

# An n.m.r. study of absorbed water in polybenzimidazole

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Polybenzimidazole (PBI) is known to absorb 15 wt% water at equilibrium. This sorbed water greatly affects the mechanical properties of this polymer. Both FTi.r. and broadline n.m.r. have been used to study the interaction between water and PBI. The results clearly show that the water in PBI is mobile and therefore does not hydrogen bond to the polymer chain.

(Keywords: n.m.r. study; absorbed water; polybenzimidazole)

## INTRODUCTION

Polybenzimidazole (PBI) is a rigid polymer which is known for its excellent mechanical and thermal properties. It is also known to absorb 15 wt% water at equilibrium in a 100% r.h. atmosphere. This water uptake is large when compared with other engineering polymers (see Table 1).

Mechanical measurements on the compressive strength of PBI have shown that the sorbed water greatly affects the mechanical properties of the polymer. Figure 1 shows compressive stress-strain curves for both the wet and the dry materials. It can be seen that the compressive strength is more than halved in the wet state. Figure 2 shows that the dynamic modulus for the wet material is also reduced to about half that of the dry material at room temperature.

Looking at the structural unit of PBI (Figure 3), it can be seen that it may be possible for intermolecular hydrogen bonding to occur in this polymer through the combination of the N and N-H groups in the imidazole ring. One possible arrangement for intermolecular hydrogen bonding is shown in Figure 4a. It is also possible for water to hydrogen bond to the polymer in two ways, as shown in Figures 4b and c.

The first possibility would occur if two water molecules were attached to each imidazole ring (see Figure 4b). In this case one water molecule could act as a proton acceptor and the other as a proton donor. This arrangement would allow a maximum of four water molecules to be attached to each polymer repeat unit. The second case involves one water molecule attached to two neighbouring imidazole rings on adjacent polymer chains (see Figure 4c). In this case the water molecule would act as both a proton acceptor and a donor. This arrangement would allow a maximum of two attached water molecules per polymer repeat unit.

The molecular weights of PBI and water are 308 and  $18 \text{ g mol}^{-1}$ , respectively. Therefore in PBI containing 15 wt% water there are approximately 2.5 water molecules per repeat unit. This value is between the two limits calculated above, and so it is possible that the high water uptake of PBI is due to the water hydrogen bonding to the polymer.

This idea is supported by work carried out by Adams *et al.*<sup>1</sup>. They used 2,6-diphenylbenzo(1,2-d;5,4-d')diimidazole tetrahydrate (see Figure 5), which they

Table 1 Water uptake in various engineering polymers

Material	Equilibrium water content (%)
PBI	15.0
Polyimide	1.2
PEEK	0.5
PC	0.3
Vectra (LCP)	0.1

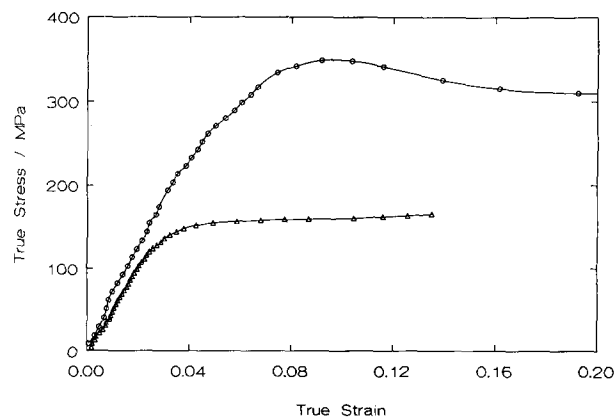


Figure 1 Stress-strain curves for (Δ) wet and (O) dry PBI

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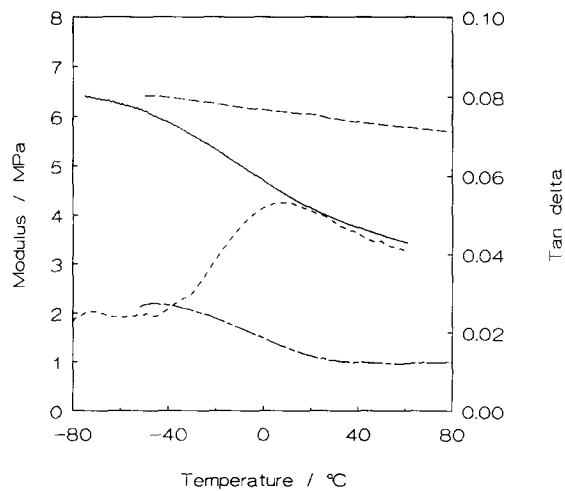


