

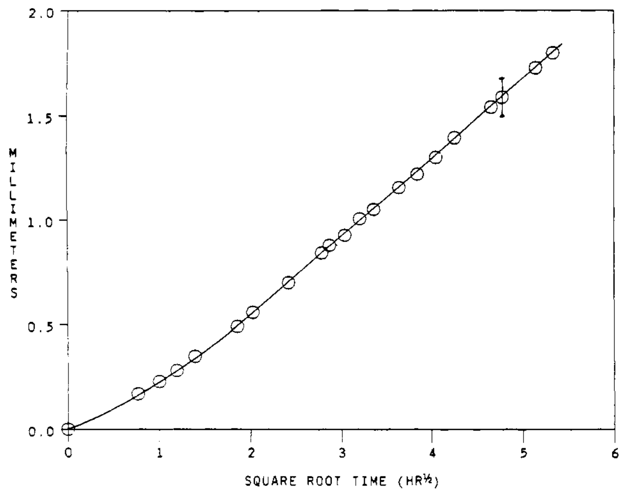

Figure 5. Diffusion front movement of MeOD into PMMA with a weight percent of water of 1.25 versus the square root of time.

the PMMA increases, the diffusion of MeOD changes from Case II to Fickian. This indicates that sufficient plasticization has taken place to increase the polymer segmental mobility to allow greater solvent penetration. The PMMA is therefore able to relax and accomodate the solvent almost immediately, and the movement of the solvent is not inhibited by the rate of polymer relaxation. This would explain the fact that the type of diffusion shifts from Case II for samples with water contents of 0.75 wt % or below to Fickian for samples with water contents of 1.0 wt % or above.

The translational diffusion coefficient, D_{MWP}, for the diffusion of MeOD into PMMA is equal to the square of the slope of a plot of the solvent front movement versus the square root of the time of diffusion. From Figure 5 it was therefore determined that, for a sample with a water content of 1.25 wt %, the translational diffusion coefficient is 3.9×10^{-7} cm^2/s. This is greater by an order of magnitude than the value of 2.4×10^{-8} cm^2/s reported by Weisenberger and Koenig[7] for the diffusion of methanol into PMMA at 60 °C for as-received PMMA rods. This indicates that the water content within PMMA enhances the diffusion of methanol into PMMA more than does the temperature.

The absorption–desorption cycling of water and methanol into and out of the PMMA rods was also studied to determine its effect on the diffusion characteristics. The effect of cycling on the water diffusion is shown in Figures 6–8 for 0.6, 0.75, and 1.0 wt % water contents in PMMA, respectively. It can be seen that there is an increase in the rate of weight gain with cycling. The increase in the rate of weight gain becomes even more evident as the initial water content in PMMA increases. This can be most clearly seen by comparing Figures 6 and 8 corresponding to the 0.6 and 1.0 wt % water contents in PMMA, respectively. This may be caused by the increased plasticization of PMMA by the water for higher water contents followed by higher methanol contents. This may have created an increased porosity within the PMMA as the solvent contents were increased.

A similar effect can be seen for the cyclic diffusion of methanol into water-soaked PMMA with water contents of 0.6 and 0.75 wt % as shown by the results of weight gain versus time of diffusion plotted in Figures 9 and 10. The percent weight gain versus time of diffusion is linear with time except for an initial lag time which is anomalous.

