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Study of Multicomponent Diffusion into Polycarbonate Rods Using NMR Imaging

Ronald A. Grinsted and Jack L. Koenig*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

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ABSTRACT: A proton NMR imaging study has been made of the diffusion of mixtures of acetone and methanol into Bisphenol A polycarbonate. Diffusion of acetone and methanol mixtures was observed for each component individually with the use of deuterated solvents. Fickian diffusion of acetone and methanol mixtures was observed, and separate diffusion coefficients were determined. Spin–spin relaxation times (T_2) of the penetrants were obtained across the diffused region as the diffusion process was taking place. These relaxation times were found to be constant for Fickian diffusion in contrast to the gradients in T_2 observed for Case II diffusion.

Introduction

Polymers in many different applications are exposed to a variety of chemical environments during their lifetime. These environments subject the polymer to several penetrants at any given time. It is therefore important to characterize the diffusion of these multicomponent systems into polymers so that their physical properties can be modified accordingly. NMR imaging (NMRI) can serve as a method to monitor multicomponent diffusion. One of the advantages of NMRI is its ability to continuously monitor the diffusion process without interruption.[1–7] For multicomponent systems, one has the capability with NMRI to independently study the diffusion front of each solvent and determine the corresponding individual diffusion coefficients.[8]

Although weight gain measurements can be used to determine sorption of a particular liquid into a material, this technique leaves many unanswered questions concerning the details of the multicomponent diffusion process. For instance, is the mixture diffusing together as one diffusant? Is one component diffusing more slowly than the other? Or, perhaps is one component not diffusing into the polymer at all? Is the diffusion process Fickian, Case II, or anomalous? Is the diffusion process the same for both components? With NMRI we can now differentiate between these possible cases using various pulse sequences without extensive sample preparation or sample handling.

With its superior mechanical and optical properties, polycarbonate (PC) has become an important engineering material. Because it is a highly transparent material it is used in many applications in which tough, high-clarity materials are needed (e.g., in windshields and protective eyewear). The clarity of this material is reduced when it is exposed to certain organic liquids such as carbon tetrachloride, aromatics, and ketones. These organic liquids cause crazing to occur in the PC, which results in the transparent material becoming opaque and therefore renders it unusable.

Acetone diffuses rapidly into PC and is an environmental stress-cracking fluid for PC.[9–11] The PC swells and begins cracking in a matter of hours of exposure to acetone. Methanol diffuses more slowly into PC than acetone, and there is no apparent stress cracking associated with its diffusion.[9] This work therefore involves the study of mixtures of acetone and methanol into polycarbonate. It is expected that, because the methanol diffuses into PC at a slower rate than does acetone, the methanol should reduce the tendency of the PC to craze. In preliminary tests, cracking of the PC was found to occur for all compositions of acetone and methanol in which the volume percent acetone was greater than 75%. These acetone-rich compositions were therefore not used for the imaging experiments because the cracking may alter the diffusion into PC by placing part of the polymer in tension and part in compression. This may induce nonuniform diffusion and affect the determination of accurate diffusion coefficients. However, compositions which contained greater than 75% acetone were used in the weight gain measurements.

Experimental Section

Bisphenol A polycarbonate (PC) rods with diameters of 0.25 in. (6.25 mm) were purchased from Commercial Plastics and Supply Corp. of Cleveland, OH. These PC rods were cut into lengths of approximately 51 mm resulting in a length to 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 perdeuterated acetone (AC-d_6), hydroxy-deuterated methanol (MeOD), and perdeuterated methanol (MeOH-d_4), which were all 99.5 atom % deuterated, and acetone, which was HPLC grade. All solvents were purchased from the Aldrich Chemical Co.

The PC rods were placed in 10-mm NMR tubes which contained solvent mixtures of 50:50, 65:35, and 75:25 v/o AC/MeOH. These solvent mixtures are reported on a volumetric basis. Volume percent in this case also happens to be equal to weight percent since acetone and methanol have the same density at room temperature. 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 by 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 (rf) 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, the three mixtures were imaged simultaneously. The PC rods laid 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 1a.[12] 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.[12] With the use of short tip angles, less time is required for the magnetization to relax back to equilibrium between acquisitions.