Figure 2 Dynamic modulus and  $\tan \delta$  for wet and dry PBI: —, wet modulus; ---, wet  $\tan \delta$ ; -.-, dry modulus; ···, dry  $\tan \delta$

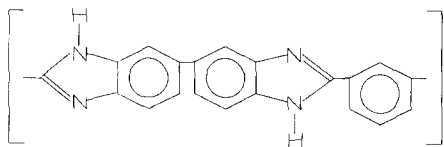


Figure 3 PBI repeat unit

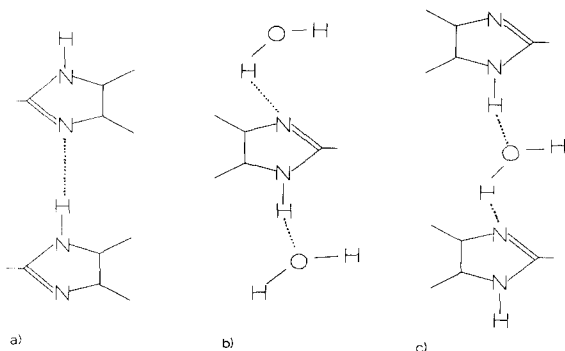


Figure 4 Hydrogen bonding in PBI: (a) dry PBI; (b) wet case 1 PBI; (c) wet case 2 PBI

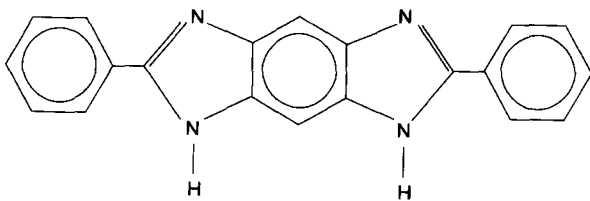


Figure 5 PBI 'model compound', see text

considered a model material for PBI polymers. Their work showed that strong hydrogen bonds formed between the imidazole rings and water and, further, that the water was incorporated into the crystalline structure of single crystals of this material.

Measurements on the rate of water uptake in PBI show that the weight gain due to moisture absorption is proportional to the square root of the time (see Figure 6), which indicates Fickian diffusion. One assumption of Fick's law is the non-interaction of the diffusing species and the matrix.

This result agrees with work by Hughs<sup>2</sup>, who measured the equilibrium water content of PBI as a function of relative humidity. He showed that the equilibrium water content was directly proportional to the relative humidity of the environment, in agreement with Henry's law and, moreover, was independent of temperature, which indicates a zero heat of solution. This is usually the situation when a molecularly dispersed, non-interacting penetrant is sorbed by an amorphous matrix<sup>2</sup>.

There is thus evidence for both interaction (hydrogen bonding) and non-interaction between water and PBI. The aim of the current work is to try to identify any such interaction.

## EXPERIMENTAL

Two techniques have been used to investigate this problem.

### FTi.r. spectroscopy

The first technique was FTi.r. using a Bomem spectrometer. Thin-film PBI (10  $\mu\text{m}$  thick), produced by casting from DMAc solution, was used for this experiment. Dry samples were prepared by drying the film in a vacuum oven for 24 h at 180°C. Wet samples were prepared by placing the film in a beaker of water overnight.

### N.m.r. spectroscopy

Broadline proton n.m.r. investigations were carried out using a Varian DP60 broadline spectrometer operated at 60 MHz. A time-averaging computer was used to add together the signals from several successive sweeps through the spectrum to improve the signal-to-noise ratio.

A 0.3056 v/v sample of distilled H<sub>2</sub>O in D<sub>2</sub>O (Fluorochem Ltd) was used as an intensity calibration standard. The magnetic field sweep was calibrated using the side bands produced by modulating the transmitter frequency at 30 kHz and running a sample of glycerol (Aldrich) at low field modulation. The frequency modulation produced side-bands at 60 MHz  $\pm n$  (30 kHz), and these appear at 7.046 G intervals in the recorded spectrum. The increment of field intensity at which the signal was sampled was approximately 0.06 G.

