

by experiments at still higher magnetic field (which we are currently attempting).

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Articles

Observation of Heterogeneous Trace (0.4% w/w) Water Uptake in Bisphenol A Polycarbonate by NMR Imaging

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The uptake of water by injection-molded bars of bisphenol A polycarbonate (Lexan 121 resin) has been monitored by a combination of one-dimensional proton NMR spectroscopy, relaxation time (T_1 and T_2) measurements, and microscopic imaging techniques. The bulk of the water absorbed in the initial stages (20–24 h) of 100 °C water exposure is uniformly distributed throughout the polymer with a trace amount of the water found in clusters of 200–300 μm in size. The water that has aggregated to form these clusters is more mobile, having a T_2 relaxation time 20 times longer than that found for the uniformly distributed water. At longer exposure times (30–40 days) the number of clusters is observed to increase. Although the total amount of water adsorbed is considerably less than 1% w/w, good-quality images are obtained, demonstrating that the NMR microimaging technique can successfully monitor even trace levels of solvent if the molecules are relatively mobile.

Introduction

Bulk polymers are permeable substances, subject to the diffusion of small molecules which can affect their physical and mechanical properties and can result in the degradation of the polymeric material. The recent development of NMR microscopic imaging has provided researchers with a noninvasive way of examining the spatial distribution of absorbed fluids in polymers.^{1–6} However, the real advantage of NMR spectroscopy over other methods is its ability to obtain chemical information about the nature and mobility of these absorbed species. In this paper, we wish to report the results of a systematic study in which the one-dimensional ^1H NMR spectra, the relaxation parameters of the components and the spatial distribution of water absorbed into injection molded bisphenol A polycarbonate bars were obtained. This particular system is of interest because of the importance of polycarbonate as the material of choice in optical storage systems where it has been suspected that water adsorption may be the critical physical process limiting its performance.^{7–9}

Experimental Section

Materials. The polycarbonate sample studied was General Electric Lexan 121 resin which was received as injection-molded izod bars (7 mm \times 12 mm cross section). The bars were cut to a cross section of 6 mm \times 7 mm and a length of 2 cm from the original 10 cm length. Distilled water was used in the study, and deuterium oxide (99.9 atom % D) was used as received from MSD isotopes.

Gravimetric Analysis. In the present study, polycarbonate pieces 2 cm \times 6 mm \times 7 mm were immersed in distilled water at 100 °C for up to 40 days, removed periodically, and dried of excess water. The sample was weighed, temporarily sealed in 10-mm-o.d. thin-walled glass NMR tubes, and then subsequently imaged. The sample was then replaced in the water bath after imaging. The limiting amount of water absorbed by the polycarbonate rods was typically <0.80% (w/w). Experiments involving the use of deuterium oxide were carried out in a similar apparatus under a blanket of dry nitrogen gas.

Spectroscopy. NMR measurements were made on a Bruker MSL 400 spectrometer equipped with a microimaging system. All experiments were performed using the proton microimaging probe supplied except that the probehead was modified by replacing the vertical saddle coil with an 11-mm horizontal solenoid coil that was demonstrated to have superior S/N and rf homogeneity characteristics. The nonselective 90° and 180° rf pulses were 9 and 18 μs , respectively. Quadrature phase cycling was used in all spectroscopic measurements.

One-dimensional ^1H NMR spectra were obtained by the standard one pulse method and by the Carr–Purcell spin-echo experiment.¹⁰ The Carr–Purcell sequence with the modification of alternating the phase of the 180° pulses as developed by

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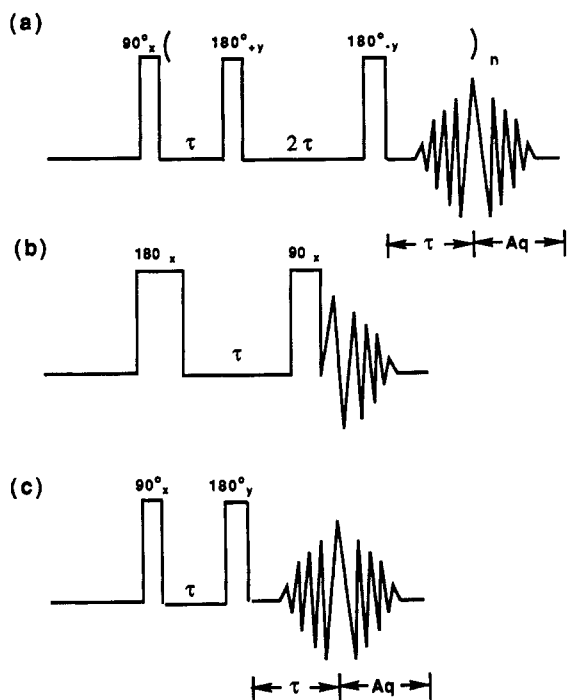