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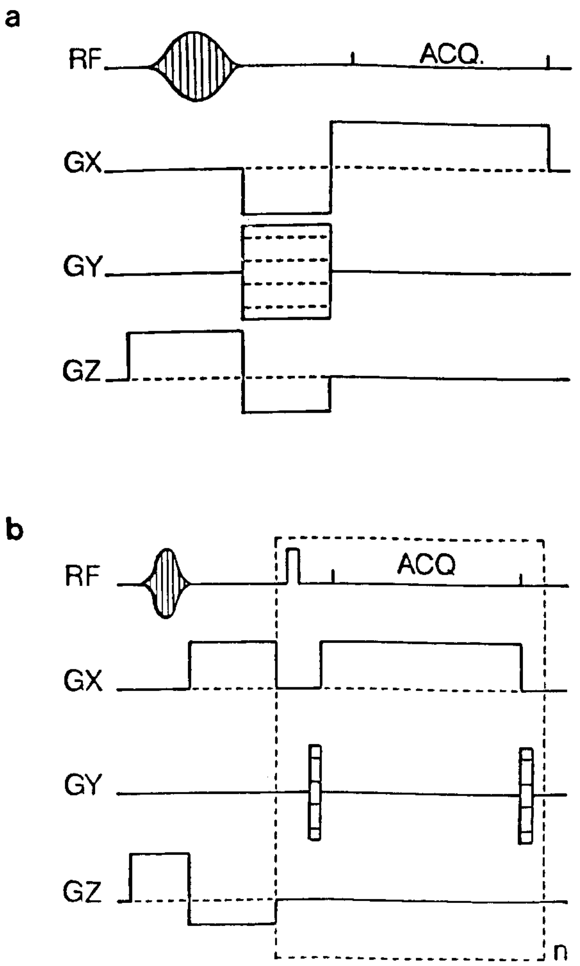

Figure 1. Timing diagram for (a) the FLASH pulse sequence and (b) the multiecho pulse sequence.

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 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. 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 25 times, resulting in a total experimental time of 25 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 chemical shift imaging (CSI). This was due to the overlap of the chemical shifts of acetone 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 T_1 between acquisitions. If 5 T_1 is used (T_1 of acetone is approximately 15 s[13]), each experiment would take over 21 h in order to acquire a 256 × 256 image. For diffusion experiments, this would be prohibitively long. The FLASH experiment in our case takes 1 min/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.

We were also interested in seeing how the mobility of the solvent changes with time as the diffusion process takes place. We therefore used the multiecho imaging experiment to determine the spin–spin relaxation time, T_2, of the solvent imbibed in the PC rod. The multiecho experiment shown in Figure 1b consists of a 90° soft or selective pulse followed by a 180° hard or non-selective pulse after a time τ. After another time τ, a spin echo then forms as in a normal spin-echo experiment. Additional 180° pulses are made 2τ from each other to generate successive spin echoes which decrease in intensity with T_2. The time frame of the experiment is slightly greater than that of a normal spin-echo experiment with the same delay between sets of echoes. In our experiment we used eight echoes to yield eight images (i.e., one for each of the echoes). These eight images can then be used to generate a T_2 image using the computer program T2EXP.[14] Instead of every pixel representing an intensity value (as in a spin-echo image), every pixel instead represents a T_2 value. In this way, T_2 values can be monitored spatially across the image as diffusion takes place.

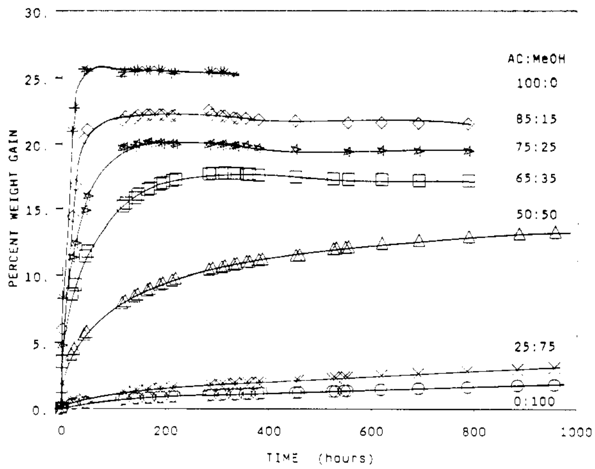

Figure 2. Weight gain versus time in hours for various concentrations of acetone/methanol diffusing into Bisphenol A polycarbonate.

