

Multinuclear Solid-State NMR Investigation of the Moisture Distribution in PEEK-PBI and PEKK-PBI Blends

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ABSTRACT: Blends of polyaryletherketones (PAEK), such as polyetheretherketones (PEEK) and polyetherketoneketones (PEKK), with polybenzimidazole (PBI) are of commercial interest due to their improved high-temperature stability and wear properties. The changes of PBI and its PEEK- and PEKK-blends (50 : 50 wt %) after immersing them in liquid H₂O and D₂O, and exposing them to D₂O steam at elevated temperatures and pressures are investigated by multinuclear solid-state NMR and IR spectroscopy. Macroscopic morphological and chemical changes on the molecular scale, which take place upon high-temperature steam-treatment and the extent and reversibility of moisture uptake have been investigated. Interactions and reactions of water, steam, and aqueous solutions of LiCl and ZnBr₂ with the functional groups of the polymer components have been studied using D₂O in combination with IR, ¹H wideline, ²H, ⁷Li, and ⁷⁹Br MAS, as well as ¹³C and ¹⁵N CP/MAS NMR spectroscopy. Different locations and types of water and protons in the blends have been described and PBI has been proven to be mainly responsible for water and salt uptake into the blends.
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INTRODUCTION

The group of polyaryletherketones (PAEK) within thermoplastic polymers,¹ including PEEK (polyetheretherketone) and PEKK (polyetherketoneketone) polymers (Scheme 1), is of growing interest in a wide range of applications that demand superior mechanical strength, corrosion resistance, and retention of dimensional and physical properties at high temperatures and pressures. One important example would be low-weight down-hole materials in oil and gas drilling and fracturing processes. While the different commercially available PAEK grades are already of benefit to the end users, the demand for even higher temperature applications continues to grow, and along with it the quest for improved tribological performance.

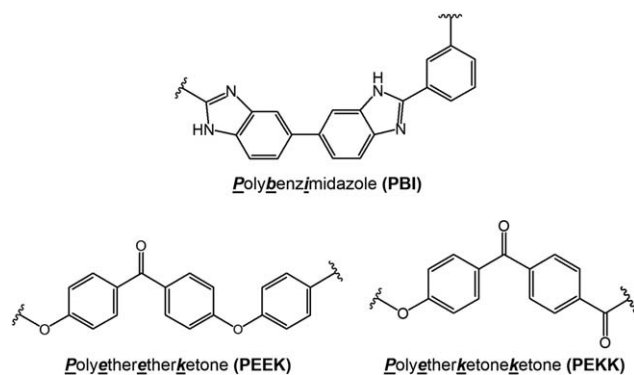
One way to meet these demands is to provide blends of PAEK polymers with PBI (polybenzimidazole) resins (Scheme 1). This strategy takes advantage of the increased service temperatures and some improvement in the wear properties afforded by the PBI component. For example, PEKK-PBI blends are manufactured primarily to elevate the service temperature of the PEKK polymer, and to improve its wear performance. A potential

drawback of PBI blends is the comparatively poor chemical stability associated with this component. Most importantly, in contrast to the pure PAEK components, the PBI addition leads to a more complex interaction of the blend with aqueous systems, such as water and steam,² as well as salt solutions. Therefore, a better understanding of the interactions of water with the functional groups of the PBI component at the molecular level is indispensable.

Furthermore, a deeper insight into how the water affinity of PBI translates to the characteristics of its blends with PEEK and PEKK is sought. More specifically, a quantification of the interactions of water with these blend systems, and the distribution of water within the morphology of the polymer blends is of importance. In this study, we will contrast the content and distribution of absorbed moisture in the pure PBI polymer and the blend pairs of interest. If there is an opportunity to understand or control the impact of absorbed moisture in these important polymer blends, 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.

Additional Supporting Information may be found in the online version of this article.

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Scheme 1. Structures of PBI, PEEK, and PEKK Polymers.

In this study, the traditional PBI (poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole]), and its 50 : 50 wt % PEEK- and PEKK-PBI blends are immersed in liquid D₂O at ambient temperature. Additionally, PBI and the PEEK- and PEKK-PBI blends are exposed to H₂O and D₂O steam at 150°C (ca. 300°F) and 315°C (ca. 600°F) for prolonged times to simulate real-life conditions, as they might, for example, be applied in oil and gas drilling and fracturing processes.