Figure 1. (a) CPMG Pulse sequence used to determine T_2 . Acquisition starts at the top of the echo. (b) Inversion-recovery pulse sequence used to determine T_1 . (c) Carr-Purcell spin-echo pulse sequence used to obtain T_2 weighted 1-D ^1H spectra. Acquisition starts at the top of the echo.

Meiboom-Gill¹¹ (CPMG pulse sequence) (Figure 1a) was used to determine the T_2 spin-spin relaxation times. The inversion-recovery pulse sequence¹² (Figure 1b) was used to determine the T_1 spin-lattice times. To obtain spectra without contributions from the broad polymer resonance, a delay of $100\ \mu\text{s}$ (ring down delay) was inserted between the 90° pulse of either the one-pulse or inversion recovery pulse sequence and the acquisition to allow for dephasing of the polymer resonance. To acquire data from both the polymer resonance and the other minor components, a short $1\text{-}\mu\text{s}$ ring-down delay was used.

Imaging. NMR imaging data were obtained by employing both the spin-echo¹³ and the gradient echo (FLASH) pulse sequences¹⁴ (Figure 2). The spin-echo pulse sequence employs a 90° rf pulse which tips the magnetization into the xy plane. The magnetization dephases with time constant known as T_2 . A 180° rf pulse is applied after a time, τ , causing the magnetization to refocus at a time 2τ . The total time from the midpoint of the 90° pulse to the middle of the acquisition time is known as the time to echo. The decay of magnetization by spin-spin relaxation (T_2) is a primary source of signal loss in samples which have a short T_2 . The production of images requires the spatial encoding the proton signals by field gradients. This is accomplished by applying three separate orthogonal gradients at appropriate points in the pulse sequence. The field gradients were generated by gradient coils mounted within the probehead. The rise time for the gradients to reach the required field strength was measured to be $50\ \mu\text{s}$. Sinc-function-shaped frequency-rf pulses were produced by a selective excitation unit. The slice selective gradient, G_x , collectively with the magnitude and duration of the selective rf pulse, selects the position and thickness of the sample in which the spins are excited and later refocused. The frequency encode (read) gradient, G_y , causes the spins to become encoded according to their spatial position in the rf coil. The imaging experiment is performed by obtaining a series of spectra in which the phase encode gradient, G_z , is incrementally increased which causes the

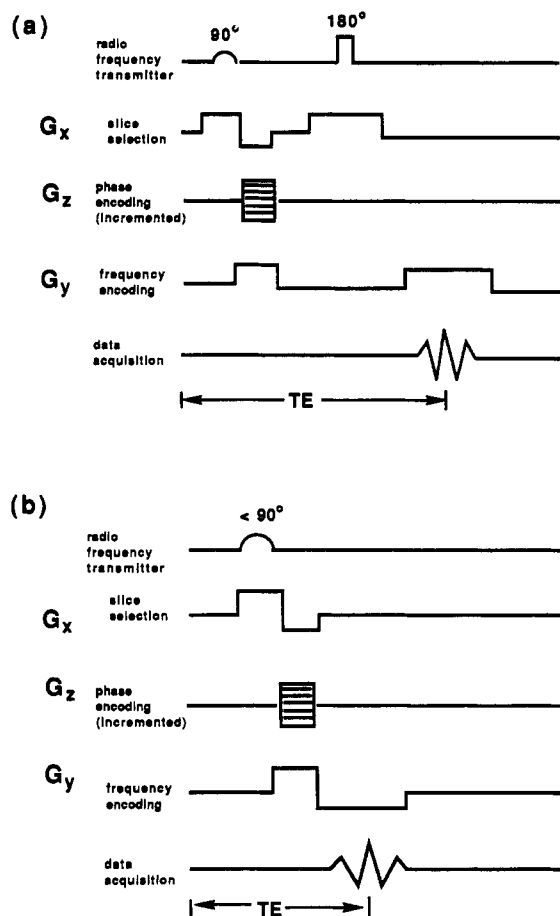


Figure 2. (a) Spin echo imaging pulse sequence. (b) Gradient echo (FLASH) pulse sequence.