NMRI was performed on two types of mixtures. The first mixture was that of acetone with fully deuterated methanol so that only the proton signal from the acetone appeared in the images. The second mixture was that of fully deuterated acetone with hydroxy-deuterated methanol so that the proton signal is generated only by the methyl group of the methanol. Both sets of mixtures were also used for weight gain measurements to confirm that diffusion occurs at the same rate regardless of whether protonated or deuterated solvents were used.

Results and Discussion

Initial experiments involved the analysis of simple weight gain measurements for a variety of acetone and methanol mixtures. Weight gain versus time in hours for various concentrations of acetone and methanol diffusing into PC are plotted in Figure 2. It can be seen that acetone diffuses and saturates PC quickly. This is accompanied by environmental stress cracking from the rapid swelling which further increases the rate by exposing more surface area for diffusion. Unlike acetone, methanol is a relatively poor solvent to PC and diffuses more slowly. The saturation content of pure methanol into PC was found to be 0.041 g of methanol/g of PC. This is consistent with the observed minimal polymer swelling. This is also supported by the reported polymer–solvent interaction parameter, χ, for the diffusion of methanol into PC. Experiments conducted by Ware et al.[9] indicated a value of $\chi = 2.06$ for this system. It is generally accepted that when the value of χ is greater than 0.5, a favorable interaction between the solvent and the polymer does not exist. In contrast, the saturation content of pure acetone into PC was determined to be 0.254 g of acetone/g of PC. This corresponds to the reported polymer–solvent inter-

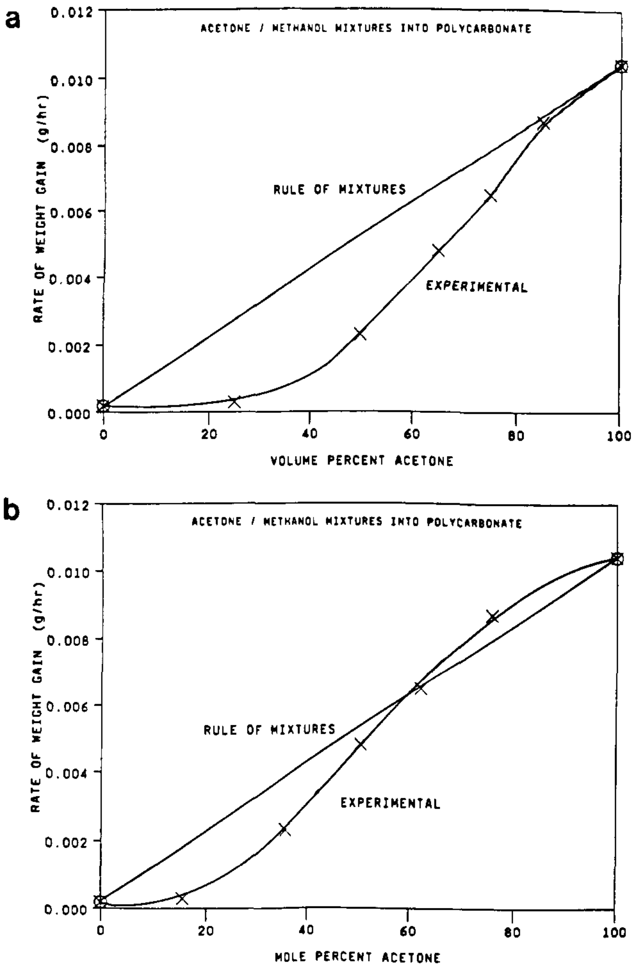

Figure 3. Weight gain rate versus (a) volume percent acetone and (b) mole percent acetone for various mixtures into PC; rule of mixtures versus experimental.

action parameter of 0.36,[9] which is less than 0.5 and therefore indicates the existence of a favorable interaction between acetone and PC. Both of these measured saturation contents are in good agreement with those reported in the literature.[9,10]

In order to determine whether a linear dependence of weight gain uptake on composition existed, the weight gain rate was plotted as a function of volume percent acetone for the various mixtures into PC, as seen in Figure 3a. The rate of weight gain was determined by dividing the weight uptake after 48 h by the total time of diffusion. If a simple rule of mixtures dependence exists, the weight gain rate would behave linearly with volume percent acetone. However, examination of the plot in Figure 3a indicates that the diffusion does not behave linearly with volume percent acetone. This was determined by the fact that the curve from the experimental results lies below the rule of mixtures line.