For polymers which are in the glassy state, the removal of diluents or small molecules may cause an increase in sorption and mass transport properties of the polymer.[24] It has been found that the removal of liquids from a polymer below its T_g can increase the porosity within the polymer.[24] This would therefore result in an increase in the rate of diffusion of diluents such as water and MeOD into PMMA. It should be noted that there was no reduction in dry weight with each successive absorption–desorption cycle of water and MeOD which would indicate

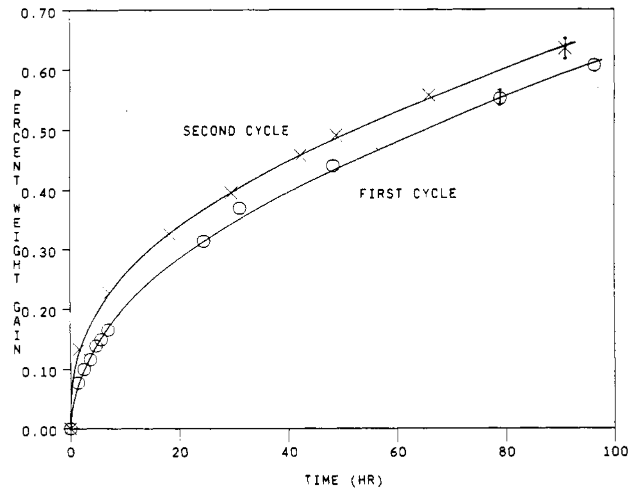

Figure 6. Weight uptake of 0.6 wt % water into dried PMMA after cyclic absorption and desorption of water and MeOD.

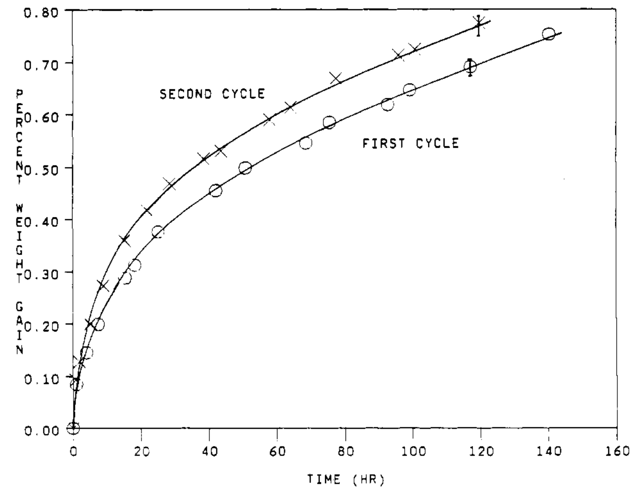

Figure 7. Weight uptake of 0.75 wt % water into dried PMMA after cyclic absorption and desorption of water and MeOD.

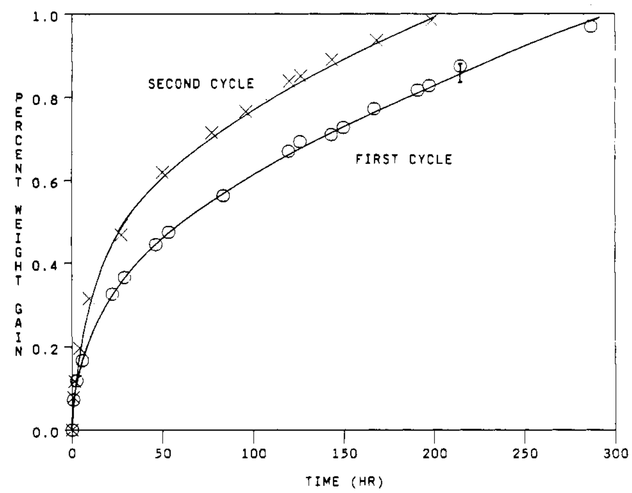

Figure 8. Weight uptake of 1.0 wt % water into dried PMMA after cyclic absorption and desorption of water and MeOD.