spins to dephase at a rate directly proportional to the magnitude of this gradient. A two-dimensional Fourier transformation of this data results in the production of an image in which the signal intensity is a function of several parameters such as the spin density, the spin-lattice (T_1) relaxation time, and the spin-spin (T_2) relaxation time. There are two main differences between the spin-echo and gradient-echo imaging sequences: (i) The gradient-echo sequence uses an excitation pulse which has a tip angle much less than 90° . (ii) The frequency encode gradient, G_y , is inverted prior to data acquisition, resulting in the formation of a gradient or field echo. Further details of the NMR imaging techniques are available in several recent reviews.¹⁵⁻¹⁷

A typical echo time for the spin-echo imaging experiments was $3.8\ \text{ms}$. The slice thickness was chosen to be $4\ \text{mm}$ because of the low concentration of sorbed water. The total acquisition time of the spin-echo imaging experiments was $4\ \text{h}$, again due to the low concentration of water absorbed (typically $0.3\% \text{ w/w}$). The in-plane resolution determined from the strength of the frequency encode gradient is $167\ \mu\text{m}$. This value was confirmed by measuring a sample of known dimensions. The spin-echo images presented in the paper have been zero-filled twice, resulting in pixel dimensions of $83.5\ \mu\text{m}$, but the real in-plane resolution is unaffected.

A typical echo time for the gradient-echo sequence was $800\ \mu\text{s}$. Such a short time to echo can be achieved by using a short ($75\ \mu\text{s}$) selective pulse coupled with a large slice selective gradient to achieve a modest slice thickness. The data acquisition time was, however, considerably longer than the spin echo sequence ($11\ \text{h}$) and since the same general details were resolved in the spin-echo image, the spin-echo sequence was used in subsequent studies.

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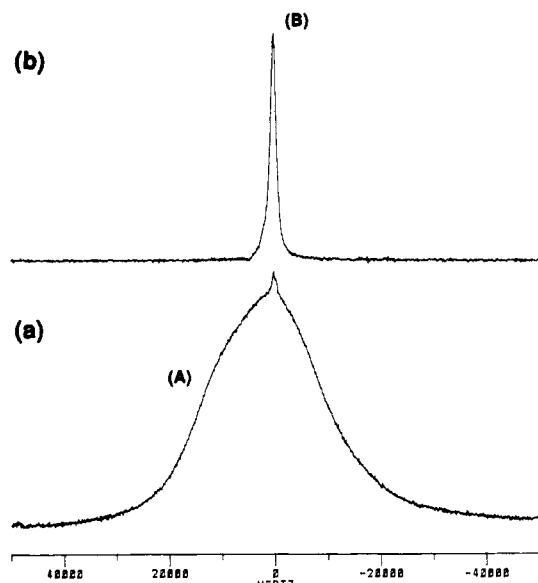


Figure 3. (a) One-pulse ^1H NMR spectrum of untreated polycarbonate rod (ring down delay = 1 μs). (b) Spin-echo spectrum (dephasing delay = 800 μs) of untreated polycarbonate rod.

Images presented in this paper follow the convention in which an inverse gray scale is used to indicate relative intensity. Thus, the black regions in the images indicate where water has diffused into the polymer. The darker the region on the image, the higher the concentration of water. Further details of the parameters used in the imaging experiments are given at the appropriate section of the text. The diffusion rate of water at room temperature is assumed to be small, and thus no artifacts from changes in concentration during the NMR experiment are expected due to the relatively large pixel sizes used and the short echo times used.¹⁶

Results and Discussion

The amount of water absorbed by commercial polycarbonate is very low: After exposure to boiling water for 24 h, the weight gain is only 0.3–0.4% w/w. The weight gain upon exposure for 30–40 days is 0.5–0.8% w/w. Some variation in weight gain was observed for different samples and is thought to be due to slight variations in the composition of the polymer rod.