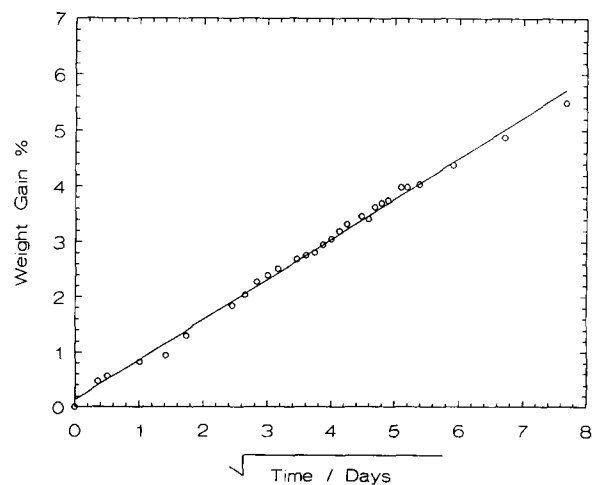


Figure 6 Water uptake in PBI

The field modulation amplitude was determined by measuring the separation between the maximum and the minimum of the derivative signal of a glycerol sample. The values of the second moments for the rigid component were thus corrected for a fixed modulation amplitude of 0.766 G using the Andrew correction<sup>3</sup>.

Two samples of PBI were machined to fit inside a 5 mm n.m.r. tube. One of the samples was placed in a vacuum oven at 180°C for 48 h to remove any absorbed moisture. The sample was then cooled under vacuum before being transferred to the n.m.r. machine for analysis. This sample is referred to as the dry sample.

The other sample was first dried using the above method. On removal from the oven the sample was weighed and then placed in boiling water. It was then weighed at various intervals until equilibrium was reached. This sample is referred to as the wet sample. All measurements were performed at room temperature.

The following procedure was used to decompose the proton n.m.r. signal of the wet PBI sample into two components: a broad-line component arising from the protons of the effectively rigid polymer chains, and a narrow component associated with mobile protons presumed to be from the absorbed water. It was assumed that the polymer gives rise to an n.m.r. signal which can be considered a Pake doublet<sup>4</sup> associated with aromatic proton pairs. This doublet is broadened by other intramolecular interactions and intermolecular interactions to give a Gaussian doublet line shape, as was observed for the dry PBI sample. To perform the decomposition, we adapted the method originally developed by Pranadi and Manuel<sup>5</sup> for the analysis of isotropic polyethylene lineshapes, and used by Clements *et al.*<sup>6</sup> in the studies of oriented poly(vinylidene fluoride).

The Gaussian doublet line shape may be defined as follows:

$$Y(\Delta H) = a_1 \left\{ \exp \left[ \frac{-(\Delta H - a_2)^2}{2a_3^2} \right] + \exp \left[ \frac{-(\Delta H + a_2)^2}{2a_3^2} \right] \right\}$$

It consists of the superposition of two identical Gaussian line shapes whose centres are separated by a field interval  $2a_2$  and whose individual second moments about their centres are  $a_3^2$ . The area under this composite curve is  $(8\pi)^{1/2} a_1 a_3$  and the second moment  $\langle \Delta H^2 \rangle = a_2^2 + a_3^2$ . The variable  $\Delta H = H - H_0$ , where  $H_0$  is the magnetic field at the centre of the doublet. Previously<sup>6,7</sup> it was possible to fit this line shape to the outer part of the experimental line with  $a_1$ ,  $a_2$  and  $a_3$  as adjustable parameters, using a non-linear least squares procedure with parabolic extrapolation<sup>8</sup> by minimizing the sum:

$$\chi^2 = \sum_i \left\{ \frac{[A_i - Y(\Delta H_i)]^2}{\sigma_i^2} \right\}$$

where  $A_i$  is the experimental value of the absorption line at the  $i$ th point,  $\sigma_i$  is the uncertainty in the data point  $A_i$  and  $Y(\Delta H_i)$  the corresponding value of the Gaussian doublet.  $\chi^2$  can be considered as a function of  $a_1$ ,  $a_2$  and  $a_3$ , represented by a three-dimensional hypersurface which must be searched for a minimum. However, the search for the global minimum of  $\chi^2$  involves choosing initial values for the parameters  $a_1$ ,  $a_2$  and  $a_3$ , and the search only converges reliably to the global minimum of  $\chi^2$  if the initial choices for the parameters are sufficiently close. When performing this analysis on the measured lineshapes for isotropic polyethylene and