The impact of water or steam on PEEK and PEKK polymers and their PBI blends has not been extensively described in the literature,^{3–5} but using a molecular model compound mimicking PBI, one report discusses two ways in which water could reside in PBI.³ It can either be present in larger aqueous domains nestled between the PBI polymer strands, or it can be bound to the N—H group in the PBI backbone by hydrogen bridges. Hereby, on average one H₂O molecule is bound per N—H group.³

PAEK and PBI polymers and their incorporation of water are in general amenable to investigation by IR spectroscopy.^{2,6,7} Changes of the carbonyl stretching band and modifications in the fingerprint area, for example, are indicators for both chemical and morphological transformations.⁶

However, solid-state NMR spectroscopy is a more powerful method for studying polymers on a molecular level and providing detailed structural and dynamic information.^{2,7–11} Chemical changes during the exposure to adverse conditions can be studied by ¹³C CP/MAS NMR,^{2,7–11} while morphological changes, involving the ratio of rigid versus mobile domains in the polymer, can be investigated by the ¹³C T₁ relaxation time characteristics.² The prerequisite for any chemical change of the polymer due to the immersion in water at room temperature or exposure to steam at elevated temperatures is that water penetrates into the polymer network.¹² Especially for mostly amorphous materials like PBI¹³ this scenario can be studied by ¹H wide-line NMR, where proton measurements of the solid samples are recorded without sample spinning.^{14–20}

In the following, solid-state NMR spectroscopy is employed to probe the interactions of H₂O and D₂O with PBI and its blends. For ¹³C NMR^{2,7–11} and ¹⁵N NMR²¹ cross polarization (CP) of magnetization from the abundant protons in the polymer sample to the measured nuclei improves the obtained signal to

noise ratio.^{10,11} Additionally, it will be demonstrated in the following that ¹H wide-line,^{14–20} and ²H,^{19,22–31} ⁷Li,³² and ⁷⁹Br MAS NMR can give valuable complementary insights into the polymer systems on the molecular level as well. Different locations and types of water and protons in PBI and in the PEEK-PBI and PEKK-PBI blends are described in the following and it will be proven that the PBI component is mainly responsible for the water and salt uptake into the blends.

EXPERIMENTAL

General Information and Procedures

All polymer samples were provided by the company Hoerbiger Corporation of America. The PEEK-PBI and PEKK-PBI are based on 50 : 50 wt % mixtures of the pure components. PBI, PEEK-PBI, and PEKK-PBI powders were dried thoroughly at 110°C for 144 h under vacuum (0.01 torr). PEEK-PBI and PEKK-PBI melt-molded samples were all ASTM D638 Type V tensile specimens, machined from solid compression molded plaques, which were rigorously dried at 110°C for 550 h under vacuum (0.01 torr). As described in the corresponding sections, the blends were either used in the shape of tensile specimens, or filed into powders with average particle diameters of about 0.5 mm before being treated or measured by solid-state NMR. The pure components and blends were either stirred in D₂O at RT for 48 h, or steam-treated in Parr pressure reactors (Model 4913) at 150°C for 48 h and at 315°C for 72 h. The maximal pressures in the closed vessels amounted to 5 bar (72 psi) and 110 bar (1600 psi), respectively. The redrying procedure consisted of removing the D₂O at 110°C under vacuum for 48 h.

Instruments and Measurements

The solid-state NMR spectra were measured on a Bruker AVANCE 400 spectrometer operating at 100.6 MHz for ¹³C, 40.5 MHz for ¹⁵N, 61.4 MHz for ²H, 400.1 MHz for ¹H, 155.5 MHz for ⁷Li NMR, and 100.3 MHz for ⁷⁹Br. For the processing of the spectra line-broadening factors of 10 Hz (¹H, ⁷Li), 20 Hz (⁷⁹Br), and 150 Hz (²H, ¹³C, and ¹⁵N) have been applied. All experiments were carried out using densely packed powders of the polymers in 4 mm ZrO₂ 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 ¹³C CP/MAS (Cross Polarization with Magic Angle Spinning) spectra were recorded at MAS rates of 10 kHz. The ¹H π/2 pulse was 2.5 μs 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 ¹³C chemical shift standard (δ = 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 ¹⁵N CP/MAS experiments were carried out at MAS rates of 6 and 10 kHz. The Hartmann-Hahn matching condition was optimized using glycine at a rotational speed of 6 kHz. Glycine also served as the external ¹⁵N chemical shift standard (δ = 7.70 ppm). All spectra were measured with a contact time of 2 ms

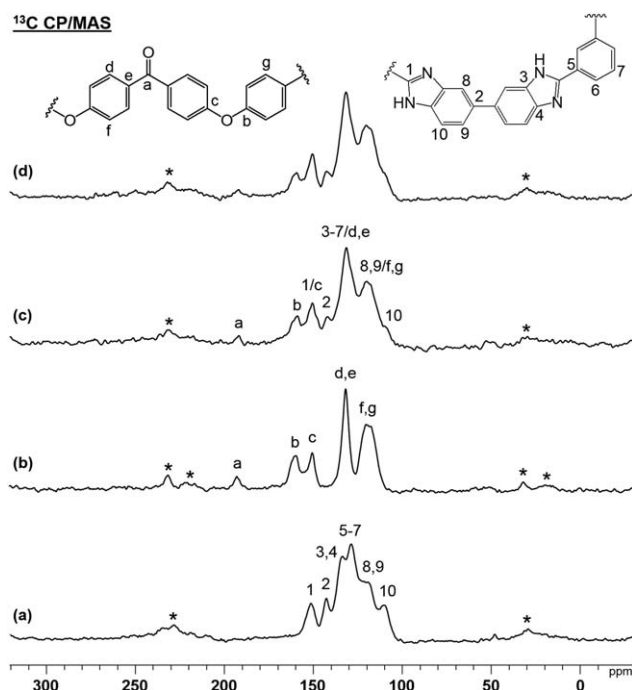


Figure 1. ^{13}C CP/MAS NMR spectra of PBI (a), PEEK (b), melt-blended PEEK-PBI (c), and a physical mixture of powdered PEEK and PBI (50 : 50 wt %) (d). The spinning speed is 10 kHz for all spectra, and the asterisks denote rotational sidebands.

and a relaxation delay of 5 s, and typically 32800 FIDs were accumulated.

