

# High-temperature steam-treatment of PBI, PEEK, and PEKK polymers with H<sub>2</sub>O and D<sub>2</sub>O: A solid-state NMR study



Jacqueline C. Pope<sup>a</sup>, Hung-Jue Sue<sup>b</sup>, Tim Bremner<sup>b, c, \*\*</sup>, Janet Blümel<sup>a, \*</sup>

<sup>a</sup> Department of Chemistry, Texas A&M University, College Station, TX 77842-3012, USA

<sup>b</sup> Department of Mechanical Engineering, Polymer Technology Center, Texas A&M University, College Station, TX 77843-3123, USA

<sup>c</sup> Hoerbiger Corporation of America, Inc., 1212 Milby Street, Houston, TX 77023, USA

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## ABSTRACT

Polyaryletherketones (PAEK) in blend systems with polybenzimidazoles (PBI) are of commercial interest due to their increased service temperature and reduction in abrasive wear against soft counterfaces when compared to PAEK alone. ASTM standard tensile specimens of PBI, polyetheretherketone (PEEK) and polyetherketoneketone (PEKK) are immersed in stirred D<sub>2</sub>O at room temperature, and additional samples are contacted with D<sub>2</sub>O steam at temperatures of 150 and 315 °C. All samples are studied by TGA, IR, <sup>13</sup>C CP/MAS, <sup>1</sup>H wideline, and <sup>2</sup>H MAS NMR. Changes in the physical appearance of the samples and the extent of D<sub>2</sub>O uptake are described. Different locations, mobilities, and types of water and protons in the polymers are identified and studied and it is proven that PBI contains the largest amounts of D<sub>2</sub>O after exposure under all conditions. PEEK and PEKK only incorporate minimal amounts of D<sub>2</sub>O even when steam-treated at 315 °C.

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## 1. Introduction

Polyaryletherketones (PAEK) represent an important group within the family of thermoplastic polymers [1]. PAEK polymers include PEEK (polyetheretherketone) and PEKK (polyetherketoneketone) polymers (Scheme 1), and these are of growing interest in a wide range of applications, where high temperatures, high differential pressures and corrosive environments are encountered. While commercially available PAEK grades from various suppliers have already become indispensable for end users, the demand for even higher temperature applications increases steadily. One approach for meeting these demands is to manufacture blends of polyaryletherketone polymers with PBI (polybenzimidazole) resins (Scheme 1). The resulting PAEK–PBI blends contribute to the increased service temperatures and some improvement in the wear properties that come with the PBI component. However, in contrast to the pure PEEK and PEKK components, the PBI blends exhibit more complex interactions with aqueous systems, such as water and steam [2], as well as salt solutions [4]. Therefore, a deeper understanding and quantification of the interactions of water with these blend systems, and the

distribution of water within the morphology of the polymer blend is of importance. In this study, we will contrast the content and distribution of absorbed moisture in the pure polymer and the blend pairs of interest. If there is an opportunity to understand or control the impact of absorbed moisture in this important polymer blend, the value is in accounting for the impact of the absorbed water on material performance and design criteria for the demanding applications that we wish to target.

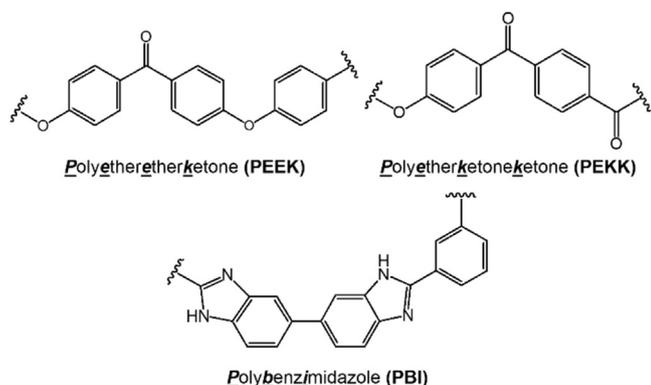
In the study presented, the traditional Celazole-type PBI (poly [2,2'-(*m*-phenylene)-5,5'-bibenzimidazole]), as well as PEEK and PEKK in the form of ASTM tensile specimens are exposed to H<sub>2</sub>O and D<sub>2</sub>O at ambient temperature. In order to simulate high-temperature exposure in a known problem area for the PBI material, the polymers have also been steam-treated with H<sub>2</sub>O and D<sub>2</sub>O at 150 °C (ca. 300 °F) and 315 °C (ca. 600 °F) for 48 and 72 h.

The impact of water or steam on PBI, PEEK, and PEKK polymers has not been extensively described by other research groups, and the few accessible reports focus on different PBI-based systems [3]. Using a molecular model compound mimicking PBI, one report, for example, discusses two ways in which water could reside in PBI [3a]. It can form larger aqueous domains nestled between the PBI polymer strands, or it can be bound to the N–H group of the benzimidazole unit by hydrogen bridges. Furthermore, a single crystal X-ray structure has been obtained, which shows the location of water molecules around a benzimidazole moiety incorporated in a cobalt complex [5].

\* Corresponding author. Tel.: +1 979 845 7749; fax: +1 979 845 5629.

\*\* Corresponding author. Department of Mechanical Engineering, Polymer Technology Center, Texas A&M University, College Station, TX 77843-3123, USA.

E-mail address: [bluemel@tamu.edu](mailto:bluemel@tamu.edu) (J. Blümel).



**Scheme 1.** Structures of Polyetheretherketone (PEEK), Polyetherketoneketone (PEKK), and Polybenzimidazole (PBI).

For analyzing the PBI, PEEK, and PEKK samples before and after exposure to  $D_2O$  under various conditions, several methods are applied. In order to assess the overall water content of the samples in a straightforward and quantitative manner, TGA analyses are performed. IR spectroscopy is employed as another powerful tool [6–9], especially when investigating potential hydrogen-bonding of water to the C=O group of PEEK or PEKK, which would lead to a decreased value of the stretching frequency for the carbonyl group [6]. Another valuable piece of information can be obtained from the different stretching and vibrational modes of  $H_2O$  and  $D_2O$ . For example, the stretching band of O–D appears at about  $2500\text{ cm}^{-1}$  [8], a spectral region that is very favorable because it is not populated by any other peaks from the polymers. In this way the O–D stretching band is also easy to distinguish from the O–H stretching peak at around  $3400\text{ cm}^{-1}$  [6,8].

Solid-state NMR spectroscopy is a powerful analytical tool that allows a multitude of diverse measurements of crystalline and amorphous compounds and materials [2,10–23]. Polymers represent the most prominent and the classic materials for solid-state NMR investigations [12,20]. The cross polarization (CP) of magnetization from the abundant protons in polymers to the measured nuclei facilitates measurements of materials such as PBI or PAEK polymers, as it improves the signal to noise (S/N) ratio in the spectra [2,12–14]. The most common nucleus for measuring polymers is  $^{13}C$  [12,13,20], followed by  $^2H$  wide-line (no spinning) and MAS (Magic Angle Spinning) NMR [10,19,23]. In this contribution it will be demonstrated that  $^1H$  wide-line NMR spectroscopy [2,10,15–18] can give valuable complementary information about the polymer systems on the molecular level as well.

$^1H$  wide-line NMR spectroscopy can distinguish protons of the immobile polymer backbone from mobile  $H_2O$  in aqueous domains. Mobile species lead to a relatively narrow signal sitting on the broad hump of the backbone signal in the  $^1H$  wide-line NMR spectra [2,10]. The method is limited when a distinction between different immobile nuclei, such as C–H and N–H protons in PBI is sought [2].