In Figure 3b, the weight gain rate is plotted as a function of mole percent acetone. Upon examination of this plot, it appears that there exist two distinct regions of interest. The first is when the mole percent acetone is less than 60%, the experimental curve falls below the rule of mixtures line. These compositions correspond to those that the polymer can accommodate without cracking. The second region includes those mixtures in which the mole percent acetone is greater than 60% and the weight gain rate is above the rule of mixtures line. In this region, the polycarbonate suffers stress cracking from the rapid swelling during the diffusion. The stress cracking of the rod makes it very difficult to accurately determine the diffusion coefficients. These compositions were therefore not examined by NMRI. Instead, the compositions in the first region were used because the stress cracking in the samples did not influence the diffusion process.

In Figure 4 is presented the first set of images for PC in acetone/perdeuterated methanol (AC/MeOH-d_4) mixtures of 75:25, 65:35, and 50:50 v/o AC/MeOH-d_4. The FLASH images show the movement of the acetone diffusion front within the PC rod after 2.25, 10.5, 22.25, and 30.33 h. The images include only the imbibed portion of the PC rods (shown in green) and the unexposed glassy core (shown in blue). The free solvent mixtures surrounding the PC 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 dynamic range of intensities between the free solvent and the imbibed solvent. As can be seen in these images, the 75:25 AC/MeOH-d_4 mixture diffuses most rapidly while the diffusion of the 50:50 AC/MeOH-d_4 mixture is the slowest.

Perdeuterated acetone/hydroxy-deuterated methanol (AC-d_6/MeOD) mixtures of 75:25, 65:35, and 50:50 v/o AC-d_6/MeOD were also studied. The images shown in Figure 5 were obtained from the signal collected from the methyl protons of methanol after 1.55, 7.55, 14.88, and 27.63 h. These images include only the imbibed portion of the PC rods and the unexposed glassy core. The solvent mixtures surrounding the PC rods were again removed. The signal to noise ratio is lower for the AC-d_6/MeOD mixtures than the AC/MeOH-d_4 mixtures due to the fact that there are twice as many hydrogen nuclei in the acetone of AC/MeOH-d_4 as there are in the methyl group of methanol in AC-d_6/MeOD. From these two sets of images we can now monitor the solvent front movement of acetone and methanol into the PC rods.

The movement of the solvent front of acetone into PC versus the square root of time is shown in Figure 6a for the 75:25, 65:35, and 50:50 AC/MeOH-d_4 mixtures. As expected from Figures 4 and 5, the diffusion into PC increases as the acetone content of the mixture increases. In addition, there is a linear dependence between the solvent front movement and the square root of time. This indicates that the diffusion of AC/MeOH-d_4 into PC is Fickian.[15] This result was anticipated since the diffusion of both pure methanol and pure acetone has previously been determined to be Fickian.[9] (Note, however, that the diffusion of pure acetone was found to be Fickian after an initial period in which the diffusion was reported to be anomalous.[9]) This may seem contrary to what is usually found for the diffusion of solvent into a glassy polymer which is below its glass transition temperature, T_g. Instead, either Case II or anomalous diffusion is most often encountered in this temperature region. This is because, below the T_g, the polymer chains are in the glassy state and are therefore not mobile enough to accommodate the solvent. In contrast, Fickian diffusion is prevalent above the T_g because the polymer chains are in the rubbery state and can therefore accommodate the solvent more readily. Though the T_g of dry PC is 149 °C, acetone and methanol diffuse into PC in a Fickian manner because the T_g is reduced to approximately −9 °C by the solvent ingress.[9] In this way, PC is able to relax and accommodate the solvent almost immediately allowing the solvent movement not to be inhibited by the rate of polymer relaxation.