The ^2H solid-echo measurements were performed at MAS rates of 6 kHz. D_2O served as the ^2H chemical shift standard ($\delta = 4.79$ ppm). All spectra were measured with a relaxation delay of 2 s and a quadrupolar echo τ delay of 6 μs . The τ delay was optimized using deuterated PMMA (polymethyl methacrylate) at a rotational speed of 6 kHz. Typically, 32800 FIDs were accumulated for the PBI and PEEK polymers and their blends.

The ^1H wideline NMR spectra were recorded using the MAS probehead without sample spinning. H_2O was used as the external chemical shift standard ($\delta = 4.79$ ppm). No background ^1H 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 μs , a deadtime of 5.6 μs , and a pulse delay of 3 s were used and typically 32 FIDs were accumulated.

Deconvolution (^1H wideline spectra) and processing of the spectra was accomplished using ACD/NMR Processor Academic Edition.³³ The quadrupolar coupling constants were derived from the ^2H MAS NMR spectra using the NMR simulation program Dmfit.³⁴

The ^7Li MAS experiments were performed at a MAS rate of 10 kHz. Polycrystalline LiCl served as the external ^7Li chemical shift standard ($\delta = 0.00$ ppm). All spectra were measured with a deadtime of 5 μs and a relaxation delay of 6 s, and typically 10500 FIDs were accumulated. There was no ^7Li background NMR signal from the probehead or rotor, when an empty rotor was measured under these conditions.

The ^{79}Br MAS experiments were carried out at a MAS rate of 10 kHz. Polycrystalline KBr served as the external ^{79}Br chemical shift standard ($\delta = 0.00$ ppm). All spectra were measured with a deadtime of 5 μs and a relaxation delay of 50 ms, and typically 300,000 FIDs were accumulated. There was no ^{79}Br background NMR signal from the probehead or rotor, when an empty rotor was measured under these conditions.

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 ~ 10 mg of the melt-molded sample into an Al_2O_3 pan. The thermal decomposition studies were performed over a temperature range of 30–700°C under air at a heating rate of 20°C/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.

RESULTS AND DISCUSSION

Characterization of PBI and Its PEEK and PEKK Blends with ^{13}C and ^{15}N CP/MAS NMR

To characterize the pure polymer components and the PEEK- and PEKK-PBI blends the ^{13}C CP/MAS NMR spectra shown in Figures 1 and 2 have been recorded. Most of the signals are resolved and only two signal groups overlap. All resonances can be assigned unequivocally to the corresponding carbon positions in the structure, in accordance with the literature.^{35–38}

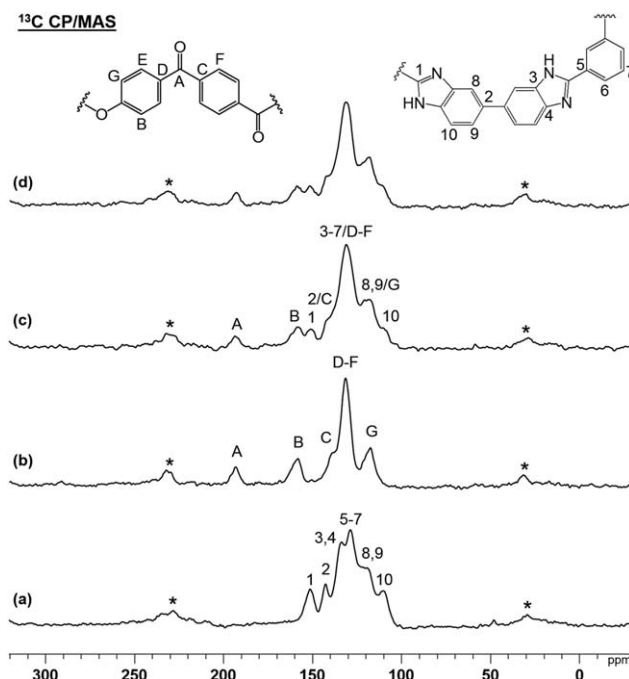


Figure 2. ^{13}C CP/MAS NMR spectra of PBI (a), PEKK (b), melt-blended PEKK-PBI (c), and a physical mixture of powdered PEKK and PBI (50 : 50 wt %) (d). The spinning speed is 10 kHz for all spectra, and the asterisks denote rotational sidebands.

