Stray field magnetic resonance imaging of the diffusion of acetone into poly(vinyl chloride)

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Stray field nuclear magnetic resonance imaging has been used to study the diffusion of acetone vapour into poly(vinyl chloride) (PVC). For the first time in a n.m.r. imaging experiment the penetrant, the swollen polymer and the rigid polymer have been simultaneously visualized. Results are presented for a range of acetone vapour activities and sample preparation temperatures, and also for a sample prepared with deuterated acetone. The profiles show that the diffusion is of Case II type. A sloping profile is observed behind the penetrant front and is interpreted in terms of a softening of the swollen polymer, which occurs over a period of hours after penetration by the acetone. The softening rate has been measured as a function of temperature.

(Keywords: n.m.r. imaging; poly(vinyl chloride); acetone diffusion)

INTRODUCTION

The diffusion of small solvent molecules into polymers has attracted considerable scientific interest in recent years because of the wide range of different phenomena which are observed, and also because of the considerable technological importance of understanding, predicting and controlling these phenomena for applications as diverse as biomedical implants and large-scale civil engineering projects. It is now well established that in many instances small molecules penetrate according to Case II, rather than Fickian (or any other), diffusion dynamics[1–3]. Case II diffusion is characterized by a sharp front between the penetrated and the unpenetrated regions of the polymer, which advances linearly, with time, into the polymer. Behind the front, the penetrant concentration is approximately constant and the polymer is usually swollen and softened. Ahead of the front, a Fickian precursor is observed, the characteristics of which vary according to the system studied. Prior to the front formation there is an induction period, during which the diffusion of the penetrant is Fickian in nature and also during which the surface concentration of the penetrant builds up to the concentration threshold which is required for front formation. The majority of recent studies of Case II diffusion have concentrated on testing the theoretical model of Thomas and Windle[1], as this model has generally been the most successful in describing the observed behaviour. The linear front advance, and the approximately zero penetrant concentration gradient behind the front, are most easily tested by mass analysis and visual inspection of exposed samples. However, these methods are not sufficiently sensitive for analysing the induction period or the Fickian precursor. Rutherford back-scattering has been applied for these more exacting tests of the theoretical models[3–5]. This method allows the surface concentration of the penetrant to be measured to depths of a few tens of micrometres. Nuclear magnetic resonance (n.m.r.) is an alternative technique which can be used to study polymer/solvent systems. N.m.r. has the advantage of being sensitive to molecular mobility on a microscopic scale via the spin–spin (T_2), spin–lattice (T_1) and spin–lattice in the rotating reference frame ($T_{1\rho}$), relaxation times. It is also sensitive to the molecular structure via the chemical shift. N.m.r. can potentially yield information on, for instance, polymer chain structure and dynamics. The development of magnetic resonance imaging techniques, initially for medical diagnosis, means that this information is now available with spatial resolution, albeit generally only for the most mobile components in the system, i.e. those with narrow n.m.r. line widths, equivalent to long T_2 relaxation times. N.m.r. imaging has been successfully used to map the concentration profile of the penetrant[6] and, in some

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studies, also to visualize the swollen polymer[7]. However, the shortness of the swollen polymer spin–spin relaxation time has prevented much quantitative study of the swollen polymer, and the rigid polymer is not visualized in most established techniques. Advances have been made in imaging solid materials with the development of techniques which overcome the difficulties associated with broad resonance line widths, namely short T_2s[8]. In an earlier study, we used the gradient echo technique[9] to study the diffusion of acetone into PVC[10]. Although this investigation established that the dynamics in this system are of a Case II type no further information was obtained because the signal-to-noise and image resolution were poor. Stray field magnetic resonance imaging (STRAFI)[11] is a relatively new technique which overcomes the short T_2 limitation of the conventional imaging experiment, and has the additional advantage of high spatial resolution. In this paper we report the first STRAFI measurements of Case II diffusion dynamics in a polymer. We show how the technique is able to map the *rigid* polymer and how it yields considerably greater information than was previously available about the swollen polymer. We have chosen to carry out these experiments on a system that has previously been studied and is known to exhibit Case II diffusion dynamics, namely acetone vapour penetrating into PVC[10].