oriented poly(vinylidene fluoride) Pranadi and Manuel<sup>5</sup> were able to calculate the value of  $a_2$  appropriate to a pair of protons in a  $\text{CH}_2$  group and  $a_3$  from theoretical second moments derived from published crystallographic data; the initial choice of  $a_1$  was made by inspection. This procedure cannot be used in this work since PBI is an amorphous polymer. For this reason the Levenburg–Marquardt<sup>9</sup> gradient expansion algorithm, which is less sensitive to the initial choices of the parameters  $a_1$ ,  $a_2$  and  $a_3$ , was used to minimize the above sum, although it is still necessary to vary the initial values of these parameters to ensure that a global minimum is found.

## RESULTS AND DISCUSSION

### FTi.r. spectroscopy

The regions of interest in the infra-red spectrum for PBI are the peaks corresponding to the free N–H stretch, the N–H···H polymer–polymer interaction and the O–H stretch for free water. These peaks occur at approximately 3420, 3150 and 3620  $\text{cm}^{-1}$ , respectively.

The traces for both wet and dry PBI are shown in Figure 7. For the dry sample it can be seen that there is a small amount of free water in this sample. This is due to the absorption of water during transfer of the sample from the oven to the spectrometer and during the FTi.r. scan (transfer time < 1 min, scan time 2.5 min). It can also be seen that there are peaks indicating both free and hydrogen bonded N–H groups. This is shown more clearly in Figure 8, which shows a scan obtained for dried PBI placed in a heated cell for 45 min at 120°C prior to scanning. (Note that this was carried out on a Perkin–Elmer dual-beam scanning spectrometer.) It is important to note in Figure 8 that there is no peak for the O–H stretch, showing that it is possible to remove the peak for the O–H stretch which occurs in Figure 7. This indicates that the O–H peak in Figure 7 is due to uptake of water in air after removal of the sample from the oven.

In the wet material it can clearly be seen that there is an increase in the free O–H peak, which corresponds to free water. In the rest of this spectral region there is an overall increase in the absorbance in the wet sample, but

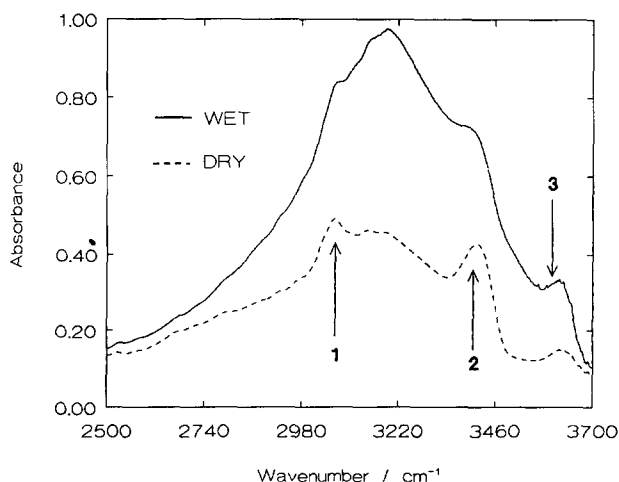


Figure 7 Infra-red spectra of wet and dry PBI films: (1) aromatic C–H stretch; (2) imidazole, free N–H stretch; (3) water, O–H stretch