The melt-blended PEEK-PBI results in the ^{13}C CP/MAS spectrum shown in Figure 1(c). The signals **b** of the PEEK and **2** of the PBI components, which do not overlap, display an approximate intensity ratio of 1 : 1. Assuming that the CP and relaxation characteristics of both components are similar,² the spectrum (c) confirms that PEEK and PBI are present in a 50 : 50 wt % ratio.

To test whether melt-blending leads to interactions of the PEEK and PBI components on a molecular level, which might be seen in the ^{13}C CP/MAS spectra, a physical mixture of PEEK with PBI powder has been measured [Figure 1(d)]. The spectrum of this mixture is practically identical with the spectrum of the melt-blended sample [Figure 1(c)]. In particular, the signal **a** of the carbonyl carbon at 194 ppm retains the same chemical shift. In the case of strong $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen bridge formation of the PBI and PEEK strands on the molecular level a shift of the carbonyl carbon resonance would have been expected.

Next, the ^{13}C CP/MAS NMR spectra of the pure components PBI and PEKK [Figure 2(a,b)], as well as the melt-blended polymer [Figure 2(c)] and a physical mixture of PBI and PEKK powder in a 50 : 50 wt % ratio [Figure 2(d)] have been recorded. Again, the signal assignments for PEKK are in agreement with the literature^{35–38} and the amounts of the components are confirmed by the $\sim 1 : 1$ intensity ratio of the signals **B** of the PEKK and **1** of the PBI component, assuming similar CP and relaxation characteristics of both components.² No obvious changes can be detected in the spectra of the melt-blended versus physically mixed samples [Figure 2(c,d)]. In particular, the carbonyl carbon resonance at about 180 ppm retains its chemical shift after the melt-blending process.

When IR spectroscopy is employed as another powerful tool,^{6,7} a very subtle, but reproducible change becomes visible in the IR spectra of a physical mixture and the melt-blended samples (Supporting Information Figure S1). The $\text{C}=\text{O}$ stretching band is found at 1653 cm^{-1} for the physical mixture, while the wavenumber is 1651 cm^{-1} for the melt-blended sample. Taking the accuracy of the instrument ($\pm 0.5\text{ cm}^{-1}$) into account, this is not a decisive wavenumber change, but it might indicate that some hydrogen bridges between $\text{C}=\text{O}$ and $\text{N}-\text{H}$ groups of different polymer strands occur after the melt-blending process.

To further investigate whether hydrogen bonding interactions between the $\text{N}-\text{H}$ groups of the PBI and the $\text{C}=\text{O}$ groups of PEEK and PEKK are visible in the chemical shift of the nitrogen nucleus, the ^{15}N CP/MAS spectra²¹ shown in Figure 3 have been recorded. Due to the low natural abundance and long relaxation time of ^{15}N in the solid state²¹ the signal to noise ratio of the spectra obtained is comparatively low. The fact that in the blends only 50% of the sample contains nitrogen nuclei from the PBI adds to this disadvantage. Together with the large linewidths of the signals and the obvious presence of more than one ^{15}N resonance in each spectrum, this renders an unequivocal interpretation of any chemical shift trend difficult. However, a cautious preliminary evaluation of the carefully referenced spectra can be undertaken.

As discussed in more detail below, the most striking change is visible in the chemical shift of the thoroughly dried PBI (113.2

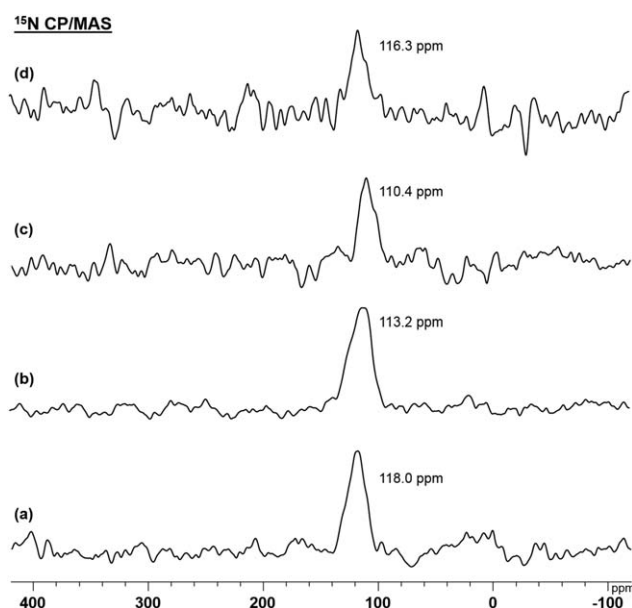


Figure 3. ^{15}N CP/MAS NMR spectra of PBI, steam-treated with D_2O at 150°C (6 kHz) (a), dried PBI (6 kHz) (b), melt-blended PEEK-PBI (10 kHz) (c), and melt-blended PEKK-PBI (10 kHz) (d).