STRAY FIELD MAGNETIC RESONANCE IMAGING

The STRAFI technique has been described elsewhere[11,12] and therefore only the salient points of the method are described here. Conventional magnetic resonance imaging is achieved by placing a magnetic field gradient across the sample, which spreads the resonance frequencies of nuclei at different locations. The transient response of the nuclei to a broadband radio frequency stimulus is recorded in the presence of the gradient and subsequently Fourier transformed to yield a one-dimensional profile. The resolution is inversely proportional to the product of the gradient strength and the encoding time, with the latter being limited by T_2. In order to achieve high spatial resolution imaging of samples with short T_2 relaxation times (i.e. broad spectral lines) it is necessary either to use a technique such as multiple pulse line narrowing, or to use a large magnetic field gradient. STRAFI takes the large gradient approach to the extreme. The sample is placed in the fringe field of a high-field magnet where the gradient can be as much as 5000 G cm^{-1}. In this very large gradient even a 'broadband' pulse excites nuclei in only a very thin slice of the sample orthogonal to the gradient. The slice thickness is typically 7–70 μm and is inversely proportional to the pulse length. Since the gradient field is neither dynamic nor controllable, the basic idea is to move the sample through the gradient and to record the signal intensity from each slice of the sample as it passes through the sensitive position. In this way, a one-dimensional profile in the gradient direction can be accumulated. No Fourier transformation of the signal is required. The method is thus more analogous to continuous wave n.m.r. techniques.

In practice, the signal intensity of a solid (dipolar) echo is recorded. Indeed, usually the intensity of each echo in an echo train is recorded, the train being generated by the radio frequency pulse sequence 90°_X–τ–(90°_Y–τ–echo–τ–)$_n$, where 90°_X denotes a 90° pulse of relative phase X, and τ is a short time interval. This particular sequence is used for two reasons. First, it uses pulses all of the same length, so that the width of the selected slice is constant for all pulses. Secondly, the solid echo partially refocuses the dipolar broadening and the sequence as a whole preserves magnetization from short T_2 components in the short τ limit. In this limit, the experiment approximates to spin locking and the echo intensities (after the first few echoes during which a pseudoequilibrium is established) decay away according to $T_{1\rho}$, the spin–lattice relaxation time in the rotating reference frame. Since the sample is moving through the gradient during the measurements the pulses experienced by the nuclei only approximate to true 90° rotations. The recorded signal intensity is thus a complex function of T_2 and $T_{1\rho}$, and other experimental parameters, such as the gradient strength, pulse length, τ and the sample velocity. The complete functional dependence of the echo intensity on these parameters, as well as on the dipolar interaction strengths in the sample, has not yet been fully evaluated. Generally, however, only long T_2 and $T_{1\rho}$ components are observed at longer echo times. This gives substantial relaxation time contrast in the profiles constructed from different echoes.

EXPERIMENTAL

PVC, manufactured by Simona, was purchased from Aquarius Plastics Ltd. This PVC was the purest form which was commercially available in large volumes. Nonetheless, it clearly contained additives which gave it a grey appearance. Sample blocks (25 mm × 25 mm × 40 mm) were cut from extruded rods prior to exposure to the acetone. The blocks were placed in a constant acetone vapour activity chamber which allowed control of both the sample preparation temperature and the equilibrium acetone concentration. The blocks were exposed either to vapour above a reservoir of liquid acetone, or to granular PVC mixed with acetone, which had been equilibrated to a known acetone/PVC ratio, ϕ. The activity of the vapour is defined as $a = \phi \exp(1-\phi)$ (ref. 4). This assumes that the polymer solvent interaction parameter is almost equal to zero. Preparation of the samples exposed to lower vapour activities follows the general procedure adopted by Hui and coworkers[4]. In every case, the reservoir was large compared to the sample, so that the sample had minimal effect on the equilibrium concentration. After exposure, the blocks were cut down to produce 10 mm cubes with only one exposed face remaining. This permitted one-dimensional profiling experiments to be carried out across the exposed face. One-dimensional profiling experiments are orders of magnitude faster to carry out than full three-dimensional analyses, and the latter would not have yielded any additional information. Between preparation and measurement each sample was stored at liquid nitrogen temperature (except for the 5 h required to transport them between Surrey, UK and Rheinstetten, Germany, during which time they were kept in a vacuum flask containing ice, itself previously cooled with liquid nitrogen). It is strongly believed that no diffusion or dynamical changes took place during this period.

The glass transition temperature of PVC swollen by acetone has been measured as a function of the activity by using differential scanning calorimetry. It is evident that in all of our experiments the equilibrated swollen polymer is above the glass transition temperature.