For cases where a differentiated picture about the various sorts of protons and water and their mobilities are needed  $^2H$  MAS can be applied [10,19,23]. This eliminates any signals from the polymer backbone.  $^2H$  is a quadrupolar nucleus with spin of 1, and therefore the Pake patterns [10,12,19,23] of  $^2H$  wide-line signals in the solid state display a splitting of the two lines with maximal intensity that allows the calculation of the quadrupolar coupling constant  $Q_{cc}$ . Sample spinning splits the Pake pattern into sets of rotational sidebands.  $Q_{cc}$  can be calculated from spectra of rotated samples as described in the experimental section and in the literature [24,25]. The mobilities of the species or functional groups containing the

measured  $^2H$  nucleus can be determined via  $Q_{cc}$  [10,19,23]. The correlation between reorientation times and the shapes of the corresponding Pake patterns has been described in detail for long deuterated alkyl chains [23].  $^2H$  MAS spectroscopy has previously been applied by us to quantify the mobilities of metallocenes adsorbed on silica surfaces [10]. But there are also examples for applications in the field of polymers in the literature, and recently  $^2H$  solid-state NMR has been applied to gain quantitative insight into different dynamic scenarios [19]. For example, the segmental mobilities of polymer chains [19h] and the plasticization of poly(vinyl acetate) adsorbed on silica have been investigated using  $^2H$  solid-state NMR [19f].

## 2. Results and discussion

### 2.1. Steam-treatment of PBI, PEEK, and PEKK with $H_2O$ and $D_2O$

For testing the moisture uptake of the corresponding tensile specimens under mild conditions at ambient temperatures, they have been stirred in liquid  $H_2O$  and  $D_2O$  for 48 h. Additionally, in order to mimic more realistic conditions of their exposure to fluids, the PBI, PEEK, and PEKK samples have also been steam-treated with  $H_2O$  and  $D_2O$ . For this purpose, the samples are placed into stainless steel pressure vessels with the glass sample holders [4]. Then the pressure vessels are filled with 150 mL of liquid  $H_2O$  or  $D_2O$  to the height of about 1.5 cm, then sealed and heated. The pressures in the closed vessels reach 5 bar (72 psi) at  $150\text{ }^\circ\text{C}$  and 110 bar (1600 psi) at  $315\text{ }^\circ\text{C}$ . The exposure of the samples to water at room temperature and  $150\text{ }^\circ\text{C}$  has been maintained for 48 h, and at  $315\text{ }^\circ\text{C}$  for 72 h.

As described qualitatively in previous work [2–4], PBI is hydrophilic and able to incorporate large amounts of water readily from the atmosphere. The affinity of the benzimidazole moiety to water becomes also obvious, for example, when contemplating the single crystal X-ray structure of a representative molecular species [5]. The water uptake of PBI is reversible when it takes place under mild conditions, and upon drying powdered samples, the material gives the original  $^{13}C$   $T_1$  relaxation time data [2] again and assumes its previous weight [4]. Hereby, the drying process is faster for powdered samples than for the molded tensile specimens due to the larger specific surface area [4]. By weighing the PBI samples as received before drying them at  $110\text{ }^\circ\text{C}$  *in vacuo* (0.1 torr) it has been determined that up to 9 wt% of the material consists of water [4].

For a more refined analysis, melt-molded PBI is subjected to steam-treatment with  $H_2O$  under controlled conditions and subsequently analyzed by TGA (Fig. S1). Immersing the tensile specimen in liquid water and stirring for 48 h leads to a moisture content of 5%. Steam-treatment with water at  $150\text{ }^\circ\text{C}$  increases the  $H_2O$  content significantly and 11% of the weight of the sample is lost during the TGA analysis. The highest temperature leads to a medium moisture content of 9%. This result is in accordance with earlier analyses performed with different NMR spectroscopic methods [2,4].

As anticipated, regarding the earlier analyses of PEEK-PBI and PEKK-PBI blends [2,4], the moisture uptake of pure PEEK and PEKK is much less than for PBI. The TGA of PEEK (Fig. S2) shows that by stirring the sample at room temperature with  $D_2O$  and during steam-treatment at  $150\text{ }^\circ\text{C}$  with  $D_2O$  basically no water is adsorbed. After steam-treatment with  $D_2O$  at  $315\text{ }^\circ\text{C}$  about 4 wt% of  $D_2O$  is incorporated into the polymer, which would correspond to a weight loss of 3.6% of non-deuterated water when taking the lower molecular weight of  $H_2O$  into account.

For PEKK the corresponding moisture contents show the same trends as for PEEK (Fig. S3). There is practically no water uptake during the treatment of PEKK with  $D_2O$  at ambient temperature and steam-treatment at  $150\text{ }^\circ\text{C}$ . After steam-treatment with  $D_2O$  at

315 °C a weight loss of only about 3% is visible in the TGA curve, which would correspond to an even lower value for the lighter H<sub>2</sub>O. It should also be noted that no moisture is found by TGA after prolonged exposure of PEEK and PEKK to the atmosphere. The NMR and IR measurements (see below) are in accordance with these results.

Overall, the TGA results corroborate the assumption that in PEEK and PEKK blends of PBI, the PBI component is the one mainly responsible for any water uptake.

## 2.2. <sup>13</sup>C, <sup>1</sup>H, and <sup>2</sup>H NMR and IR spectroscopy for probing different H<sub>2</sub>O sites in PBI, PEEK, and PEKK

After gaining an overview of water in general incorporated into PBI, PEEK, and PEKK, a more differentiated picture is sought. For this purpose, besides IR and <sup>13</sup>C solid-state NMR analysis, <sup>1</sup>H wideline NMR and <sup>2</sup>H MAS are applied in the following. For <sup>2</sup>H solid-state NMR spectroscopy the samples have been treated with D<sub>2</sub>O instead of H<sub>2</sub>O. Since the largest amount of moisture obviously resides in the PBI, it will be discussed first.

## 2.3. Analysis of PBI after exposure to H<sub>2</sub>O and D<sub>2</sub>O as liquid and steam

When a melt-molded sample of PBI is stirred in water at ambient temperatures, changes in its appearance are immediately obvious. Its color darkens (Fig. 1), but no obvious change of its texture takes place. The surface of the material remains smooth and it does not become brittle. The same observation is made after steam-treatment with D<sub>2</sub>O at 150 °C, although some first defects on the surface become visible. However, after steam-treatment at 315 °C for 72 h the color is lighter again and the material becomes brittle. Its surface is rough and some pieces have chipped off at the edges of the specimen (Fig. 1). It is noteworthy that D<sub>2</sub>O practically does not differ in its reactivity from H<sub>2</sub>O, and the same observations are made using the latter for steam-treatment.

Since there are massive changes in the appearance of the material occurring after steam-treatment, the IR spectra of PBI have been recorded (Fig. 2). IR spectroscopy shows that the only major change when steam-treating the PBI with D<sub>2</sub>O at 150 °C is that water is incorporated into the polymer network. This can be concluded from the large broad signal in the middle spectrum of Fig. 2, with the lowest transmission at 2256 cm<sup>-1</sup> [8]. The largest difference between the IR spectra is found when proceeding to steam-treatment at 315 °C (Fig. 2, top). The polymer backbone seems to be affected, as the whole region from 1447 to 600 cm<sup>-1</sup> is largely changed. In particular, the peaks at 1447, 1377, and 1308 cm<sup>-1</sup>, representing the D<sub>2</sub>O and H<sub>2</sub>O bending modes [8], are shifted. At the same time, the broad water O–H stretching peak around 3100 cm<sup>-1</sup> increases in intensity. Overall the IR spectra

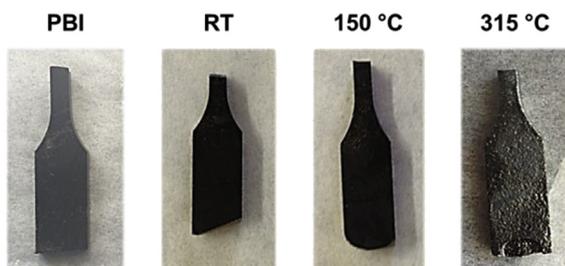


Fig. 1. Change of physical appearance of melt-molded PBI after stirring in D<sub>2</sub>O at RT, and steam-treatment with D<sub>2</sub>O at 150 °C and 315 °C.