ppm) [Figure 3(b)] and PBI steam-treated with H_2O at 150°C (not shown, 120.6 ppm). When deuterated water, D_2O , is used for the steam-treatment, the ^{15}N NMR signal appears at 118.0 ppm [Figure 3(a)]. This means that the N nuclei in the PBI are affected by the steam-treatment reagent at 150°C , supporting our later hypothesis that $\text{N}-\text{H}$ protons are exchanged by deuterium in the course of the steam-treatment. Furthermore, there are chemical shift changes between the thoroughly dried PBI [Figure 3(b)] with 113.2 ppm, the melt-blended PEEK-PBI [Figure 3(c)] (110.4 ppm), and the melt-blended PEKK-PBI [Figure 3(d)] with 116.3 ppm. One might very cautiously interpret this as reflecting an increased potential for $\text{N}-\text{H}\cdots\text{O}=\text{C}$ hydrogen-bonding between the PEKK and PBI components, as compared with PEEK-PBI. Overall, we conclude that the $\text{N}-\text{H}$ groups of the benzimidazole unit of PBI are in the “center of the action” when steam-treatment is performed, and the ^{15}N resonance is sensitive to the second component in PBI blends and seems to “sense” the difference between PEEK and PEKK.

Macroscopic Water Removal and Rehydration of PBI, PEEK-PBI and PEKK-PBI at Moderate Temperatures

As described qualitatively in previous work,² PBI is hydrophilic and prone to take up water readily from the atmosphere. To obtain a more quantitative estimate of this characteristic, PBI powder and melt-molded tensile specimens have been dried under vacuum (0.1 torr) at 110°C for 144 h (6 days) and 600 h (25 days), respectively. This process is monitored in a straightforward manner by weighing the samples at given time intervals. The drying curves are displayed in Supporting Information Figures S2 and S3. The PBI powder shows no more weight loss after about 4 days while the melt-molded tensile specimens still retain residual moisture after 25 days. This result demonstrates that whenever rigorously dried PBI is needed, a powder should

be used. Due to its larger specific surface area it allows the absorbed water to leave the sample more quickly. The slightly different curves obtained for the three tensile specimens (Supporting Information Figure S3) corroborate the assumption that the surface area of the samples is crucial for the drying rate. Since constant weight is achieved after drying the PBI powder we assume that the moisture content of this particular sample amounts to about 9% of its weight. This value is in the same range (5–11%) as the moisture contents found by TGA for PBI tensile specimens treated with water and steam under different conditions.³⁸

For PEEK and PEKK blends of PBI, it is generally assumed that the PBI component is mainly responsible for the water uptake. To quantify this effect, the weight loss of the blends has been recorded over time. When PEEK-PBI and PEKK-PBI (50 : 50 wt %), as received, are dried *in vacuo* at elevated temperatures, the curves displayed in Supporting Information Figures S4–S9 are obtained.

The PEEK-PBI powder reaches constant weight after about 50 h (Supporting Information Figure S4), while PEKK-PBI initially loses the moisture much faster and is completely dry after roughly 45 h (Supporting Information Figure S6). This result nicely confirms earlier assumptions that PEEK is slightly more prone to take up and retain moisture from the environment than PEKK. The total amount of weight loss, however, is about the same for both blends with about 4.3% (Supporting Information Figures S4 and S6). This is nearly half the amount of water found for PBI, which indicates that practically all the water of the 50 : 50 wt % PEEK-PBI and PEKK-PBI blends is residing in the PBI component.

As in the case of PBI, and to test the reproducibility, three tensile specimens have been submitted to the drying procedure for both the PEEK-PBI and the PEKK-PBI blends (Supporting Information Figures S5 and S7). There is only a minimal difference between the drying progress of the three samples of each material, which might again be attributed to slightly different sizes and surface areas of the samples. The PEEK-PBI starting material releases more moisture than the PEKK-PBI blend within the given time frame. After 25 days of drying *in vacuo* about 14 mg of water per 1 g of PEEK-PBI is lost (Supporting Information Figure S5), but only about 9 mg per g of PEKK-PBI (Supporting Information Figure S7).

It has been demonstrated earlier by ¹³C T₁ relaxation time measurements that the uptake of water in PBI blends is reversible as long as the conditions are relatively mild.² To quantify this effect the dried PEEK-PBI and PEKK-PBI tensile specimens have been exposed to water at ambient and elevated temperatures. Both PEEK-PBI and PEKK-PBI samples take up moisture readily (Supporting Information Figures S8 and S9), but at room temperature only about 10 mg of H₂O have been absorbed per g of material within 220 h. However, at 100°C both blends take up moisture vigorously and in excess of what the samples contained when received. Again, PEEK-PBI has a stronger affinity to H₂O than PEKK-PBI, as it takes up 50 mg per 1 g of material within 220 h, versus only about 40 mg in the latter case.