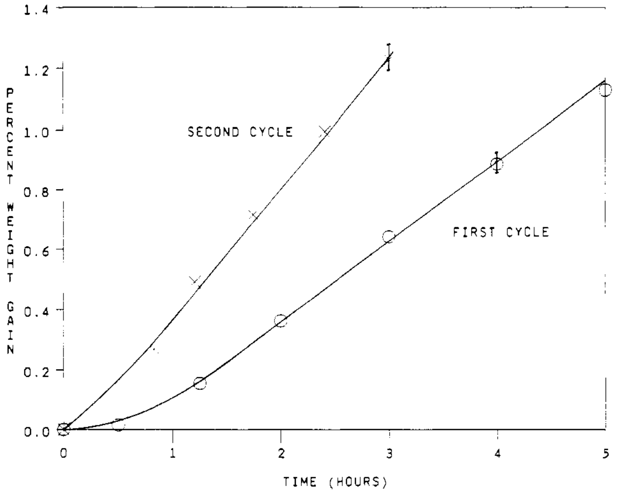

Figure 9. Weight uptake of MeOD into 0.6 wt % water in PMMA after cyclic absorption and desorption.

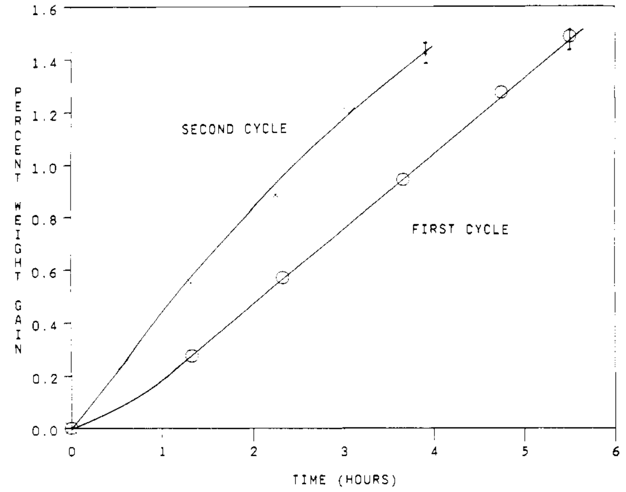

Figure 10. Weight uptake of MeOD into 0.75 wt % water in PMMA after cyclic absorption and desorption.

initially that unreacted monomer and other small molecules were not leaching out. This would also indicate that the initial drying was sufficient to remove unreacted monomers and other small molecules from the PMMA rods and none were further released by the absorption–desorption of methanol and water.

In a sense, this conditioning of the PMMA rods allows the uptake of increased amounts of solvent with each successive cycle.[35] These increased uptakes may be attributed to reduced packing or lack of reconsolidation, when the solvent is removed from the swollen polymer in the glassy state.[24,35] It may be suggested that increases in uptake are due to an increase in free volume,[35] though any increase in dry volume was not observed. It is possible that not all the methanol was removed in the drying process and there may have been some loss of other low molecular weight materials such as unreacted monomer from the PMMA sample. It has been well-established that it is difficult to remove solvents or monomers from polymers.[36] The PMMA rods were kept in a vacuum at 60 °C until no further weight loss was apparent.

It has been shown in previous experiments[24] that when PMMA is exposed to solvents such as MeOH, unreacted monomer present within the material will leach out. It is expected that, after drying the polymer to remove the solvent that has diffused into PMMA, the zero weight of the sample should decrease. However, the zero weight of the samples analyzed in this experiment remained the same. This indicates that not all of the methanol that diffused into the PMMA is removed during the drying periods between the absorption cycles.

In addition to using weight gain measurements to describe the effects of cycling on the diffusion characteristics of water and methanol in PMMA, NMRI was used to observe the solvent front movements within the PMMA rods.

In Figure 11 proton NMR images are shown of the diffusion of MeOD into three different PMMA samples. These three samples had previously been subjected to 0, 1, and 2 cycles of the absorption and desorption of MeOD. The FLASH images show the movement of the MeOD diffusion front within the PMMA rods after 5.92, 18.75, 23.70, and 31.20 h. The images are only of the imbibed region of the PMMA rod (shown in green) and the unexposed glassy core (shown in blue). The zero cycle corresponds to MeOD diffusion into dry PMMA. The 1- and 2-cycle PMMA rods each contained a 0.6 wt % initial water content before MeOD was introduced. It can be seen from the images in this figure that the diffusion of MeOD increases with an increase in the number of cycles. This corresponds to our previous weight gain experiments.