Untreated Polycarbonate. The ^1H NMR spectrum of the untreated polycarbonate material consists of a homogeneously broadened peak (A) with a width at half-height of approximately 25 kHz (Figure 3a). This is typical for protons in a rigid polymer which have large dipolar interactions in the solid state. The spin-lattice (T_1) and spin-spin (T_2) relaxation time constants for this peak are presented in Table I. The extremely short T_2 of 10–30 μs precludes observation of the polymeric material in the types of imaging experiments performed in this work. This can be clearly seen from a comparison of the normal one-pulse ^1H NMR spectrum and the spin-echo (Carr-Purcell) spectrum obtained after a dephasing delay of 800 μs (Figure 3b). After 800 μs , all of the signal from the polymer has decayed via T_2 relaxation.

A second very small peak (B) is observed at 0.55 ppm in the spin-echo spectrum (Figure 3b, dephasing delay of 800 μs) which has a much narrower line width than the polycarbonate peak. The narrower line width and the T_2 value of 1.5 ms indicates that this material is more mobile than the polycarbonate and may be due to a processing additive (such as polyethylene) or perhaps water absorbed from the atmosphere. It is thought that this component is absorbed atmospheric water for the following reasons: (i) It has a chemical shift position of 0.5 ppm relative to the HOD peak (4.65 ppm) in D_2O which is possible for

Table I. T_1 and T_2 Relaxation Times of the Various Species in Untreated and Exposed Polycarbonate

treatment	peak ^a	T_1 , ms	T_2 , ms
untreated	A	430	0.001–0.003
untreated	B	430	1.5
20–24 h	C	762	1.8
20–24 h	D		36
20–30 days	C	786	1.6
20–30 days	D		56

^a Peak A is the polycarbonate resonance; peak B is the resonance at 0.55 ppm arising from adsorbed atmospheric water; peak C is the resonance at 1.73 ppm due to adsorbed water; peak D is the resonance at 5.2 ppm due to the water that has aggregated into small pools. The HOD impurity in D_2O was used as the external reference ($\delta = 4.65$ ppm).

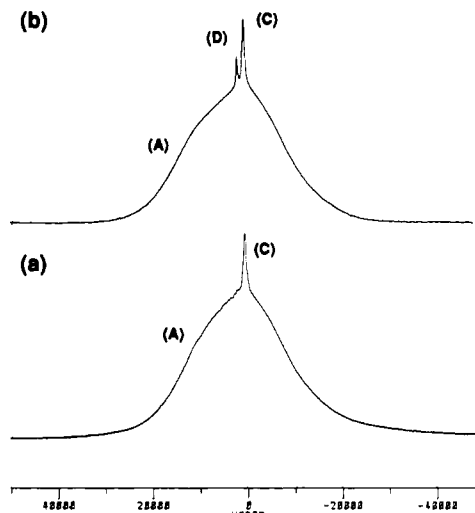


Figure 4. (a) One-pulse ^1H NMR spectrum of polycarbonate rod after exposure to refluxing H_2O for 24 h (ring down delay of 1 μs). (b) One-pulse ^1H NMR spectrum of polycarbonate rod after exposure to refluxing H_2O for 45 days (ring down delay of 1 μs).

water dissolved at low concentration in a solid organic matrix and is thus strongly interacting with the organic functional groups of the polymer. (ii) A decrease in intensity is observed for this peak upon treatment of the sample with refluxing $\text{D}_2\text{O}/\text{N}_2$, which indicates that the substance undergoes hydrogen-deuterium exchange. (iii) Polycarbonate is known to be slightly hygroscopic, and the absorption of trace amounts of atmospheric water is not unreasonable.^{7–9}

An attempt was made to obtain a spin-echo image of this mobile component in the untreated material. A large number of transients were required to observe the signal (18-h acquisition time), and a faint uniform signal from the entire polymer rod was observed. This indicates that the mobile component which corresponds to the second peak in the spin-echo spectra is distributed evenly throughout the polymeric material in terms of the 167- μm resolution of the experiments.