Steam-Treatment of PBI and Its PEEK and PEKK Blends with H₂O and D₂O

All samples have been stirred in liquid water for the above indicated amounts of time. In order to mimic more realistic conditions of exposure to fluids, powdered PBI and tensile specimens of PEEK-PBI and PEKK-PBI have also been subjected to steam-treatment with H₂O. For this purpose, the samples are placed into stainless steel pressure vessels, which are filled with 150 mL of liquid water to the height of about 1.5 cm, then sealed and heated. The pressures reached in the closed vessels are 5 bar (72 psi) at 150°C and 110 bar (1600 psi) at 315°C. The exposure of the samples to water at room temperature and 150°C has been maintained for 48 h, and at 315°C for 72 h. Interestingly, the initially used stainless steel grids holding the samples in place above the liquid phase in the reactor corrode significantly where they are exposed to steam, while they stay intact in the liquid phase (Supporting Information Figure S10). Therefore, special glass sample holders with longer lifetimes have been designed and manufactured (Supporting Information Figure S10).

When melt-molded PBI samples are immersed in water at RT and exposed to steam at 150°C and 315°C, and subsequently subjected to TGA analysis, 5, 11, and 9% of moisture are found, respectively.³⁸ So, the highest water content in the PBI samples is found after steam-treatment at 150°C, in accordance with the findings after complementary analyses.²

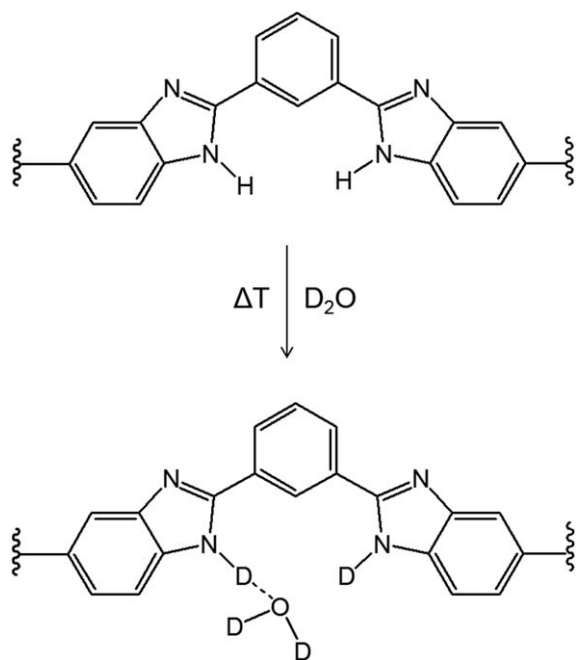
The TGA results after exposing PEEK-PBI and PEKK-PBI to water at RT, 150, and 315°C are shown in Supporting Information Figures S11 and S12. For both blends, the highest moisture contents of 6 and 7% are found after steam-treatment at 150 and 315°C. A slight difference of about 1% favors moisture in the PEEK-PBI blend (4%, Supporting Information Figure S11) after immersion in liquid water at ambient temperature as compared with the PEKK-PBI (3%, Supporting Information Figure S12). These data show that especially at higher temperatures the PEEK and PEKK components of the blends reduce the amount of water that pure PBI would incorporate.

¹³C, ²H, and ¹H NMR Spectroscopy for Probing Different H₂O Sites in PBI, PEEK-PBI, and PEKK-PBI

Following this global assessment of water incorporated into PBI and its blends, a more differentiated picture is sought. For this purpose, besides ¹³C solid-state NMR analysis, ¹H wideline and ²H MAS spectroscopy will be applied. In the latter case, the samples have been treated with D₂O instead of H₂O. Since the largest amount of moisture obviously resides in the PBI it will be discussed next.

Analysis of PBI after Exposure to D₂O as Liquid and Steam

It is obvious from the darkening color of PBI powder after stirring it in water at ambient temperatures that there are changes in the appearance of the material occurring already under these mild conditions (Supporting Information Figure S13). Steam-treatment of the PBI powder at 150°C leads to a further deepening of the color and visible morphological changes. After steam-treatment of the sample at 315°C with D₂O the powder makes a “baked” black and charcoal-type impression. It should be pointed out that D₂O practically does not differ in its



Scheme 2. Exchange of protons versus deuterium and hydrogen bonded D_2O in PBI.

reactivity from H_2O , and the same observations are made using the latter for steam-treatment.

Intrusion of water into the polymer network is the crucial factor 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 the 1H and 2H solid-state NMR analysis, it is important to reflect on the possible locations of water and protons in hydrated PBI. There are two sorts of backbone protons, aryl protons bound to carbons of the benzene rings, and N-H protons. Aryl C-H protons do not exchange, even under the harsh conditions of steam-treatment at $315^\circ C$. This is proven by subjecting the molecular model compound benzimidazole, $C_7H_6N_2$, to steam-treatment in the pressure vessels at $150^\circ C$. No traces of C-D groups have been found. Additionally, molecular benzophenone has been steam-treated at $315^\circ C$ for 72 h, but no H/D exchange has been observed. Therefore, one can assume that the hydrogen atoms of the PBI, PEEK, or PEKK backbones are not exchanged either. Nitrogen-bound protons, however, can in principle exchange with protons of H_2O , or deuterium, in case D_2O is offered (Scheme 2). The potentially formed N-D groups are expected to retain the deuterium when PBI is subjected to redrying after D_2O exposure.