A plot of the diffusion front movement of MeOD into PMMA versus time is shown in Figure 12 for 0, 1, and 2 cycles of water and MeOD. As expected from the images, the rate of MeOD diffusion increases with cycling. A linear dependence of the solvent front movement with time can be seen for the PMMA samples subjected to 0 and 1 cycle. This indicates that Case II diffusion is occurring after an initial time period of anomalous diffusion. However, as shown in Figure 13, the MeOD front movement for the second cycle is not linear with time but rather is linear with the square root of time. After an initial lag period of anomalous diffusion, the front movement for the second cycle behaves in a Fickian manner. This indicates that the diffusion characteristics of the PMMA are altered with absorption–desorption cycling.

The slopes of the curves for the samples subjected to 0 and 1 cycle in Figure 12 yield the solvent front velocities for Case II diffusion of 12.6 and 14.5 nm/s, respectively. These values are more than twice the magnitude of those found by Thomas and Windle[15] and Weisenberger and Koenig[5,7] for methanol diffusion in PMMA. This can be explained by the fact that the water content and drying treatment of the PMMA were never taken into account in their experiments. The removal of water and the leaching out of unreacted monomer were also not considered. The increases in diffusion of MeOD may be accounted for the plasticization by water of PMMA which can be demonstrated between the 0 and 1 cycle. The increased plasticization allows for the increased rate of relaxation of the polymer chains and a greater solvent front velocity.

A plot of the solvent front movement versus the square root of the time of diffusion is shown in Figure 13. From the square of the slope of the resulting line, the translational diffusion coefficient was determined to be 4.0×10^{-7} cm^2/s. This values is greater by an order of magnitude than the value of 2.4×10^{-8} cm^2/s for the diffusion of methanol into PMMA at the elevated temperature of 60 °C reported by Weisenberger and Koenig[7] for as-received PMMA rods. This shows that, even at a low concentration, the cyclic absorption–desorption of water and MeOD has a more significant effect on the characteristics of the methanol diffusion into PMMA than does the temperature at which diffusion occurs. The value of 4.0×10^{-7} cm^2/s for the diffusion of MeOD after two cycles of

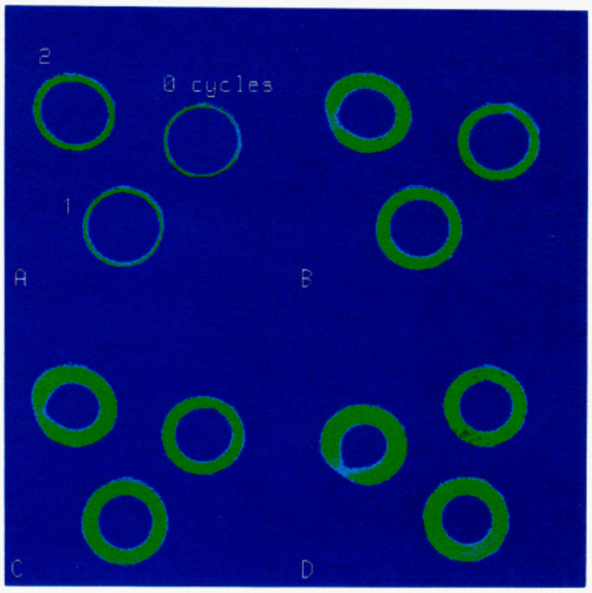

Figure 11. Proton NMR images of the diffusion of MeOD into 0.6 wt % water in PMMA rods after 0, 1, and 2 cycles of absorption and desorption; (A) 5.92 h, (B) 18.75 h, (C) 23.70 h, (D) 31.20 h.