20–24-h Exposure to Refluxing Water. In the ^1H NMR spectrum of polycarbonate exposed to refluxing H_2O , two peaks are clearly seen (Figure 4a). The broad peak (A) with a half-height >25 kHz is again clearly due to the rigid polycarbonate. The sharp peak (C) with a chemical shift position of 1.73 ppm must be due to the adsorbed water due to the lack of a signal when D_2O is used as noted above. The relative area of the small, narrow peak is also in approximate agreement with the percentage gain in weight. Relaxation measurements of this sharp peak (C) yield T_1 and T_2 relaxation times of 762 and 1.8 ms, respectively (Table I). The short T_1 and T_2 values suggest

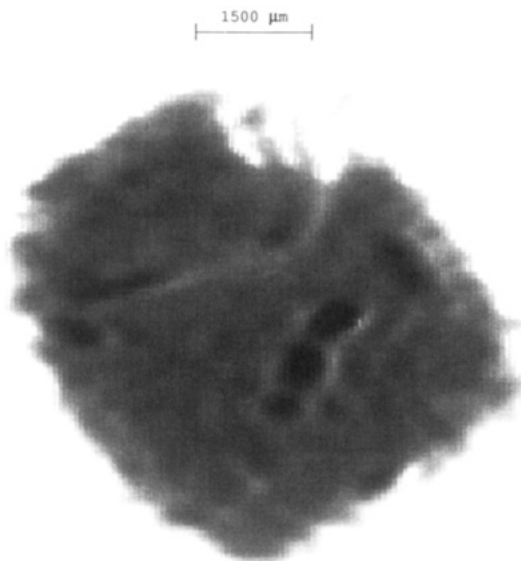


Figure 5. FLASH image of polycarbonate exposed to refluxing H₂O for 24 h. Slice gradient strength 27.4 G/cm, slice thickness = 2.2 mm, time to echo = 810 μs, frequency encode gradient strength 13.7 G/cm, phase encode gradient strength = 23.0 G/cm incremented through 128 experiments, in-plane resolution = 133 μm, pixel dimensions of image = 66.5 μm.

that the water is in a restricted environment and is not freely mobile. The chemical shift position and relaxation times of this resonance are similar to that observed for the mobile component in the untreated polycarbonate, again in agreement with it being due to water.

While investigating the T_2 relaxation behavior of the water signal via the CPMG pulse sequence, a very small third peak (D) 3.4 ppm downfield of the water signal was clearly observed, especially at longer echo times. This peak at 5.2 ppm has a much longer spin-spin relaxation time, on the order of 40 ms, and is present at only a very small concentration in the polycarbonate which has been boiled for 20–24 h. Due to its small concentration and close proximity to the large water peak at 1.73 ppm, it was not possible to accurately determine its spin-lattice relaxation time in this sample. We believe that this component is also absorbed water but is clustered, occupying a larger volume, and is thus much more mobile.

A FLASH (gradient echo) image (TE = 810 μs) of polycarbonate exposed to boiling water for 24 h was obtained (Figure 5). In addition to a uniform signal from the water distributed over the entire polymeric rod, as expected, small, very intense pools of signal can be observed due to the third mobile component described above. A spin-echo image, TE = 3.8 ms (Figure 6), of polycarbonate gives rise to the same type of image, a uniform grey signal being observed together with several areas of much higher signal intensity.

An attempt was made to obtain a FLASH and a spin-echo proton image from a sample of polycarbonate that had been placed in refluxing D₂O for 24 h. The weight gains of the samples exposed to refluxing D₂O were similar to that observed for those exposed to refluxing H₂O (0.4% w/w), but no signals were observed. The absence of a signal again suggests that the polycarbonate itself is not being observed in the imaging experiments. In addition, it indicates that any signals that are observed in the images under the conditions used are due to absorbed water.

20–30-Day Exposure to Refluxing Water. The ¹H NMR spectrum of polycarbonate (Figure 4b) exposed to refluxing water for 20–30 days shows the same general features observed for 20–24-h exposure. The proportion