In order to characterize mass equilibrated samples of PVC exposed to acetone and deuterated acetone vapour, the hydrogen spin–spin relaxation time was measured at 30 MHz, at room temperature, as a function of exposure temperature for samples prepared using the liquid acetone reservoir. This was done by using Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences with pulse gaps of 140 and 800 μs, and by additionally recording the free induction decay (FID) up to the first refocusing pulse in order to record the shortest components. Best fits to the data are obtained using three-component exponential decays. These have T_2 values of 90 μs, 2.0 ms and 25 ms ($\pm$20%), with relative amplitudes of 0.21, 0.17 and 0.62, respectively. When repeated with samples prepared with deuterated acetone the T_2 values obtained in this case were 90 μs, 1.5 ms and 30 ms ($\pm$20%), with relative amplitudes of 0.52, 0.32 and 0.16, respectively. We suggest that the long T_2 component is primarily due to the absorbed mobile acetone and that the short component is attributable to the swollen PVC. The long component exhibited by the sample exposed to deuterated acetone is possibly due to chemical exchange occurring during the long preparation period. The middle component is a little more interesting and requires more investigation. Two possible explanations are that it is due to broken, and hence more mobile, swollen polymer chains, or that it is due to bound acetone and PVC. The results seem largely independent of the exposure temperature. Samples left above the liquid acetone reservoir increased in mass by 35$\pm$5% and in volume by 95$\pm$5%.

Figure 1 shows a typical one-dimensional profile which was obtained using the STRAFI technique. The sample was prepared at 20°C over a period of 48 h using the liquid acetone reservoir. Before presenting further results the principal features are explained. The pixel resolution is 78 μm and the echo time used is $2\tau = 100$ μs. The profile is the result of summing a train of four echoes and includes 256 averages. The gradient strength is 5000 G cm^{-1} and the pulse length is 10 μs. The n.m.r. frequency used is 160 MHz and the profile is recorded at room temperature. Unless stated otherwise, these n.m.r. parameters are used throughout. The acetone has penetrated the sample from the left, with the front face of the PVC being at 0 mm on the scale. The main peak is the combined signal coming from the penetrating acetone and from the swollen PVC. It is slightly rounded on the left due to surface drying, and on the right as a result of diffusion dynamics. The downward slope of the main peak, to between one third and one half the maximum intensity, as it goes into the sample, is characteristic of all of the samples that we have studied, as is the sharp diffusion front, seen here at ~3 mm. Behind the front, the rigid PVC is seen up to a distance of 11 mm. The small peak at 11 mm is a signal from the 'Superglue' used to mount the sample on to the probe. The acetone/swollen PVC shows as a considerably more intense peak than the rigid PVC. This, in part, is due to the extra hydrogen present, but the greater part of the increase results from the longer spin–spin relaxation time of these components so that more signal is remaining at the time of the echoes. It should be noted that the spin–spin relaxation time of the rigid polymer is significantly less than τ, whereas the spin–spin relaxation times of the other components are significantly longer. This is the first n.m.r. polymer diffusion experiment in which the rigid polymer has been seen as well as the more mobile components.

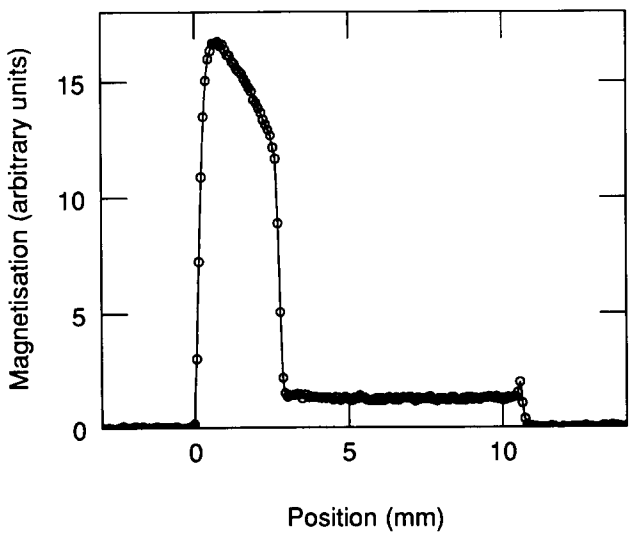

Figure 1 A one-dimensional profile of PVC exposed to acetone vapour above a liquid acetone reservoir for 48 h at 20°C; the line connecting the data points is added for ease of viewing only