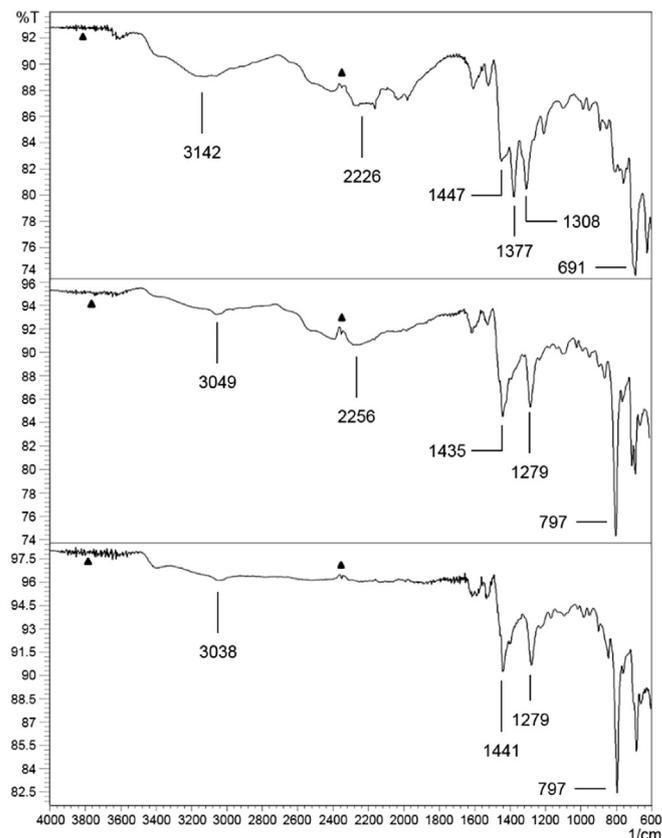
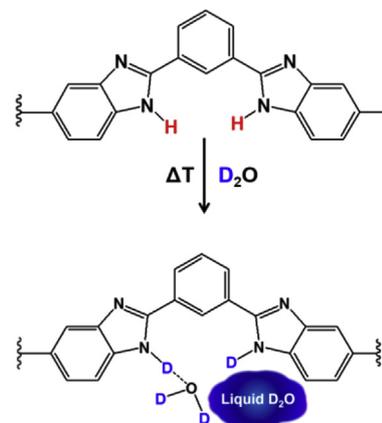


Fig. 2. IR spectra of rigorously dried PBI powder (bottom), and a PBI tensile specimen after steam-treatment with D<sub>2</sub>O at 150 °C (middle) and 315 °C (top). The triangles denote artifacts from the instrument and traces of CO<sub>2</sub>.

suggest that D<sub>2</sub>O is incorporated into the PBI and that at 315 °C the PBI also undergoes morphological changes.

The uptake of water into the polymer network plays a crucial role when the materials change their morphology or break down due to chemical reactions. Therefore, the interactions of water with the polymers will be studied in more detail in the following. For this purpose, the different water and proton sites in fully hydrated PBI need to be contemplated (Scheme 2).

As depicted in the top structure of Scheme 2, rigorously dried PBI contains two sorts of backbone protons, aryl protons bound to carbons of the benzene rings and N–H protons. Aryl C–H protons of



Scheme 2. Changes on the molecular level after steam-treatment of PBI with D<sub>2</sub>O.

benzimidazole are not exchangeable, even under the harsh conditions of steam-treatment at 315 °C [4]. Furthermore, C–H protons of non-fused aryl rings do not exchange, even in the presence of a C=O substituent, as demonstrated by steam-treating triptycene and benzophenone with D<sub>2</sub>O at 315 °C. Nitrogen-bound protons, on the other hand, can in principle be exchanged with protons of H<sub>2</sub>O, or deuterium from D<sub>2</sub>O (Scheme 2). However, the N–D groups will not lose the deuterium atom when PBI is redried after D<sub>2</sub>O exposure [4].

Besides the covalently bound hydrogen and deuterium atoms, D<sub>2</sub>O can form hydrogen bonds with the N–H or N–D groups, as shown in Scheme 2. In previous work it has been demonstrated with the use of a molecular model compound that at least one water molecule is hydrogen-bonded per N–H group [3]. The adsorbed water molecules can migrate along the PBI strands [3]. Another publication describes the single crystal X-ray structure of a complex incorporating a benzimidazole moiety [5], which shows multiple water molecules attached to the ligands. The water can either form hydrogen bridges with the free electron pair at the N via its hydrogen atoms or interact with N–H protons via the oxygen atom [5]. Hydrogen-bonded water can be removed entirely when redrying the PBI rigorously [4].

Finally, water can also be present in the polymer as a liquid, residing in pockets of the polymer network (Scheme 2). Water molecules in the liquid domains can exchange with adjacent hydrogen-bonded water. This water in aqueous domains is lost most easily during a redrying process. While backbone C–H and N–H protons and N–D deuterium atoms are practically immobile, disregarding movements of the polymer chains, hydrogen-bonded H<sub>2</sub>O and D<sub>2</sub>O have some mobility even in the solid materials. The water in liquid domains, depending on their size, represents the species with the highest degree of mobility in the polymer. The water molecules in large aqueous domains can even approach liquid-type mobilities with reorientation times in the ns range [4].

Since the steam-treatment of PBI leads to obvious changes of the material (Figure 1), <sup>13</sup>C CP/MAS NMR has been applied to probe whether decomposition at the molecular level can be detected. Fig. 3 shows the <sup>13</sup>C CP/MAS NMR spectra of all PBI tensile specimens before and after exposure to D<sub>2</sub>O at the listed conditions. The signal assignments are in agreement with the literature [2,21,22]. Slight changes are already visible when PBI is stirred in liquid D<sub>2</sub>O at room temperature. The overlapping signal of the carbons 5–7 in the center grows, while those for carbons 8,9, and 10 start to lose some intensity. After steam-treatment of the PBI at 150 °C basically the same overall signal shape is obtained. However, after steam-treating the sample at 315 °C for 72 h, the resonances for carbons 8–10 and 2 are mostly gone. Only the signals for carbons 1 and the shoulder for 3 and 4, besides the signals 5–7 of the benzene ring remain. Since the outcome of any solid-state NMR measurement is always determined by the pulse programs and parameters in a major way, one needs to contemplate these to decide whether the changed spectra indicate any decomposition of the sample, or the scenario is just a consequence of the exchange of <sup>1</sup>H by <sup>2</sup>H.

The spectra in Fig. 3 are all recorded with cross polarization [12–14], which means that the <sup>13</sup>C signal intensities are boosted by magnetization transfer from the proton reservoir to the corresponding carbon nuclei. Since hydrated PBI contains large amounts of protons in adsorbed water, as visible, for example, in the X-ray structure of a benzimidazole-containing complex [5], a short contact time of 1.5 ms is sufficient to obtain spectra with good signal-to-noise ratio that show all signals. This also indicates that adsorbed H<sub>2</sub>O stays long enough in one place to allow for the magnetization transfer.