The solvent front was also monitored for the AC-d_6/MeOD mixtures. For the mixtures of 75:25, 65:35, and 50:50 AC-d_6/MeOD into PC, similar behavior was also seen in Figure 6b where the methyl resonance of methanol was

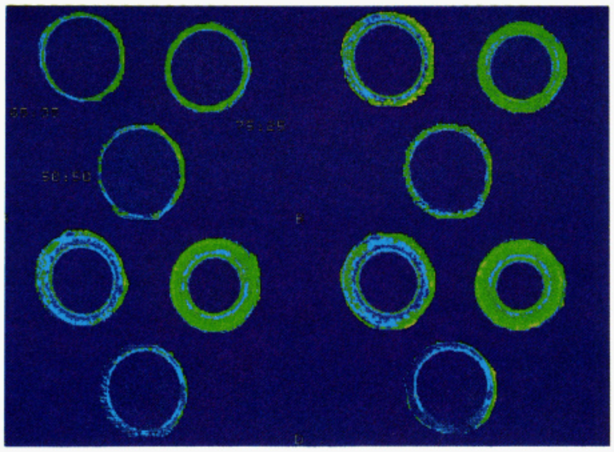

Figure 4. Proton NMR images of the diffusion of acetone/methanol-d_4 mixtures into PC rods with time: (a) 2.25 h, (b) 10.50 h, (c) 22.25 h, (d) 30.33 h.

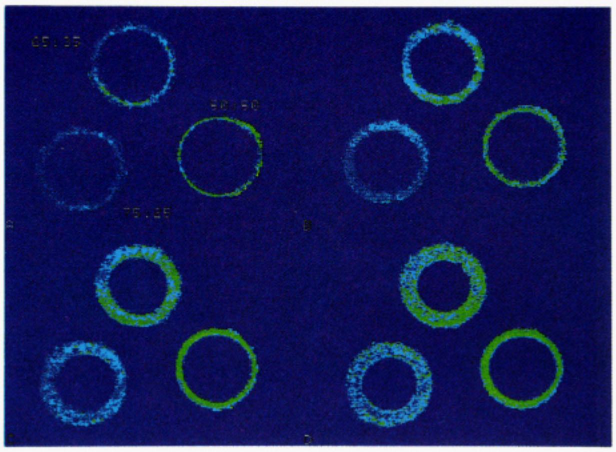

Figure 5. Proton NMR images of the diffusion of acetone-d_6/methanol-d mixtures into PC rods with time: (a) 1.55 h, (b) 7.55 h, (c) 14.88 h, (d) 27.63 h.