Besides these covalently bound hydrogen or deuterium atoms, D_2O 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 one water molecule is hydrogen-bonded per N-H group.³ Adsorbed water molecules can migrate along the PBI strands and exchange with water molecules in adjacent liquid domains.³ Hydrogen-bonded water is expected to be removed when redry-

ing the PBI rigorously. Finally, water can also be present in the polymer, residing as a liquid in pockets of the polymer network, which can also be removed upon drying. While backbone C-H and N-H protons and N-D deuterium atoms are basically immobile, as long as the polymer chains are rigid, hydrogen-bonded H_2O and D_2O have some mobility even in the solid, rigid materials. The water in liquid domains, depending on their size, should be the species with most mobility in the polymer system. The water molecules in large liquid domains can even approach liquid-type mobility with reorientation times in the ns range.¹⁹

Since the steam-treatment of PBI leads to obvious changes of the material (Supporting Information Figure S13), ^{13}C solid-state NMR has been applied to probe whether decomposition at the molecular level can be detected. Figure 4 shows the ^{13}C CP/MAS NMR spectra of all PBI samples before and after exposure to D_2O at the listed conditions. First changes are already visible when PBI is stirred in liquid D_2O at ambient temperatures. The previously merged signals of the carbon nuclei 8 and 9 are split into two signals [Figure 4(b)]. Steam-treatment of the PBI at $150^\circ C$ leads to an increase of signal intensities of carbons 5–7. Interestingly, after steam-treatment at $315^\circ C$, all signals of the benzimidazole moiety are basically gone, while those of the benzene ring and carbon 1, which is directly bound to it, persist [Figure 4(d)]. To distinguish whether this result indicates potential decomposition of the imidazole unit, or is due to the exchange of 1H by 2H nuclei, one needs to reflect on the measurement method.

The spectra in Figure 4 are all recorded with CP,^{9–11} which means that the ^{13}C signal intensities are boosted by magnetization transfer from protons. Since the original material contains

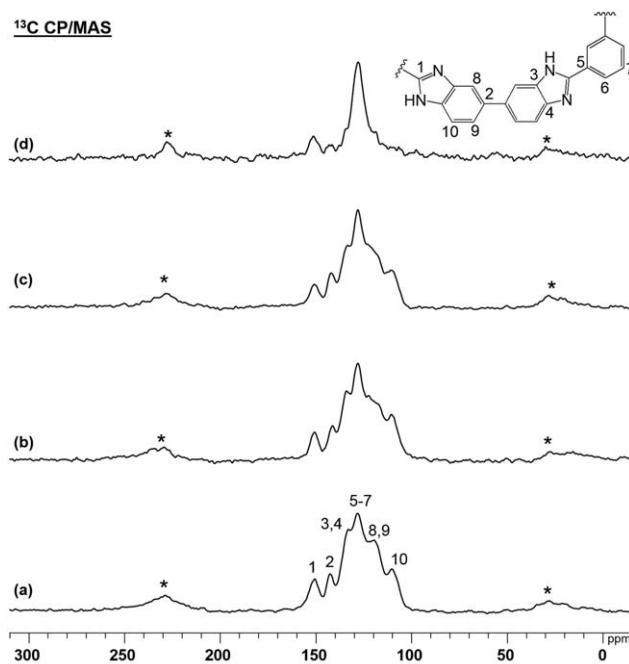


Figure 4. ^{13}C CP/MAS NMR spectra of PBI powder after drying at $110^\circ C$ for 144 h (a), stirring in liquid D_2O at RT (b), steam-treatment with D_2O at $150^\circ C$ (c), and at $315^\circ C$ (d).

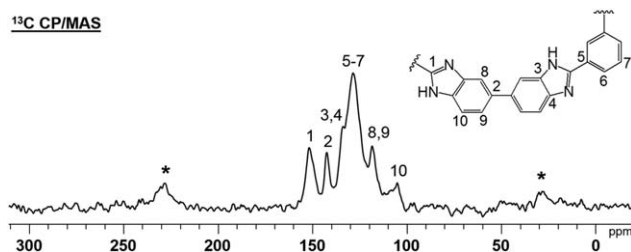


Figure 5. ^{13}C CP/MAS NMR spectrum of PBI powder after treatment with D_2O at 315°C , recorded with a contact time of 10 ms for CP.