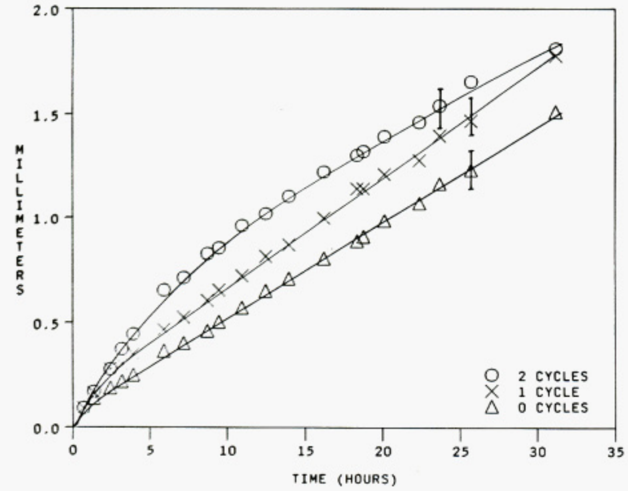

Figure 12. Diffusion front movement of MeOD into 0.6 wt % water in PMMA rods versus time after 0, 1, and 2 cycles of absorption and desorption.

absorption–desorption of water and MeOD appears to be comparable to that of MeOD diffusion in PMMA for a high water content (1.25 wt %) as reported earlier in this paper.

Conclusions

NMR imaging can be used to monitor the diffusion of penetrants into polymers and complements the results of the weight gain measurements. We have determined by NMRI that, as the water content in PMMA increases, the diffusion rate of methanol also increases. With increasing water content, the diffusion of methanol changes from Case II to Fickian. This may be caused by the polymer chains being sufficiently plasticized to allow the methanol to diffuse in more readily or possibly the hydrophilic interaction of water and methanol would attract a greater quantity of methanol to the water-soaked PMMA rods.

The cyclic effects of absorption–desorption were also investigated. With each cycle, the absorption of MeOD into PMMA increased for the 0.6 wt % water-soaked PMMA rods. Between the first and second cycles of water and methanol, the diffusion kinetics of MeOD were altered from Case II diffusion to Fickian diffusion. This change in the type of diffusion may be explained by the increase in porosity of the PMMA which occurs as increased amounts of monomer are leached out. The increase in porosity of the PMMA thus would increase the rate of diffusion. In addition, complete removal of the water and methanol that had diffused into the PMMA samples was not achieved. This residual water and methanol was therefore able to plasticize the PMMA and change the type of diffusion from Case II to Fickian.

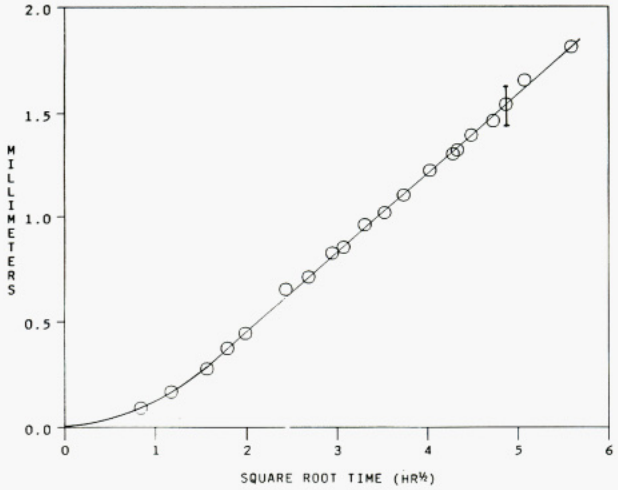

Figure 13. Diffusion front movement of MeOD into 0.6 wt % water in PMMA versus the square root of time after 2 cycles of absorption and desorption.

It has been shown that the water content within PMMA dramatically affects the diffusion of methanol. This is demonstrated by the increase in the solvent front velocities and the diffusion coefficients when compared to those found in the literature.[5,7,15] It has also been shown that there is an increase in the diffusion of methanol and water into PMMA with each absorption–desorption cycle.

Acknowledgment. We thank the National Science Foundation through the Materials Research Group for their support of this research.

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