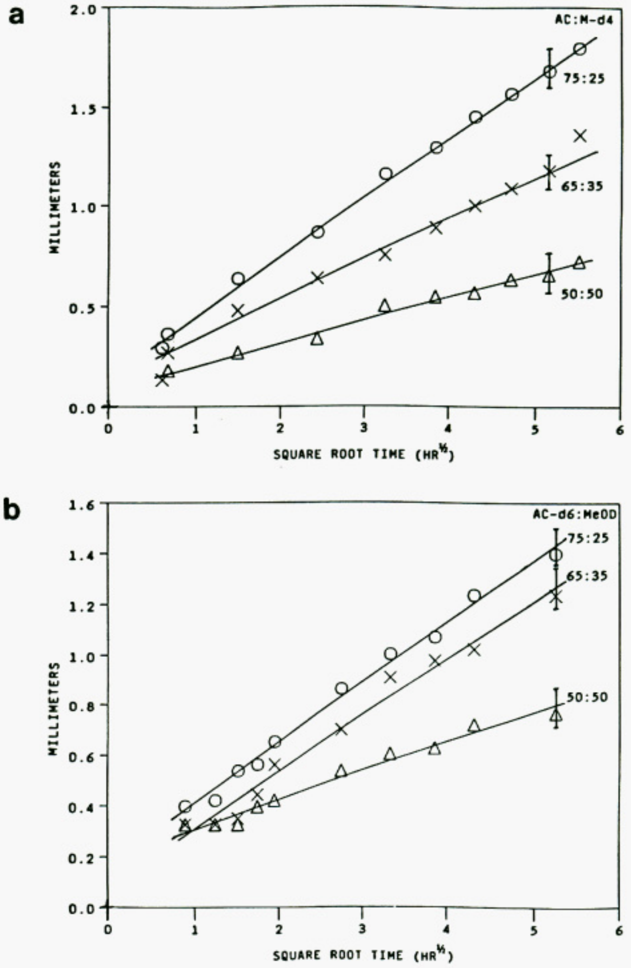

Figure 6. Solvent front movement of (a) acetone into PC for the 75:25, 65:35, and 50:50 v/o AC/MeOH-d_4 mixtures and (b) methanol into PC for the 75:25, 65:35, and 50:50 v/o AC-d_6/MeOH-d mixtures versus the square root of time.

monitored. There is an increase in the rate of the front movement as the acetone content increases as well as a linear dependence of the front movement with the square root of time. This linear dependence indicates Fickian diffusion.

We were interested in determining whether the solvent fronts move at the same or different rates for the same acetone to methanol ratio. Comparison of the rates of the solvent front movements in Figure 7a of the 65:35 AC/MeOH-d_4 and the 65:35 AC-d_6/MeOD mixtures revealed that they were equal within experimental error. There is an overlapping of the front movement when plotted as a function of the square root of time. This indicates that acetone and methanol are diffusing jointly through the PC rod in a Fickian manner and do not appear to separate. Similar behavior is also found in comparing the 50:50 AC/MeOH-d_4 and the 50:50 AC-d_6/MeOD mixtures (not shown).

It may be proposed that this joint diffusion through PC is the result of acetone diffusing into the polymer first, thereby lowering the T_g of the polymer. The acetone would increase the mobility of the polymer chains and allow for methanol to diffuse more readily into PC. The methanol could then proceed at nearly the same rate as acetone. This was observed when there was an equal or greater molar quantity of methanol in the mixture. This can be demonstrated in Figure 7a for the 65:35 v/o AC/MeOH mixtures as well as for the 50:50 v/o AC/MeOH mixtures. As the mole fraction of acetone in the mixture increases above 50%, acetone and methanol no longer diffuse at the same rate. The 75:25 AC/MeOH-d_4 and 75:25 AC-d_6/MeOD mixtures in Figure 7b start to show a slight deviation from each other in the solvent front movements through the PC rods as the diffusion time increases. This may be explained by the fact that the 75:25 v/o composition corresponds to a mole ratio of 62:38 AC/MeOH so there exists an excess of acetone compared to methanol. This allows a greater quantity of acetone to proceed first into the PC rod. It would then be expected that the acetone would diffuse at a slightly faster rate than the methanol as shown in Figure 7b.

In parts a and b of Figure 7, the front movements are plotted as a function of the square root of time for the AC/MeOH mixtures having a concentration ratio of 65:35 and 75:25 v/o, respectively. The translational diffusion coefficients, D_{AMP}, can then be determined as being equal to the square of the slope of the resulting plots. In Figure 8 the logarithm of the resulting diffusion coefficients plotted as a function of the volume percent acetone are shown. From Figure 7a, it can be seen that the slopes of the resulting lines in the 65:35 mixtures are nearly equal. It therefore was not unexpected to find that the 65:35 AC/MeOH v/o mixtures have the same translational diffusion coefficients within experimental error. The same was found for the 50:50 v/o AC/MeOH mixtures which also have corresponding diffusion coefficients. A difference in the diffusion coefficients begins to be seen with the 75:25 v/o AC/MeOH mixtures. This can be explained