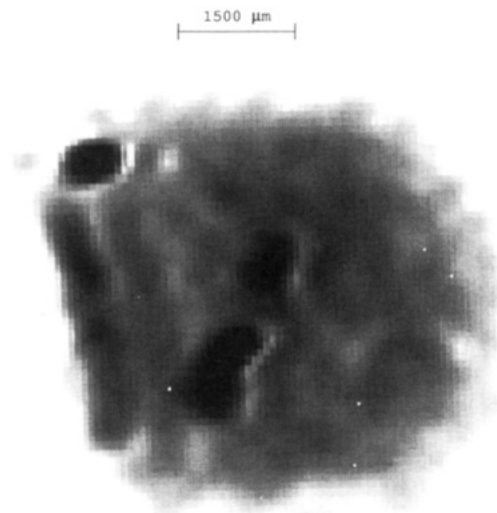


Figure 6. Spin echo image of polycarbonate exposed to refluxing water for 24 h. Slice gradient strength 1.7 G/cm, slice thickness = 5.4 mm, time to echo = 3.8 ms, frequency encode gradient strength 2.74 G/cm, phase encode gradient strength = 4.8 G/cm incremented through 128 experiments, in-plane resolution = 167 μm, pixel dimensions of image = 83.5 μm.

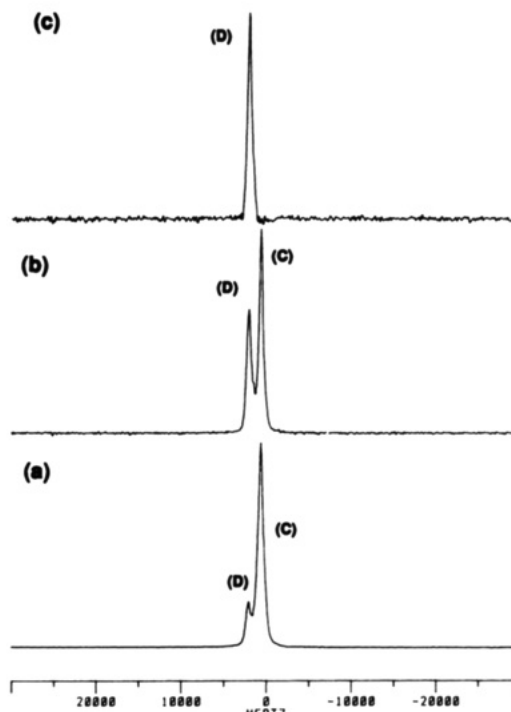


Figure 7. (a) Carr-Purcell spin-echo spectrum of polycarbonate exposed to refluxing water for 30 days (dephasing delay = 810 μs). (b) Carr-Purcell spin-echo spectrum of polycarbonate exposed to refluxing water for 30 days (dephasing delay = 3.8 ms). (c) Carr-Purcell spin-echo spectrum of polycarbonate exposed to refluxing water for 30 days (dephasing delay = 22.3 ms).

of the peak (D) at 5.2 ppm relative to the peak (C) at 1.73 ppm has increased substantially from much less than 1% to approximately 5%, and the relaxation parameters of the three components are essentially unchanged. Again, the total peak intensities relative to the broad component are in approximate agreement with measured weight gain.

A series of Carr-Purcell spin-echo spectra were taken at different time to echo values, corresponding to those used to obtain a FLASH image (810 μs, Figure 7). This pulse sequence is an effective way of examining spectroscopically the proportions of the various components which will contribute to a given image since the data are acquired

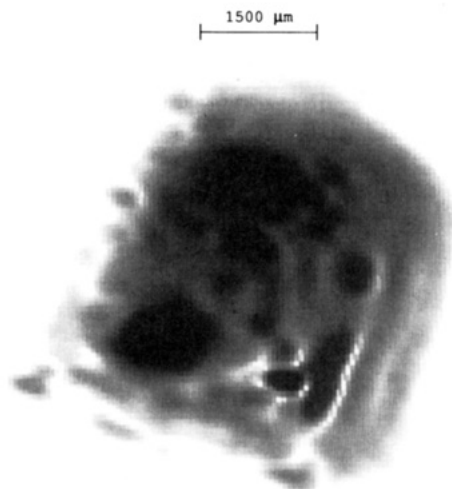


Figure 8. Spin-echo image of polycarbonate exposed to refluxing water for 30 days. Slice gradient strength 1.7 G/cm, slice thickness = 5.4 mm, time to echo = 3.8 ms, frequency encode gradient strength 2.74 G/cm, phase encode gradient strength = 4.8 G/cm incremented through 128 experiments, in-plane resolution = 167 μm, pixel dimensions of image = 83.5 μm.