For those PBI samples, however, where <sup>1</sup>H is largely exchanged with <sup>2</sup>H by steam-treatment with D<sub>2</sub>O, the magnetization has to be transferred from the remaining aryl protons. But cross polarization

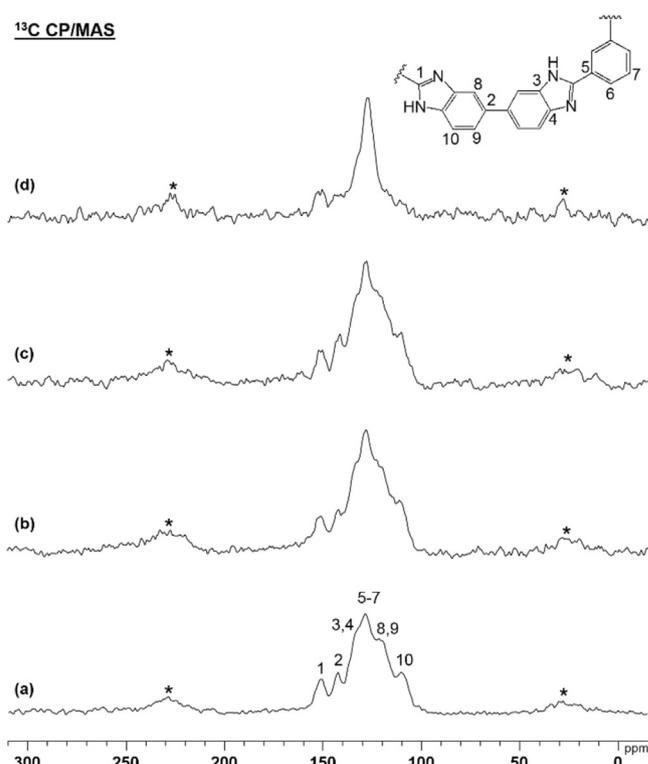


Fig. 3. <sup>13</sup>C CP/MAS NMR spectra of melt-molded PBI after drying at 110 °C for 550 h (a), stirring in D<sub>2</sub>O at RT (b), steam-treatment with D<sub>2</sub>O at 150 °C (c), and steam-treatment with D<sub>2</sub>O at 315 °C (d). The spinning speed is 10 kHz for all spectra; the asterisks denote rotational sidebands.

from aryl protons to heteronuclei requires longer contact times [12,14].

To test this hypothesis, PBI, steam-treated with D<sub>2</sub>O at 315 °C, has been measured with a contact time of 10 ms. As the <sup>13</sup>C CP/MAS spectrum in Fig. 4 shows, all <sup>13</sup>C signals that do not overlap with the peak in the center are visible again with about the same intensities as seen in the spectrum for the original PBI (Fig. 3a). The loss of <sup>13</sup>C benzimidazole signals after treatment with D<sub>2</sub>O and their boost with the longer contact time means that the H<sub>2</sub>O and the newly incorporated D<sub>2</sub>O mostly reside around the benzimidazole moieties in the polymer. This is in accord with the X-ray analysis described in the literature [5]. The carbon signal 1 persists throughout, because its signal profits from magnetization transfer of the close-by aryl protons 6 and 7. Furthermore, the result indicates that the N–H proton and the protons of the H<sub>2</sub>O molecule hydrogen-bonded to the N–H group are a source for magnetization transfer to the <sup>13</sup>C nuclei of the benzimidazole moiety.

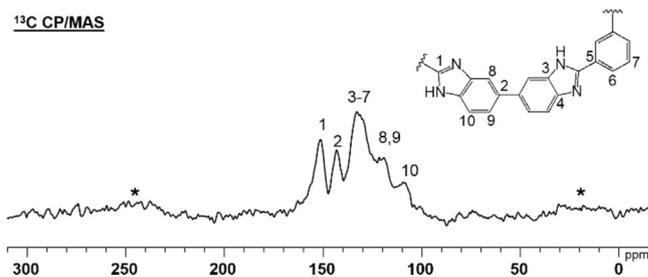


Fig. 4. <sup>13</sup>C CP/MAS NMR spectrum of melt-molded PBI after steam-treatment with D<sub>2</sub>O at 315 °C, recorded with a cross-polarization contact time of 10 ms. The spinning speed is 10 kHz, and the asterisks denote rotational sidebands.

In order to further probe the different  $^1\text{H}$  locations and characteristics,  $^1\text{H}$  solid-state NMR spectroscopy has been applied.  $^1\text{H}$  MAS NMR, recorded with high spinning speeds of up to 35 kHz is analytically not very favorable for the polymers investigated here, because only one narrow signal is obtained, which is surrounded by the corresponding sets of rotational sidebands. However, as demonstrated earlier [2,4],  $^1\text{H}$  wideline NMR spectroscopy without sample spinning provides valuable information for distinguishing protons of the immobile backbone from those in mobile  $\text{H}_2\text{O}$  molecules in aqueous domains within the polymer network. Mobile species result in a relatively narrow signal sitting on the broad resonance of the polymer backbone  $^1\text{H}$  NMR signal [2,4].

Fig. 5 displays the  $^1\text{H}$  wideline NMR spectra of melt-molded PBI prior to and after exposure to  $\text{D}_2\text{O}$  under different conditions. Spectrum (a) shows that after drying the sample *in vacuo* for 550 h at  $110^\circ\text{C}$  only immobile C–H and N–H backbone protons are present, which result in a broad resonance with a line width of about 26.8 kHz. After stirring PBI at room temperature in  $\text{D}_2\text{O}$ , the proton wideline spectrum (b) shows a narrow line on top of the 27.7 kHz broad backbone signal, whose half width can be determined to be about 8.3 kHz after deconvolution [24]. The narrow signal might originate from residual, strongly adsorbed  $\text{H}_2\text{O}$  that has been liberated into aqueous domains by exchange with  $\text{D}_2\text{O}$ . Independent of the origin of the protons resulting in the narrow resonance one can conclude that even at room temperature  $\text{D}_2\text{O}$  can migrate into the polymer and participate in proton exchange. After steam-treatment of the PBI sample with  $\text{D}_2\text{O}$  at  $150^\circ\text{C}$  (c) and  $315^\circ\text{C}$  (d), narrow peaks are present with line widths of 5.8 and 7.3 kHz, respectively. The scenario shows that for (c) the water content is highest, in accordance with the TGA (Fig. S1) and earlier results obtained with different methods [2,4]. Obviously at the higher temperature of  $315^\circ\text{C}$  the equilibrium water content is lower.

Fig. 6 displays the  $^2\text{H}$  MAS spectra obtained before and after exposure of PBI to  $\text{D}_2\text{O}$  under various conditions. After immersing a tensile specimen of PBI in  $\text{D}_2\text{O}$  at RT, two signals with very different characteristics are visible in the  $^2\text{H}$  MAS spectrum (a). The central signal must be due to mobile  $\text{D}_2\text{O}$  present in aqueous domains within the polymer based on its small half width of 3.7 kHz and the fact that it is not a Pake pattern. The second signal represents a classical Pake pattern that is split into rotational sidebands because of the spinning frequency of 6 kHz. The residual line widths of the rotational sidebands is small with only about 500 Hz. The quadrupolar coupling constant  $Q_{cc}$  with a value of 194 kHz indicates that

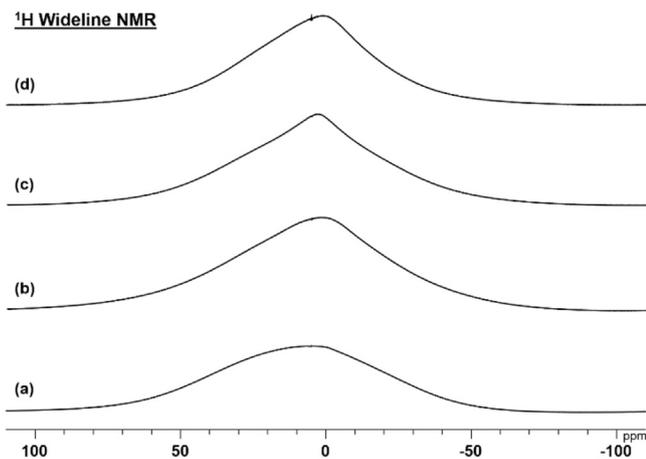


Fig. 5.  $^1\text{H}$  Wideline NMR spectra of melt-molded PBI after drying at  $110^\circ\text{C}$  for 550 h (a), stirring in  $\text{D}_2\text{O}$  at RT (b), steam-treatment with  $\text{D}_2\text{O}$  at  $150^\circ\text{C}$  (c), and steam-treatment with  $\text{D}_2\text{O}$  at  $315^\circ\text{C}$  (d).