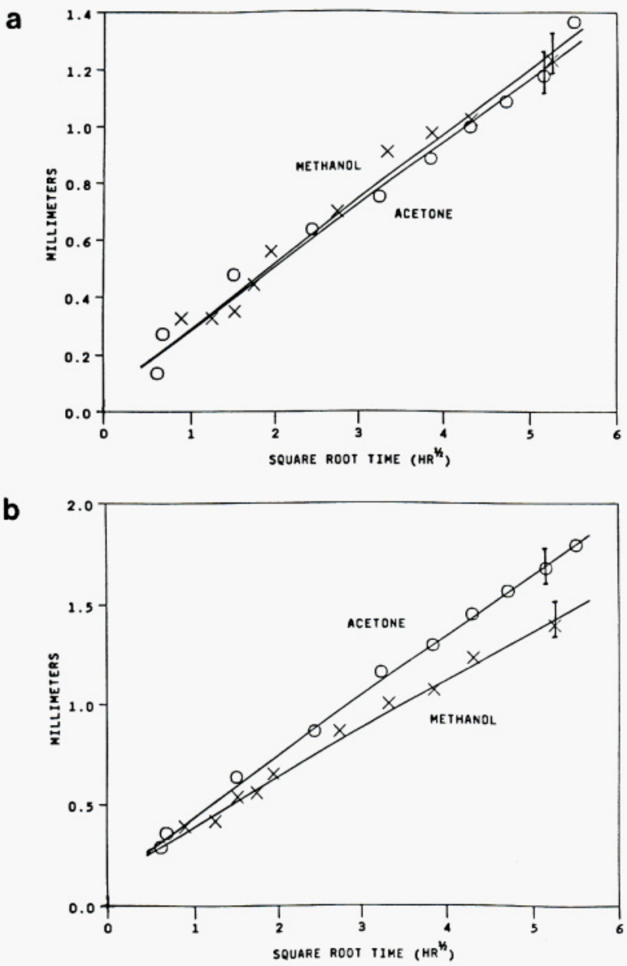

Figure 7. Comparison of solvent front movement for (a) the 65:35 AC/MeOH-d_4 and the 65:35 AC-d_6/MeOH-d mixtures and (b) the 75:25 AC/MeOH-d_4 and the 75:25 AC-d_6/MeOH-d mixtures.

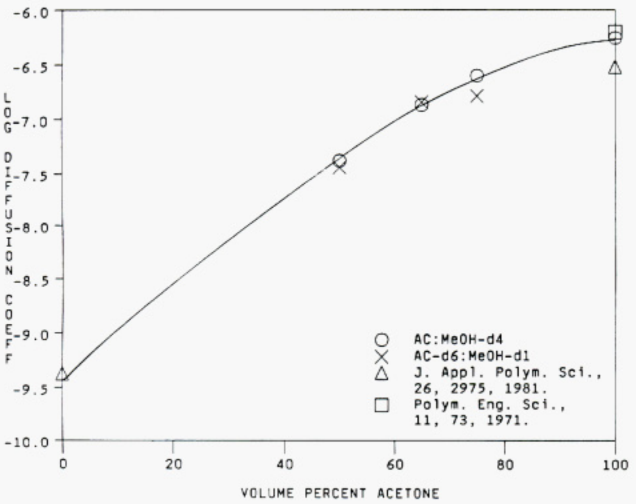

Figure 8. Logarithm of the diffusion coefficients, D_{AMP}, versus volume percent acetone: (○) AC/MeOH-d_6, (×) AC-d_6/MeOH-d, (△) ref 9, and (☐) ref 10.

by the fact that an excess of acetone would diffuse at a greater rate than the methanol.

The change in mobility of the solvent with time as the diffusion process advances was also monitored. The multiecho imaging experiment was used to determine the spin–spin relaxation time, T_2, of the solvent imbibed in the PC rod. The T_2 is a sensitive measure of the change in mobility of the solvent. A multiecho experiment consisting of eight

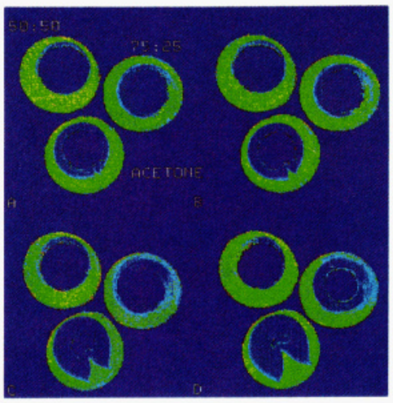

Figure 9. T_2 images of the diffusion of the 50:50, 75:25, and 100:0 AC/MeOH-d_4 mixtures into PC with time: (a) 1.78 h, (b) 3.32 h, (c) 16.35 h, (d) 27.57 h.