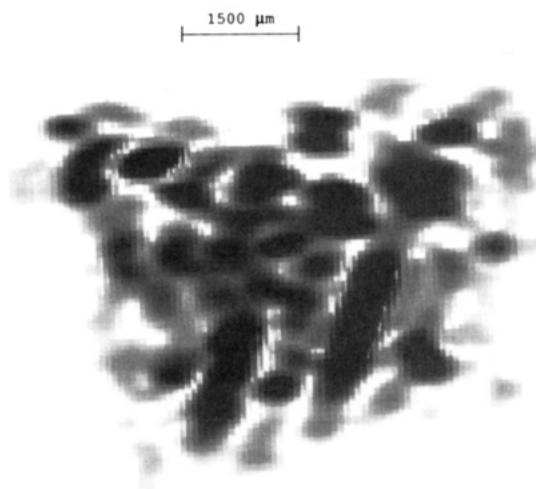


Figure 9. Spin-echo image of polycarbonate exposed to refluxing water for 30 days. Slice gradient strength 1.7 G/cm, slice thickness = 5.4 mm, time to echo = 23.8 ms, frequency encode gradient strength 2.74 G/cm, phase encode gradient strength = 4.8 G/cm incremented through 128 experiments, in-plane resolution = 167 μm, pixel dimensions of image = 83.5 μm.

under conditions where there will be identical decays in the magnetization before data acquisition as will occur in the corresponding imaging experiments. The contributions to the intensities in the images may thus be directly related to the signals observed in the one-dimensional ^1H spectra.

The major contribution to the image at an echo time of 810 μs is from the peak at 1.73 ppm. The intensity of the smaller peak at 5.2 ppm is directly proportional to the dephasing time (τ) due to its longer T_2 relaxation time. At 22 ms, only contributions from the peak at 5.2 ppm will remain. Thus, an image taken at an echo time of 22 ms will reflect only the distribution of the minor, slowly dephasing and very mobile component.

In the spin-echo images taken at 3.8 (Figure 8) and 22 ms (Figure 9) large numbers of pools are now observed. A low-level signal from the entire rod is still visible in the 3.8 ms image. The pools in the 22-ms spin-echo image are due solely to the peak at 5.0 ppm since the peak at 1.8 ppm has completely dephased by this time. Within the limited resolution of the imaging experiment, the dimensions of the pools of "free" water can be estimated as being approximately 200–300 μm in diameter. After 30 days, visible damage is observed on "slicing up" the sample.

Material exposed to refluxing water for 30 days was subsequently exposed to refluxing D_2O for 16 h. A very substantial reduction in the signal intensity for both the peak at 1.73 ppm and the peak at 5.2 ppm is observed. A residual signal is observed due to the traces of HOD in the D_2O and perhaps also to traces of processing materials. This suggests strongly that both peaks are due to absorbed water which has different environments. The water which has aggregated into pools has a chemical shift similar to water in the pure liquid (5.2 vs 4.65 ppm).

Conclusions

Although the total amount of water absorbed by bulk polycarbonate is less than 1% w/w, good-quality images can be obtained, demonstrating that the microimaging technique can successfully monitor even trace levels of

sorbed species if the molecules are relatively mobile and short times to acquisition are used. The protocol of measuring ^1H one-pulse spectra, Carr–Purcell spin-echo spectra, and the relaxation parameters of the various components and then correlating these data to the images obtained under different conditions is a very effective one in the study of the chemistry of solvent/polymer interactions.

In contrast to either type I or type II Fickian diffusion processes commonly observed for bulk polymers, the diffusion into polycarbonate is a two-stage process which is heterogeneous in nature. In the initial stages of water absorption, the water is evenly distributed throughout the polymer matrix inside the slice (4 mm) and within the in-plane resolution of 167 μm. A small number of pools of "free" water with dimensions of approximately 200–300 μm in which the water has aggregated are also visible. As the exposure to the water continues, the number of these pools increases and the proportion of the total water in these pools increases, ranging from 5 to 10% of the total sorbed water.

Due to the importance of this system and the potential of improving the performance of polycarbonate in optical storage systems if water absorption can be suppressed, we plan to continue work in this area and investigate the effects of additives and processing conditions. An advantage of the microscopic imaging technique is that it can examine the effects that surface properties may have on the absorption process and the properties of the bulk since thin films are not required. From the data presented in this study, it should be possible to investigate the distribution of the pools of free water using considerably thinner slices.

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