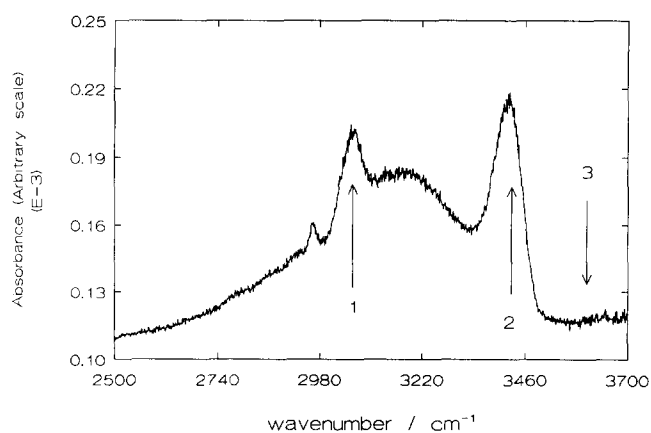


Figure 8 Infra-red spectrum of PBI film at 120°C. Stretches as in Figure 7

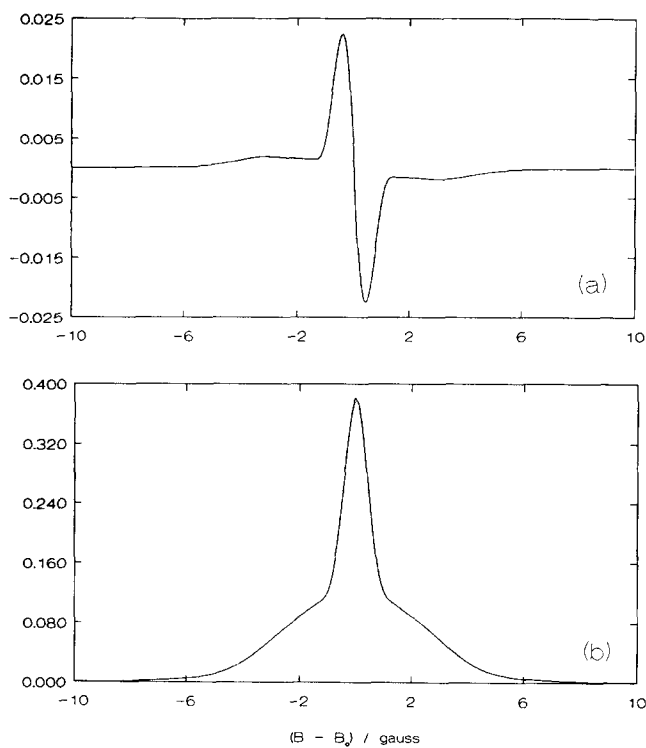


Figure 9 Derivative (a) and absorption (b) n.m.r. spectra for wet PBI sample. The abscissae are in gauss and the ordinates represent absorption normalized to unit-integrated intensity

no specific information about hydrogen bonding can be deduced.

*N.m.r. spectroscopy*

Figure 9 shows the derivative and absorption broad-line n.m.r. spectra for the wet sample of PBI. Figures 10 and 11 illustrate the corresponding spectra for the dry sample and for the calibration sample of H<sub>2</sub>O in D<sub>2</sub>O. These spectra may be compared directly, since they have all been normalized to unit-integrated intensity. It is clear that the spectrum for the wet sample is a composite spectrum, composed of a broad doublet superimposed on a narrow singlet. In comparison, the spectrum for the dry sample would appear to be a simple one, just a single broad line. The existence of two distinct components of different widths in the wet spectrum is entirely consistent with one component, the broad doublet, arising from

protons of the polymer, and the other component, the narrow singlet, arising from protons of the absorbed water. The apparent absence of the narrow singlet in the spectrum of the dry sample confirms these observations, although, as will be seen below, a small amount of free water is also present in the dry sample, due to absorption during the experiment. To reduce the noise of the resultant spectrum the sum of several sweeps was taken.