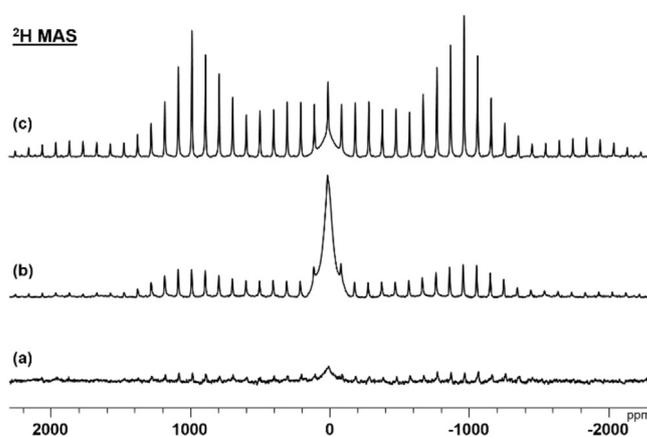


Fig. 6.  $^2\text{H}$  MAS NMR spectra of melt-molded PBI after stirring in  $\text{D}_2\text{O}$  at RT (a), steam-treatment with  $\text{D}_2\text{O}$  at  $150^\circ\text{C}$  (b), and immediately after steam-treatment with  $\text{D}_2\text{O}$  at  $315^\circ\text{C}$  (c). The Pake patterns are split into rotational sidebands (spinning frequency 6 kHz for all samples). Their  $Q_{cc}$  values are given in Table 1.

the  $^2\text{H}$  nuclei responsible for the signal are basically immobile [23]. Therefore, we conclude that this Pake pattern stems from strongly adsorbed  $\text{D}_2\text{O}$  or N–D groups.

The quadrupolar coupling constants  $Q_{cc}$  of all  $^2\text{H}$  MAS spectra are summarized in Table 1, together with key data obtained earlier [4]. The  $Q_{cc}$  values have been obtained after deconvolution [24] and simulating the Pake patterns in the spectra [25]. The simulated spectra generated as described in the experimental section and in the literature [25] are quite accurate. Fig. S4 shows as an example the simulated spectrum in gray fitting the measured spectrum of PBI after steam-treatment with  $\text{D}_2\text{O}$  at  $315^\circ\text{C}$  (Fig. 6c).

As Fig. 6 shows, after steam-treatment of the PBI sample with  $\text{D}_2\text{O}$  at  $150^\circ\text{C}$  (b) and  $315^\circ\text{C}$  (c), the same two unstructured center signals with half widths of only about 3.6 and 3.7 kHz, are again visible. The main difference is that the signal assigned to mobile  $\text{D}_2\text{O}$  in liquid domains is more intense after steam-treatment at  $150^\circ\text{C}$  (b), while it shrinks again after  $315^\circ\text{C}$  (c). This is in accordance with the TGA and  $^1\text{H}$  MAS results. The Pake pattern, however, is most intense after steam-treating the PBI at  $315^\circ\text{C}$ . Its  $Q_{cc}$  value matches the ones obtained after steam-treatment of its PEEK and PEKK blends very well (Table 1). It can tentatively be assigned to strongly adsorbed  $\text{D}_2\text{O}$  or deuterium nuclei in N–D groups, also taking into account that it has previously been found that the Pake patterns do not disappear after redrying the PEEK–PBI and PEKK–PBI blends [4].

The chemical shift for  $\text{D}_2\text{O}$  is the same whether it resides in liquid domains or is hydrogen-bonded, and  $\delta(^2\text{H})$  for N–D should be similar. Therefore, taking the large residual line width and the huge signal span of  $^2\text{H}$  in the solid state into account, even the rotational sidebands of the MAS signals of these species overlap.

Table 1

$Q_{cc}$  (quadrupolar coupling constant) values [kHz] of melt-molded samples treated with  $\text{D}_2\text{O}$  as liquid at RT and steam at  $150$  and  $315^\circ\text{C}$ . – indicates that no Pake pattern has been observed.

Melt-molded	RT	$150^\circ\text{C}$	$315^\circ\text{C}$
PBI	194	196	184
PEEK	–	–	186 <sup>a</sup>
PEKK	–	–	182 <sup>a</sup>
PEEK–PBI [4]	–	197	184
PEKK–PBI [4]	–	195	183

<sup>a</sup> Indicates signals with low intensity. The data for the melt-blends (50:50 wt%) have been taken from the literature [4]. Error margins of the  $Q_{cc}$  values are  $\pm 0.5$  kHz.

This is why the rotational sidebands of the Pake patterns which stem from the different species are not split into several sets of lines but give only one set. Another consideration is that the D<sub>2</sub>O molecules bound via hydrogen bridges undergo fast exchange with the D<sub>2</sub>O molecules in contiguous liquid domains. This means that the  $Q_{cc}$  values connected to specific types of <sup>2</sup>H environments are averaged out and variable to some degree in the presence of liquid domains. In the absence of liquid D<sub>2</sub>O, there is no longer any exchange and only the signal for N–D groups with maximal  $Q_{cc}$  is present [4]. Table 1 shows that the  $Q_{cc}$  values for melt-molded PEEK–PBI, PEKK–PBI, and PBI after steam-treatment with D<sub>2</sub>O at 315 °C are practically the same. Taking into account that at this temperature the amount of water in liquid domains is minimal (Fig. 6c), one can conclude that the Pake pattern stems from N–D groups and that any water uptake of the blends is basically due to the PBI component. The  $Q_{cc}$  values of PBI and its blends (Table 1) are larger after treatment with liquid D<sub>2</sub>O and steam at 150 °C, although the exchange of deuterium nuclei with the increased amount of water in aqueous domains can take place and therewith a diminished splitting of the Pake patterns should be expected. Therefore, a morphological change influencing the overall polymer chain mobility has to take place at the higher temperature of 315 °C. This assumption is in accordance with the sample becoming more brittle after this treatment (Fig. 1), with the IR results presented above, and with earlier <sup>13</sup>C T<sub>1</sub> relaxation time measurements [2].

#### 2.4. Analysis of PEEK after exposure to D<sub>2</sub>O as liquid and steam

In the following melt-molded PEEK samples are exposed to liquid D<sub>2</sub>O and its steam as described for PBI above. Fig. 7 shows that at ambient temperature and 150 °C only the color changes slightly, while the texture of the sample remains the same. After steam-treatment with D<sub>2</sub>O at 315 °C, however, the color of the sample changes to black, and it becomes deformed and brittle with a charcoal-type texture.

As pointed out above, PEEK and PBI polymers and their incorporation of water are in general amenable to investigation by IR spectroscopy [2,4–8]. Changes of the carbonyl stretching band and modifications in the fingerprint area, for example, are indicators for both chemical and morphological transformations [4]. Fig. S5 displays the IR spectrum of the original PEEK sample, which is practically identical with the spectrum after steam-treatment at 150 °C, and after steam-treatment at 315 °C. The constant value of the C=O stretching band of the PEEK sample at 1647 cm<sup>-1</sup> does not support the presence of a large number of D<sub>2</sub>O molecules bound via hydrogen bridges, as this should decrease its wavenumber. The same observation is made regarding the C–O stretching band of the ether group of the PEEK at 1219 cm<sup>-1</sup>. However, the two low intensity bands at the shoulder of this peak around 1300 cm<sup>-1</sup> experience a change. While they have equal intensities in the IR

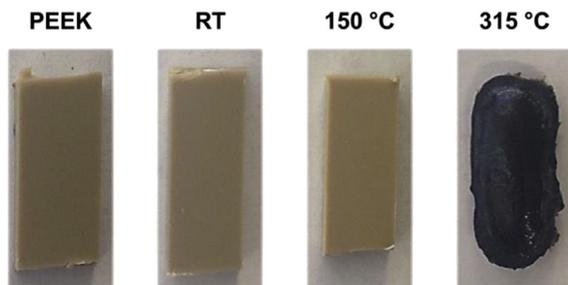


Fig. 7. Change of physical appearance of melt-molded PEEK after stirring in D<sub>2</sub>O at RT, and steam-treatment at 150 °C and 315 °C.

spectrum of the original sample, the band with the higher wavenumber loses intensity after the steam-treatment. This effect has been reported in the literature, and attributed to an increase in crystallinity of the sample [9]. This is again in accord with the <sup>2</sup>H MAS results described above and in earlier investigations [2].