RESULTS AND DISCUSSION

STRAFI has been used to study the onset of front formation in Case II diffusion as a function of acetone activity. *Figure 2* shows profiles obtained for samples exposed at 20°C for 48 h with vapour activities of 0.13, 0.35, 0.60 and 0.82. The 0.35 activity profile is particularly interesting in that a front has just formed, while the 0.13 activity profile shows no evidence of a front at all. The insets, *Figures 2b* and *2c*, show these two profiles in more detail. The Fickian precursor shows clearly in the 0.35 activity sample. Indeed, it is evident in most of the samples that were studied, although a sufficient number of averages have to be accumulated to observe it. The profile shown is the result of 256 averages and the summation of four echoes. The precursor extends a surprisingly long way into the sample, ranging over 3 mm. The 0.13 activity profile shows only the Fickian precursor, and since this is below the threshold for front formation the diffusion kinetics will remain Fickian in nature.

An experiment was performed using two samples that had been identically prepared at 20°C, at 0.82 activity for 48 h, except that in one case acetone-d_6 was used. *Figure 3* shows the measured profiles normalized to the same rigid PVC intensity, in order to account for slight experimental variations (i.e. sample mounting and size, and spectrometer drift). The difference profile is also shown, and from this it is concluded that, to a very great extent, the sloping contribution to the main peak is due to the swollen polymer and the rectangular pedestal is due to uniformly absorbed acetone.

The same assignment of two components in the main peak is supported in another way. Study of an echo train of profiles shows that by the 16th echo profile the sloping part of the signal has decayed away and that only the rectangular pedestal remains (see *Figure 4*). These profiles were recorded from samples prepared with a vapour activity of 0.82 for 48 h at 20°C. The acetone has a longer relaxation time than the swollen polymer and hence it is observed out to considerably later echoes in the series. Mass analysis also indicates that the acetone