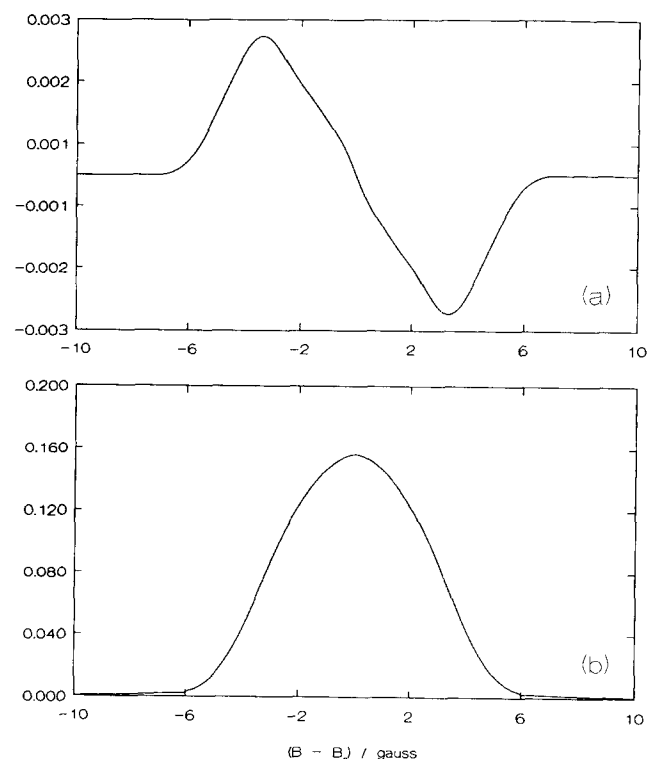


Figure 10 Derivative (a) and absorption (b) n.m.r. spectra for dry PBI sample

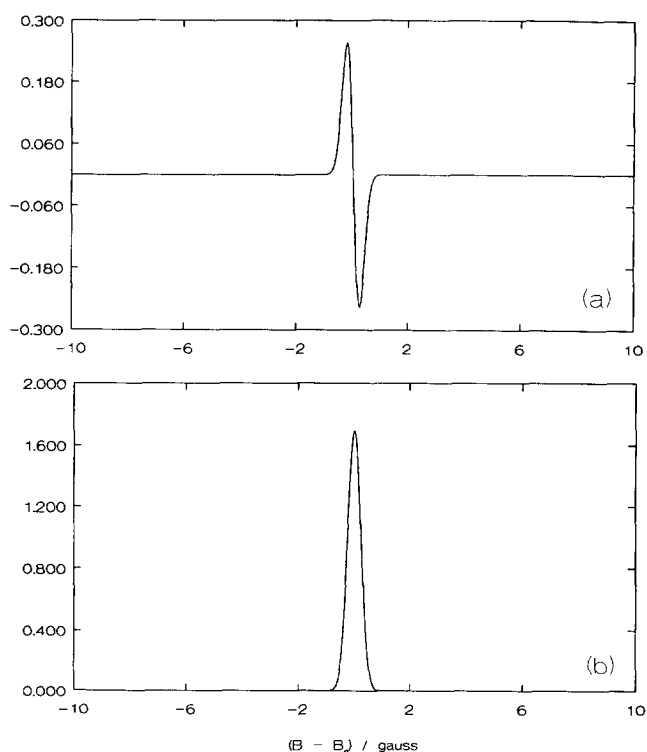


Figure 11 Derivative (a) and absorption (b) n.m.r. spectra for 0.3056 v/v H<sub>2</sub>O in D<sub>2</sub>O

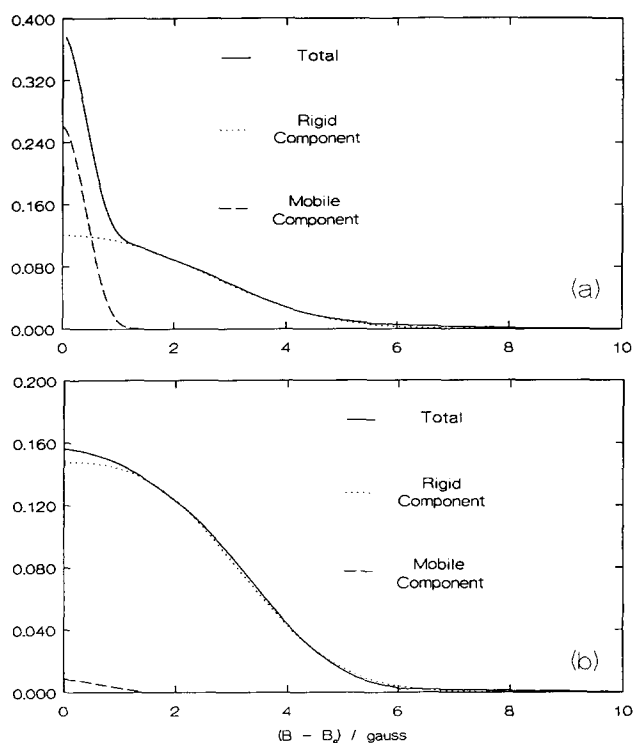


Figure 12 Absorption n.m.r. spectra for (a) wet and (b) dry PBI samples showing the fitted double Gaussians and the residual singlet

Table 2 Mobile fraction,  $f_w$ , and second moments for the Gaussian doublet  $\langle \Delta H^2 \rangle_d$  and singlet  $\langle \Delta H^2 \rangle_w$  components of the n.m.r. absorption for wet and dry samples of PBI