The <sup>13</sup>C CP/MAS NMR spectra of PEEK samples before and after exposure to D<sub>2</sub>O under the indicated conditions are displayed in Fig. 8. All signals can be assigned in accordance with the literature [4,22]. After stirring the dried PEEK (a) at room temperature in D<sub>2</sub>O (b), steam-treatment at 150 °C (c) and at 315 °C with D<sub>2</sub>O (d), no obvious changes are visible in the <sup>13</sup>C CP/MAS spectra. In particular, the resonance a for the carbonyl carbon at 193.4 ppm does not change its chemical shift. Therefore, one can conclude that the carbonyl group does not undergo hydrogen-bonding with potentially incorporated H<sub>2</sub>O or D<sub>2</sub>O. The same accounts for the signals b and c of the carbon nuclei at 160.5 and 161.2 ppm, bound to the ether oxygen atom. None of the <sup>13</sup>C CP/MAS signals changes its intensity.

Regarding the cross polarization mechanism discussed above [12–14], one can conclude that either no magnetization transfer from exchangeable protons to the carbon nuclei takes place in the original sample, or that the D<sub>2</sub>O does not replace any protons in PEEK even under harsh reaction conditions. The following <sup>1</sup>H wideline and <sup>2</sup>H MAS NMR results show that the first interpretation is the most likely. As observed for the non-condensed phenyl ring in PBI, the aryl protons of PEEK are not exchanged and it can be concluded that PEEK does not contain adsorbed H<sub>2</sub>O that contributes to the magnetization transfer.

The <sup>1</sup>H wideline NMR spectra of the melt-molded PEEK samples before and after treatment with liquid D<sub>2</sub>O and D<sub>2</sub>O steam are displayed in Fig. 9. The absence of any substantial proton signals with smaller line widths on top of the broad resonances with half widths of ca. 29 kHz in the spectra (a) and (b) reveals that under ambient conditions the melt-molded sample does not contain adsorbed and mobile H<sub>2</sub>O. This is in accordance with its TGA curves and the IR and <sup>13</sup>C CP/MAS results. However, after steam-treatment at the higher temperatures of 150 and 315 °C (c, d), low intensity signals with half widths of about 1.7 and 2.6 kHz appear. These are

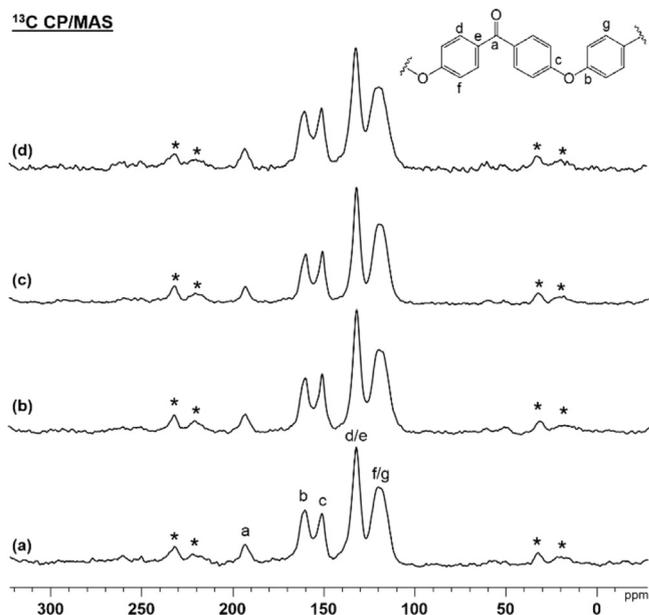
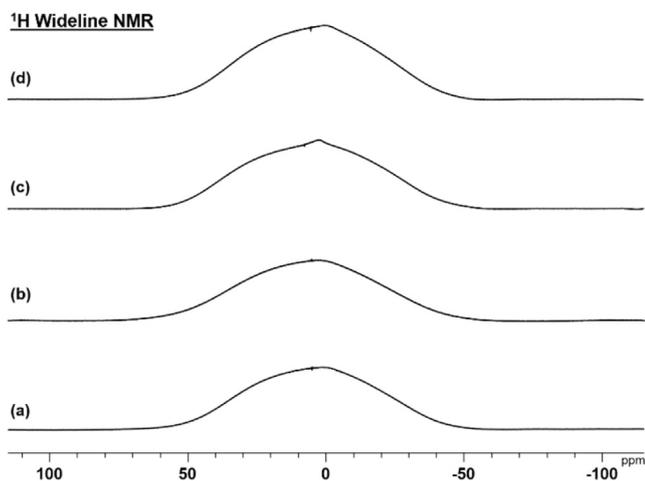


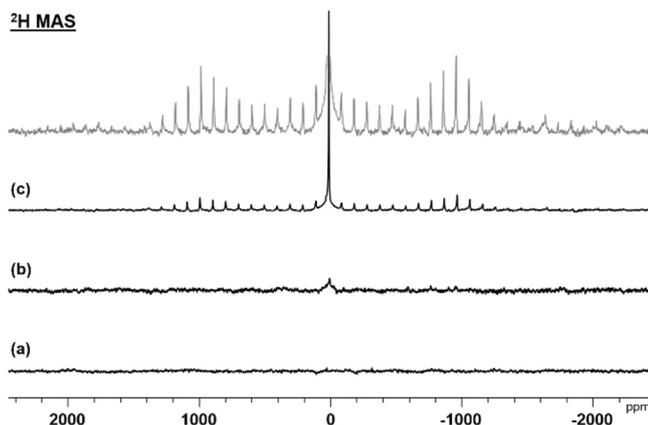
Fig. 8. <sup>13</sup>C CP/MAS NMR spectra of melt-molded PEEK after drying at 110 °C for 550 h (a), stirring in D<sub>2</sub>O at RT (b), steam-treatment with D<sub>2</sub>O at 150 °C (c), and immediately after steam-treatment with D<sub>2</sub>O at 315 °C (d).



**Fig. 9.**  $^1\text{H}$  Wideline NMR spectra of melt-molded PEEK as received (a), after stirring in  $\text{D}_2\text{O}$  at RT (b), steam-treatment with  $\text{D}_2\text{O}$  at  $150\text{ }^\circ\text{C}$  (c), and immediately after steam-treatment with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$  (d).

tentatively attributed to tiny amounts of exchangeable protons in the original sample, potentially stemming from traces of plasticizers. Their decomposition might also explain the color change of PEEK when exposed to the most demanding conditions (Fig. 7). It is noteworthy that molecular benzophenone does not exchange protons of the phenyl rings for deuterium atoms when steam-treated at  $315\text{ }^\circ\text{C}$  for 72 h.

As the  $^2\text{H}$  MAS NMR spectra displayed in Fig. 10 show, it takes steam-treatment at  $315\text{ }^\circ\text{C}$  to bring at least some  $\text{D}_2\text{O}$  into the melt-molded PEEK samples. No  $^2\text{H}$  MAS signal is found after exposure of PEEK to  $\text{D}_2\text{O}$  at RT even after prolonged measurement times. After steam-treatment at  $150\text{ }^\circ\text{C}$  a low intensity central signal with a half width of about 2 kHz appears, indicating traces of mobile  $\text{D}_2\text{O}$ . A low intensity Pake pattern is obtained after steam-treatment with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$ . In contrast to the PBI samples, where the Pake pattern becomes obvious after only 512 scans, the PEEK measurements require 32,000 scans to render the Pake pattern visible (Fig. 10 c). Besides the Pake pattern with a  $Q_{\text{CC}}$  value of 186 kHz (Table 1), a central signal attributable to mobile  $\text{D}_2\text{O}$ , adsorbed or in liquid domains in the polymer, emerges with a half width of about 200 Hz.