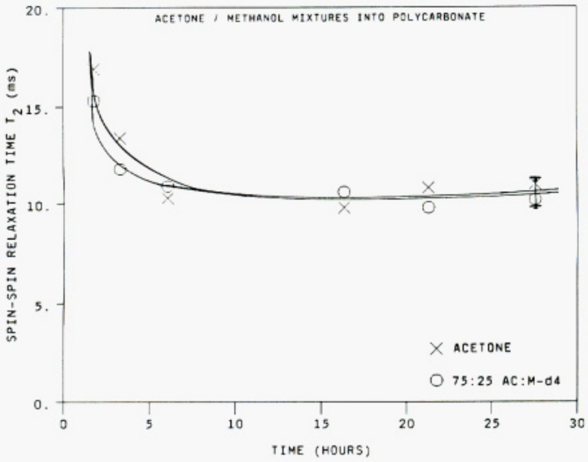

Figure 10. T_2 values in the diffused region of PC versus time for (○) 75:25 AC/MeOH-d_4 and (×) acetone.

echoes was used to generate eight images of decreasing intensity. These were then computer processed to generate a T_2 image in which every pixel represents a T_2 value. In this way, T_2 values could be spatially monitored across the image as the diffusion takes place.

T_2 images of 50:50, 75:25, and 100:0 AC/MeOH-d_4 mixtures diffusing into PC are shown in Figure 9. The dark blue regions represent short T_2's of less than 2 ms in the glassy core into which the solvent has not penetrated. The red regions represent T_2's of 200 ms or greater and can be attributed to the random noise in the original eight images. The green-yellow regions correspond to the free solvent mixtures and the lighter blue regions to the imbibed solvent in the PC rod. In the pure acetone image, evidence of the stress cracking can be seen to occur over time. The diffusion fronts are easily seen in the T_2 images for the 75:25 v/o mixture and the pure acetone. However, because there is distortion of the image for the 50:50 v/o mixture, accurate T_2 information could not be obtained for this sample.

The T_2 values of the acetone in both the 75:25 v/o AC/MeOH-d_4 mixture and the pure acetone were obtained from the multiecho experiment with eight echoes. The T_2 values start at approximately 16–17 ms in the imbibed region and decrease with time to approximately 11 ms after 5 h, as shown in Figure 10. They then remain constant throughout the diffusion process and are uniform across the imbibed regions. This indicates that the motions of the solvents diffused into PC are unaffected by the relaxations of the PC as diffusion takes place. This is because the rate of relaxation of the PC is much greater than the rate of diffusion of the solvent, which is a requirement for Fickian diffusion.[16] This is opposite to what is found for Case II diffusion[16] where there is a gradient in the T_2 values across the imbibed region resulting from the fact that the polymer relaxation rate is slower than the rate of solvent diffusion.[15] The T_2 value can now be used as a parameter for differentiating between Fickian and Case II diffusion into a material.

Conclusions

NMR imaging is a useful analytical technique with which to monitor multicomponent diffusion into polymers. We have determined by NMRI that AC/MeOH mixtures diffuse into PC in a Fickian manner as shown by the square root of time dependence of the diffusion rate. The diffusion coefficients of these mixtures increase as the acetone content in the mixture is increased. Acetone and methanol diffuse at nearly the same rates in the mixtures though the 75:25 v/o AC/MeOH mixture begins to show the existence of two separate diffusion fronts forming with time. The excess acetone diffuses first and is then followed by the methanol. The T_2's of acetone in the 75:25 AC/MeOH-d_4 mixture and pure acetone were shown to remain constant, after the initial diffusion front, and were found to be uniform throughout the diffused region. This indicates that the motions of the solvents diffused into PC are unaffected by the polymer relaxations. This reveals that the diffusion process is Fickian since the rate of polymer relaxation is much greater than the diffusion rate. This is in contrast to the gradients in T_2 found for Case II diffusion[16] where the diffusion rate is much greater than the polymer relaxation rate. The T_2 value in this way has been introduced as a parameter for differentiation of Fickian and Case II diffusion.

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