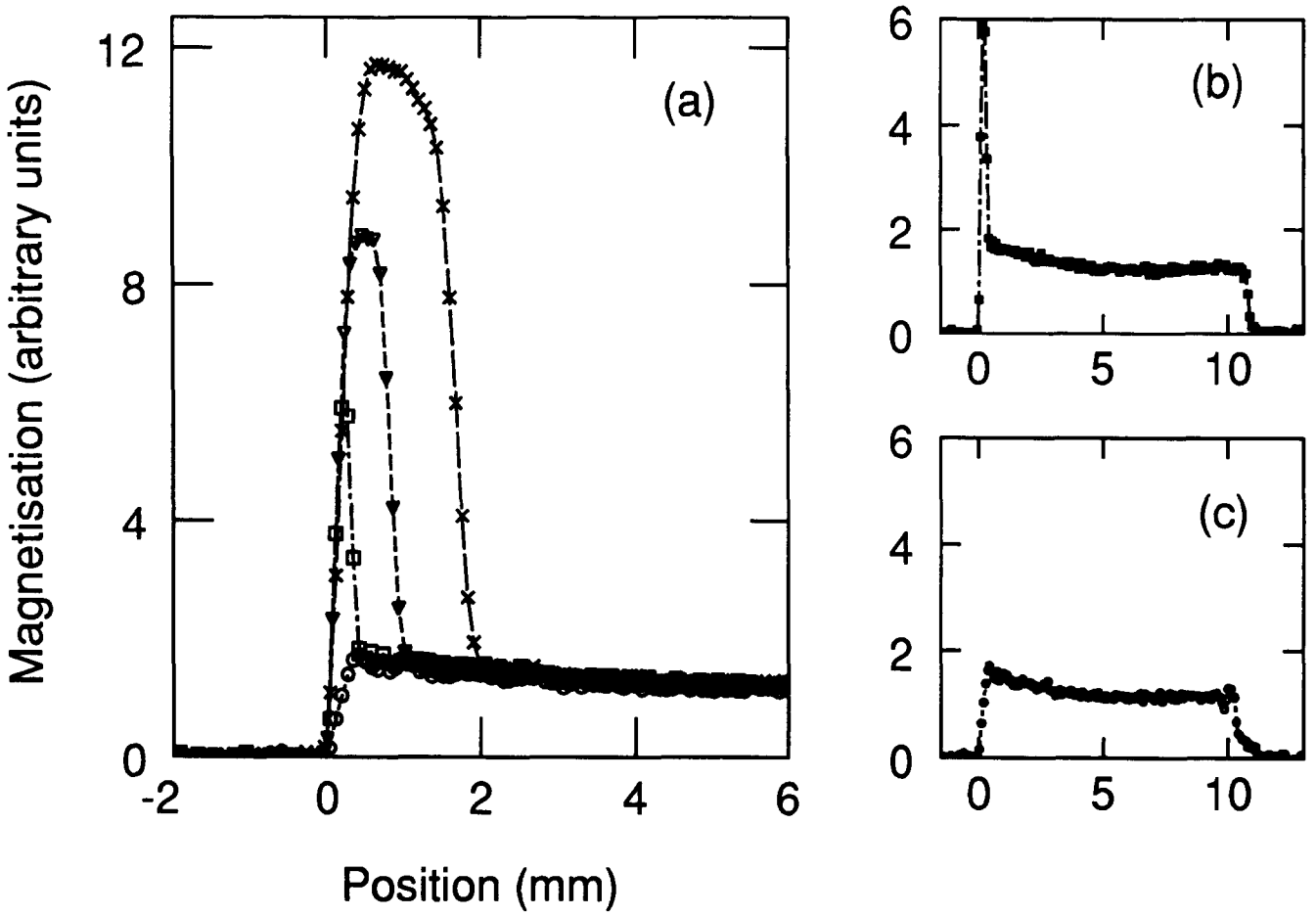

Figure 2 One-dimensional profiles of PVC exposed to acetone vapour of different activities for 48 h at 20°C: (○) 0.13; (□) 0.35; (▽) 0.60; and (×) 0.82. The insets (b) and (c) show the profiles in more detail for activities of 0.35 and 0.13, respectively; the lines connecting the data points are added for ease of viewing only

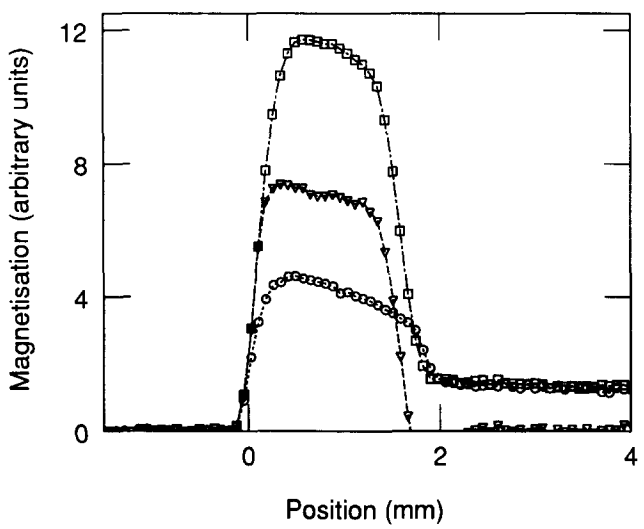

Figure 3 One-dimensional profiles of PVC that has been exposed to acetone vapour with an activity of 0.82 for 48 h at 20°C: (□) after exposure to acetone vapour; (○) after exposure to deuterated acetone; and (▽) difference profile, showing the concentration of acetone in the sample. Lines connecting the data points are added for ease of viewing only

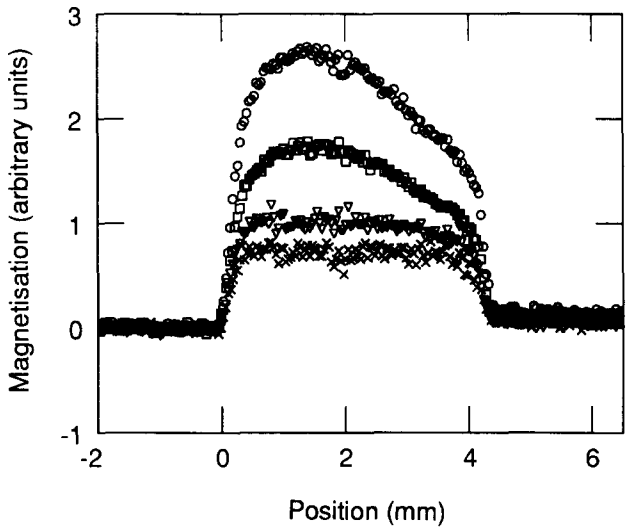

Figure 4 Representative one-dimensional profiles of PVC exposed to acetone vapour above a liquid acetone reservoir for 48 h at 50°C, shown for: (○) the 2nd echo; (□) the 4th echo; (▽) the 10th echo; and (×) the 16th echo

concentration is approximately uniform in the swollen region, which is consistent with the profile. With this assignment, however, the problem is to account for the significant slope in the polymer profile. Clearly, the PVC concentration is uniform across the swollen region. Each peak is, in effect, a time course experiment, with the time axis running from right to left and with the origin at the penetrant front edge. One explanation of the slope is that the n.m.r. relaxation time of the polymer on the left is longer than that on the right, perhaps because it has been