**Fig. 10.**  $^2\text{H}$  MAS NMR spectra of melt-molded PEEK after stirring in  $\text{D}_2\text{O}$  at RT (a), steam-treatment with  $\text{D}_2\text{O}$  at  $150\text{ }^\circ\text{C}$  (b), and immediately after steam-treatment with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$  (c). The gray top trace shows the vertical expansion of (c) to improve the visibility of the Pake pattern, which is split into rotational sidebands (spinning frequency 6 kHz for all samples). The  $Q_{\text{CC}}$  value is given in Table 1.

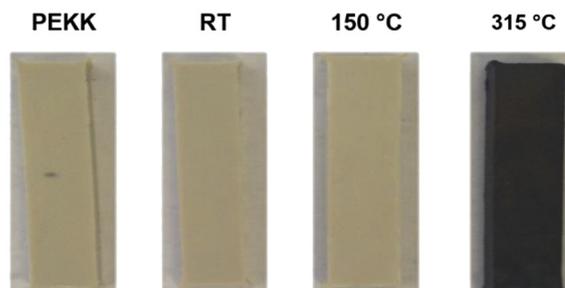
## 2.5. Analysis of PEKK after exposure to $\text{D}_2\text{O}$ as liquid and steam

When melt-molded PEKK is exposed to  $\text{D}_2\text{O}$  under various conditions, the physical appearance of the specimen changes as displayed in Fig. 11. Stirring the sample in liquid  $\text{D}_2\text{O}$  and steam-treatment at  $150\text{ }^\circ\text{C}$  leaves the color of the sample practically unchanged. The surface also remains smooth under these conditions. However, steam-treatment of PEKK with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$  leads to a notable color change to black, while astonishingly, the surface of the polymer remains smooth (Fig. 11).

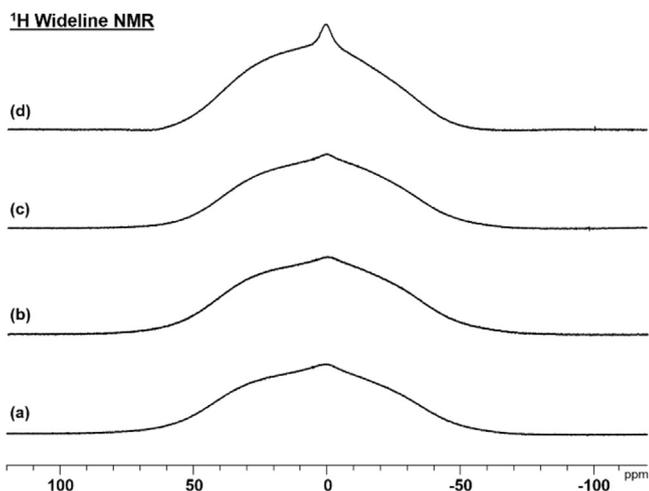
The IR spectra of the original melt-molded PEKK sample and the PEKK samples after steam-treatment at  $315\text{ }^\circ\text{C}$  are displayed in Fig. S6. There are no obvious differences in the spectra and in particular the wavenumbers of the  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$  stretching bands retain their values of  $1647\text{ cm}^{-1}$  and  $1231\text{ cm}^{-1}$ , respectively. Therefore, one can conclude that there is practically no  $\text{D}_2\text{O}$  hydrogen-bonded to the carbonyl or ether groups in the treated sample, as this would lead to weaker  $\text{C}=\text{O}$  and  $\text{C}-\text{O}$  bonds and therewith lower wavenumbers of their stretching bands.

The  $^{13}\text{C}$  CP/MAS NMR spectra of melt-molded PEKK samples follow the trend observed for PEEK, when treated with  $\text{D}_2\text{O}$  at ambient and elevated temperatures (Fig. S7). After treatment of the original sample (a) with  $\text{D}_2\text{O}$  at RT and  $150\text{ }^\circ\text{C}$  (c) there are no major changes in the  $^{13}\text{C}$  CP/MAS signals. However, steam-treatment with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$  leads to a different result (d) as compared to the PBI and PEEK polymers. Disregarding negligible changes of the intensities of all signals, the spectrum (d) is indistinguishable from the spectra (a) to (c). Therefore, taking the CP characteristics discussed for PBI and PEEK into account, one can conclude that untreated PEKK does not contain any significant amount of  $\text{H}_2\text{O}$  in its network, which could be replaced by  $\text{D}_2\text{O}$  during the steam-treatment and subsequently change the CP dynamics of the sample. This is in accordance with the TGA and IR results presented above, which indicate that PEKK contains only traces of water when in equilibrium with the atmosphere or exposed to it under the harsh conditions of steam-treatment at  $315\text{ }^\circ\text{C}$ .

The  $^1\text{H}$  NMR spectra of melt-molded PEKK before and after exposure to  $\text{D}_2\text{O}$  are displayed in Fig. 12. The original sample shows traces of water in the form of a narrow signal with a half width of about 5 kHz on top of the broad resonance from the polymer backbone protons with a half width of ca. 30 kHz (a). Stirring the molded specimen in  $\text{D}_2\text{O}$  at ambient temperature and steam-treatment at  $150\text{ }^\circ\text{C}$  basically do not change the appearance of the signals, as seen in the traces (b) and (c). This suggests that  $\text{D}_2\text{O}$  does not penetrate into the polymer network, as in this case changes of the narrow resonance on top of the backbone signal would be expected. Steam-treatment of the PEKK sample with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$ , however, liberates more  $\text{H}_2\text{O}$ , and the narrow signal with a half width of about 2 kHz on top of the 26 kHz broad hump



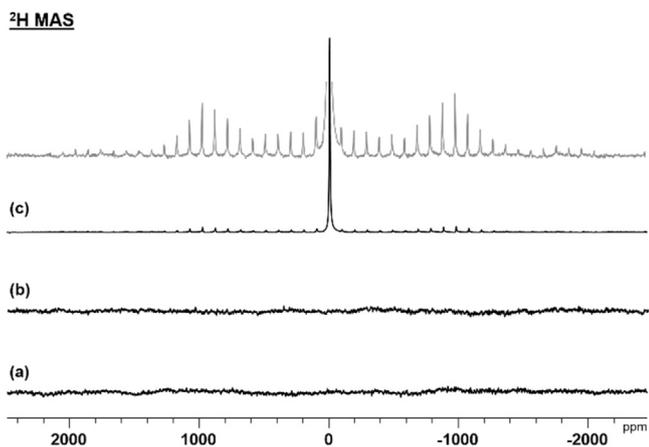
**Fig. 11.** Change of the physical appearance of melt-molded PEKK after stirring in  $\text{D}_2\text{O}$  at RT, and steam-treatment at  $150\text{ }^\circ\text{C}$  and  $315\text{ }^\circ\text{C}$ .



**Fig. 12.**  $^1\text{H}$  Wideline NMR spectra of melt-molded PEKK as received (a), after stirring in  $\text{D}_2\text{O}$  at RT (b), steam-treatment with  $\text{D}_2\text{O}$  at  $150\text{ }^\circ\text{C}$  (c), and immediately after steam-treatment with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$  (d).

increases in intensity (d). This result is in agreement with the TGA analysis, and it can be concluded that very harsh conditions are needed to bring at least moderate amounts of  $\text{D}_2\text{O}$  into the PEKK polymer.