Sample	$f_w$	$\langle \Delta H^2 \rangle_d$ (G <sup>2</sup> )	$\langle \Delta H^2 \rangle_w$ (G <sup>2</sup> )
Wet	0.29	4.90	0.16
Dry	0.02	5.30	0.15

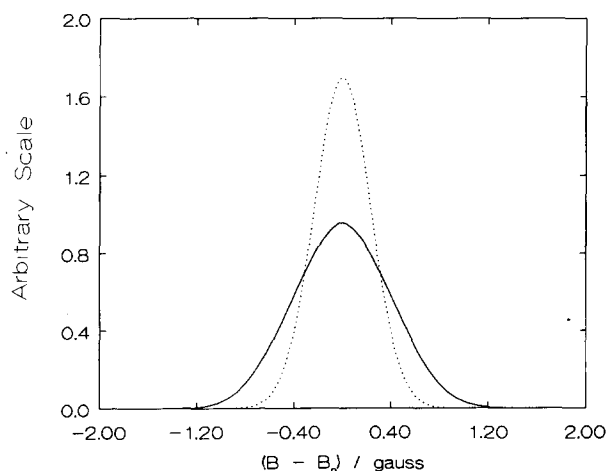


Figure 13 Absorption n.m.r. spectra of (---) 0.3056 v/v H<sub>2</sub>O in D<sub>2</sub>O ( $\langle \Delta H^2 \rangle = 0.055 \text{ G}^2$ ) and (—) the residual singlet of wet PBI ( $\langle \Delta H^2 \rangle = 0.16 \text{ G}^2$ )

The absorption signals of the wet and dry samples were decomposed using the method outlined above and the results are shown in Figure 12. Table 2 shows the ratio of the integrated intensity of the residual singlet to the total integrated intensity,  $f_w$ , which can be associated with the volume fraction of water absorbed in both the wet and the dry samples. The second moments calculated from this decomposition procedure are also given, where  $\langle \Delta H^2 \rangle_d$  is the calculated second moment of the fitted

Gaussian doublet and  $\langle \Delta H^2 \rangle_w$  is the calculated second moment of the residual singlet. Although a certain line broadening of the water spectrum shown in Figure 11 is inevitably produced by the field modulation used to record the spectrum, a qualitative assessment is still possible. If we compare the residual singlet of the wet sample with the water of the calibration sample, shown in Figure 13, we can draw the following conclusions:

1. The absorbed water in the wet sample is free water, undergoing rapid tumbling to produce the narrow singlet observed. This is a clear indication that the water molecules are not bonded to the polymer chains.
2. The ratio of the integrated intensity of the residual singlet to the total integrated intensity,  $f_w$ , is 0.29 for the wet sample and 0.02 for the dry sample. If all the water in PBI is free then the expected value for  $f_w$  is 0.294 since there are 12 protons per monomer of PBI and approximately 2.5 water molecules per monomer at equilibrium. This is clearly in agreement with the value  $f_w = 0.29$  for the wet sample. For the wet sample,  $f_w$  corresponds to 15 wt% or about 2.5 water molecules per PBI repeat unit, and for the dry sample 1 wt%.
3. The fitted Gaussian doublet of the wet sample is narrower and has a smaller second moment than that of the dry sample. The reduction in second moment, which depends on the sum of  $r_{ij}^{-6}$  for all proton pairs, is consistent with the 3.3% swelling that occurs in the wet polymer.

## CONCLUSIONS

The FTi.r. results are not conclusive. At first there is a reduction in free N-H stretch absorption in the wet samples, perhaps because of water-polymer hydrogen bonding. However, this apparent decrease in absorbance might be due to the large overall increase in absorption in this region of the spectrum.

PBI is known to have the highest compressive yield stress of any polymer<sup>10</sup>. These FTi.r. results provide no evidence to suggest that this is due to strong intermolecular hydrogen bonding in the dry state being disrupted in the wet state.

The n.m.r. results show very clearly that the majority of water in PBI is effectively mobile, and therefore not bonded to the polymer. The loss in mechanical properties in wet PBI could be due to the reduction in van der Waals forces and possibly hydrogen bonding interactions between chains as a consequence of the swelling of the wet material.

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