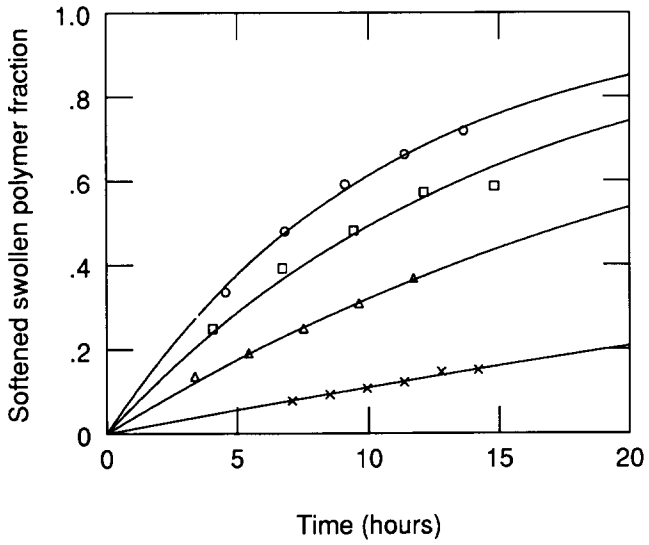

Figure 5 The softening rate of the swollen polymer for samples of PVC exposed to acetone vapour, as deduced from STRAFI profiling experiments, measured at various temperatures: (×) 20°C; (△) 30°C; (□) 40°C; and (○) 50°C. The continuous lines are fits to the function $(1-\exp(-t/\tau_c))$ where $\tau_c = 86$, 26, 15 and 11 h, respectively

in contact with acetone for a considerably longer period of time. A suitable model is based on the concepts of a multicomponent/relaxation time system with averaging in which $1/T_{2\,\text{observed}} = \sum(f_i/T_{2i})$ and f_i is the fraction of the ith component. However, attempts to fit exponential decays, with a constant amplitude and variable relaxation time, to the polymer part of the profile intensity, as a function of echo time for various positions across the profile peak, suggests that this is not the case. Indeed, if anything, and the effect is slight, the relaxation time on the left is shorter.

An alternative explanation is that the swollen polymer is slowly softening for some considerable period after the acetone has penetrated and that the softened polymer exhibits a distinct, longer relaxation time than the unsoftened polymer, the signal of which, therefore, does not contribute significantly to the profile intensity. Hence the value of the signal amplitude, measured by extrapolation back to zero time from a series of echoes as a function of position, is a measure of the fraction of softened, swollen polymer as a function of the time for which the polymer has been in contact with acetone. This analysis is based on a multicomponent system without averaging. *Figure 5* shows the signal amplitude as a function of acetone/PVC contact time (deduced from the position and front velocity). The samples are prepared at temperatures of 20, 30, 40 and 50°C, above a liquid acetone reservoir. In obtaining this data, all the profiles used were normalized to the same rigid PVC intensity. The data have been fitted to exponential functions $A(1-\exp(-t/\tau_c))$ where τ_c^{-1} is a 'softening rate'. Since the PVC/acetone density of fully-mass-equilibrated samples is known to be independent of sample exposure temperature, the pre-exponential factor, A, is constant (normalized to 1) in each case. The softening rate increases dramatically with temperature. The measured values of τ_c are 86, 26, 15 and 11 (±10%) h for the samples exposed at 20, 30, 40, and 50°C, respectively. An increase in chain mobility with acetone contact time is plausible on the grounds of chemical breakdown of the chains, or more likely, changes in the chain conformation/tertiary structure, and is an example of the kind of information which can be gained from this kind of experiment. High resolution ^{13}C cross polarization/magic angle spinning (CP/MAS) n.m.r. experiments are planned to test for changes in the primary chain structure or conformation which might support these suggestions. Additionally, ongoing experiments are seeking evidence for changes in the amplitudes of the different relaxation time components of the system with time after the establishment of mass equilibration, i.e. after the sample has absorbed its full complement of acetone.

CONCLUSIONS

STRAFI has been shown to be a powerful new technique for the study of the diffusion of small molecules into polymers. The ability of this method to visualize broad line (short T_2) components means that quantitative dynamical information about the polymer, as well as the penetrant, can be obtained. The experiments reported here suggest that changes in the molecular dynamic processes are occurring for some considerable time after the penetrant has entered the polymer.

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