The  $^2\text{H}$  MAS spectra (a) and (b) displayed in Fig. 13 corroborate the  $^1\text{H}$  wideline NMR results. After treatment with  $\text{D}_2\text{O}$  at RT and  $150\text{ }^\circ\text{C}$ , no  $^2\text{H}$  NMR signals emerge even after prolonged measurement times. Block averaging techniques prove that the absence of a signal is not due to any instrument malfunction. This means that under these conditions no  $\text{D}_2\text{O}$  penetrates into the polymer network, which is in agreement with the hypothesis that PEKK should fend off water when teaming up with PBI in PBI-PEKK blends [2,4]. Steam-treatment of a PEKK sample with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$  leads to a  $^2\text{H}$  MAS spectrum with two signals (Fig. 13c). An unstructured central signal with a half width of merely 200 Hz, attributable to mobile water in the polymer, is the dominant feature. The second signal emerges as a low intensity Pake pattern with a  $Q_{\text{cc}}$  of 182 kHz. Only a large vertical expansion of the spectrum renders this signal visible (Fig. 13c, gray trace). Clearly, most of the water incorporated in the PEKK resides in aqueous domains and



**Fig. 13.**  $^2\text{H}$  MAS NMR spectra of melt-molded PEKK after stirring in  $\text{D}_2\text{O}$  at RT (a), steam-treatment with  $\text{D}_2\text{O}$  at  $150\text{ }^\circ\text{C}$  (b), and immediately after steam-treatment with  $\text{D}_2\text{O}$  at  $315\text{ }^\circ\text{C}$  (c). The gray top spectrum shows the vertical expansion of (c). The Pake pattern is split into rotational sidebands (spinning frequency 6 kHz). The  $Q_{\text{cc}}$  value is given in Table 1.

only a trace might be present hydrogen-bound to  $\text{C}=\text{O}$  or  $\text{C}-\text{O}$  groups. Regarding the  $Q_{\text{cc}}$  values in Table 1 it should also be noted that the Pake patterns found for PEEK and PEKK have the largest deviation from the values of 183 and 184 kHz obtained for PBI, PEEK-PBI, and PEKK-PBI. Therefore, the Pake patterns in the pure PEEK and PEKK might also be the consequence of proton exchange in traces of plasticizer in the polymers. However, in the PBI component and its blends clearly the Pake patterns are associated with  $\text{D}_2\text{O}$  either strongly adsorbed to the PBI strands, or to  $\text{N}-\text{D}$  groups of the benzimidazole moiety after proton exchange.

### 3. Conclusions

In this contribution it has successfully been demonstrated that the single components of important PAEK-PBI blends, namely PBI, PEEK, and PEKK, can be characterized by  $^{13}\text{C}$  CP/MAS and all signals can be assigned due to the favorable signal resolution. Furthermore, the molded samples can be analyzed by TGA, IR,  $^1\text{H}$  wideline solid-state NMR, and  $^2\text{H}$  MAS NMR after steam-treatment. When the samples are stirred at ambient temperature in  $\text{D}_2\text{O}$  or steam-treated with it at  $150\text{ }^\circ\text{C}$ , only the PBI sample takes up large amounts of water. Under harsh conditions of steam-treatment at  $315\text{ }^\circ\text{C}$ ,  $\text{D}_2\text{O}$  is incorporated in trace amounts and mainly in the form of liquid domains into the PEEK and PEKK samples. The PBI, however, incorporates a smaller amount of  $\text{D}_2\text{O}$  into its polymer network when subjected to steam-treatment at  $315\text{ }^\circ\text{C}$ , as compared to the outcome at lower temperatures. The physical appearance of the samples implies that PEEK is least resistant to steam-treatment at the highest temperature of  $315\text{ }^\circ\text{C}$ , showing signs of major decomposition. The PEKK sample keeps up best, and only undergoes a color change to black, while PBI becomes more brittle and rough on its surface. Overall it can be concluded that both PEEK and PEKK are valuable components in blends with PBI, being able to fend off water even under harsh reaction conditions. PEEK-PBI and PEKK-PBI blends, and their salt uptake are being investigated in a parallel project.

### 4. Experimental section

#### 4.1. General information and procedures

All polymer samples were provided by the company Hoerbiger Corporation of America, Inc. PBI, PEEK, and PEKK were dried thoroughly at  $110\text{ }^\circ\text{C}$  for 550 h under vacuum (0.01 torr) prior to treatment with  $\text{D}_2\text{O}$ . Unless mentioned otherwise in the text, the melt-molded polymer samples were all ASTM D638 Type V tensile specimens, machined from solid compression-molded plaques. To prepare fine powders for solid-state NMR spectroscopy, solid samples were filed into shavings with average particle diameters of about 0.5 mm. The polymers were either stirred in  $\text{D}_2\text{O}$  at RT for 48 h, or steam-treated in Parr pressure reactors (Model 4913) at  $150\text{ }^\circ\text{C}$  for 48 h and at  $315\text{ }^\circ\text{C}$  for 72 h. The maximal pressures in the closed vessels amounted to 5 bar (72 psi) and 110 bar (1600 psi), respectively. Unless mentioned otherwise, the drying procedure consisted of removing the  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  at  $110\text{ }^\circ\text{C}$  under vacuum for 48 h.

#### 4.1.1. Instruments and measurements

The solid-state NMR spectra were measured on a Bruker AVANCE 400 spectrometer operating at 100.6 MHz for  $^{13}\text{C}$ , 61.4 MHz for  $^2\text{H}$ , and 400.1 MHz for  $^1\text{H}$ . For the processing of the spectra line-broadening factors of 10 Hz ( $^1\text{H}$ ) and 150 Hz ( $^2\text{H}$ ,  $^{13}\text{C}$ ) have been applied. All experiments were carried out using densely packed powders of the polymers in 4 mm  $\text{ZrO}_2$  rotors. In case no signal was observed in a spectrum, block averaging measurements

were performed to prove that the absence of any resonance was not merely due to a spectrometer malfunction.

The  $^{13}\text{C}$  CP/MAS (Cross Polarization with Magic Angle Spinning) spectra were recorded at MAS rates of 10 kHz. The  $^1\text{H}$   $\pi/2$  pulse was 2.5  $\mu\text{s}$  and TPPM decoupling was used during the acquisition. The Hartmann–Hahn matching condition was optimized using the polymer Victrex 450P at a rotational speed of 10 kHz. Adamantane served as the external  $^{13}\text{C}$  chemical shift standard ( $\delta = 37.95$  and 28.76 ppm). All spectra were measured with a contact time of 1.5 ms and a relaxation delay of 3.0 s, and typically 1024 FIDs were accumulated.

The  $^2\text{H}$  solid-echo measurements were performed at MAS spinning speeds of 6 kHz.  $\text{D}_2\text{O}$  served as the  $^2\text{H}$  chemical shift standard ( $\delta = 4.79$  ppm). All spectra were measured with a relaxation delay of 2 s and a quadrupolar echo  $\tau$  delay of 6  $\mu\text{s}$ . The  $\tau$  delay was optimized using deuterated PMMA (polymethyl methacrylate) at a rotational speed of 6 kHz. Typically 32,800 FIDs were accumulated for the PBI, PEEK, and PEKK samples.

The  $^1\text{H}$  wideline NMR spectra were recorded using the MAS probehead without sample spinning.  $\text{H}_2\text{O}$  was used as the external chemical shift standard ( $\delta = 4.79$  ppm). No background  $^1\text{H}$  NMR signal of the probehead, loaded with an empty rotor, was obtained when a spectrum was recorded with the measurement parameters used for the polymer samples. A  $\pi/2$  pulse of 2.7  $\mu\text{s}$ , a deadtime of 5.6  $\mu\text{s}$ , and a pulse delay of 3 s were used and typically 32 FIDs were accumulated.

Deconvolution ( $^1\text{H}$  wideline spectra) and processing of the spectra was accomplished using ACD/NMR Processor Academic Edition [24]. The quadrupolar coupling constants were derived from the  $^2\text{H}$  MAS NMR spectra using the NMR simulation program Dmfit [25].

The IR spectra were recorded on a Shimadzu IRAffinity-1 FTIR spectrometer by placing the powdered polymers on top of a Pike Technologies MIRacle ATR diamond plate. Typically 100 scans were accumulated for optimal spectrum quality.

The TGA curves were recorded on the TA Instruments Q500 TGA by placing approximately 10 mg of the melt-molded sample into an  $\text{Al}_2\text{O}_3$  pan. The thermal decomposition studies were performed over a temperature range of 30–700  $^\circ\text{C}$  under air at a heating rate of 20  $^\circ\text{C}/\text{min}$ . Nitrogen was used as the balance gas at a rate of 40 mL/min and air was used as the sample gas at a rate of 40 mL/min.

### Author contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interests.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2014.07.027>.

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