large amounts of protons, a short contact time of 1.5 ms is sufficient to obtain spectra with good signal-to-noise ratio that show all signals. However, in the materials where ^1H is largely exchanged with ^2H by steam-treatment with D_2O , the magnetization has to be transferred from the remaining aryl protons, which are further away from the corresponding ^{13}C nuclei of the benzimidazole unit. This can be achieved by applying a longer contact time.¹¹ Indeed, when PBI, steam-treated with D_2O at 315°C is measured with a contact time of 10 ms, all ^{13}C signals are visible again (Figure 5). This spectrum allows three conclusions. First, the lines are narrower than in any of the spectra in Figure 4, which indicates that the PBI has changed its morphology and is more crystalline after the high-temperature steam-treatment, in accordance with earlier results obtained by ^{13}C T_1 relaxation time measurements.² Secondly, the loss of ^{13}C benzimidazole signals after treatment with D_2O and their boost with the longer contact time means that the H_2O and the newly incorporated D_2O mostly reside around the benzimidazole moieties in the polymer. The carbon signal 1 persists throughout, because its signal profits from magnetization transfer of the close-by aryl protons 6 and 7. The third piece of information is that the N—H proton and the protons of the H_2O molecule hydrogen-bonded to the N—H group are a source for magnetization transfer to the ^{13}C nuclei of the benzimidazole unit. Furthermore, this result suggests that the hydrogen-bonded H_2O molecules must stay long enough in the same environment to allow magnetization transfer.

To further probe the different ^1H and ^2H locations and characteristics, ^1H and ^2H solid-state NMR spectroscopy have been applied. ^1H MAS NMR, even at very high rotational frequencies of 35 kHz is only of limited use for the polymers investigated here, because only one narrow signal is obtained, surrounded by the corresponding sets of rotational sidebands. However, as demonstrated earlier,^{2,19,21} ^1H wideline NMR spectroscopy without sample spinning is analytically valuable for distinguishing protons of the immobile backbone from mobile phases,^{2,14,15} or from H_2O molecules in aqueous domains within the polymer network. Mobile species result in a relatively narrow signal sitting on the broad resonance of the backbone signal.²

Figure 6 displays the ^1H wideline NMR spectra of PBI powder before and after exposure to D_2O under different conditions. Spectrum (a) shows that after drying the sample *in vacuo* for 144 h at 110°C only immobile C—H and N—H backbone protons are present, which result in a broad resonance with about 28 kHz linewidth. After stirring PBI at room temperature in

D_2O , the proton wideline spectrum (b) shows a narrower line on top of the backbone signal whose half width can be determined to be around 4.9 kHz after deconvolution.³³ The narrow signal might stem from residual, strongly adsorbed H_2O that has been liberated into aqueous domains by exchange with D_2O , or the generated HDO. An alternative explanation, also for the narrow signals in the following ^1H wideline NMR spectra, would be the plasticization of parts of the PBI.¹⁵ This would lead to an increase in the mobility of the polymer chains, and a relatively narrow signal of the corresponding C—H protons could merge with the narrow $\text{H}_2\text{O}/\text{HDO}$ signal. More quantitative and dedicated experiments would be needed to disentangle this effect from the H_2O signal that has to be visible in the ^1H wideline spectra based on the measurement conditions and the large amount of water in the samples as determined by TGA. The following ^2H MAS experiments (see below) prove that adsorbed D_2O constitutes at least the major part of the narrow signals. Although plasticization¹⁵ cannot be excluded at this point, for the sake of clarity, in the following only adsorbed water is mentioned in regards to the narrow signals.

Independent of the origin of the protons resulting in the narrow resonance one can conclude that even at room temperature water can easily move into the polymer and participate in proton exchange. After steam-treatment of the PBI with D_2O at 150°C [Figure 6(c)] and 315°C (d), narrow peaks are present with line widths of 2.5 and 4.5 kHz, respectively, but their intensity is diminished as compared with the signal in spectrum (b). Obviously, at the higher temperatures, the exchange of protons by deuterium is more complete, leading to reduced ^1H signals of exchangeable protons, because under these conditions more water can penetrate into the polymer network within the given time frame and leave it again. The line widths of the broad signals in Figure 6 changes from about 29–22 kHz in the sequence from (a) to (d). Although the lines are too broad to speak of plasticization,¹⁵ this line narrowing indicates a morphological change of the polymer backbones, which ultimately

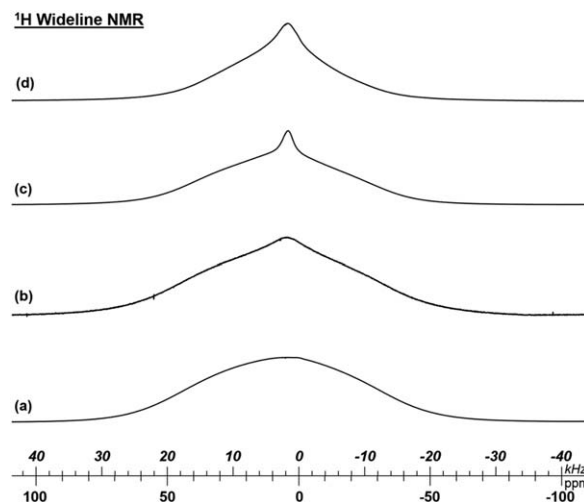


Figure 6. ^1H Wideline NMR spectra of PBI powder after drying at 110°C for 144 h (a), stirring in D_2O at RT (b), and steam-treatment with D_2O at 150°C (c) and 315°C (d).

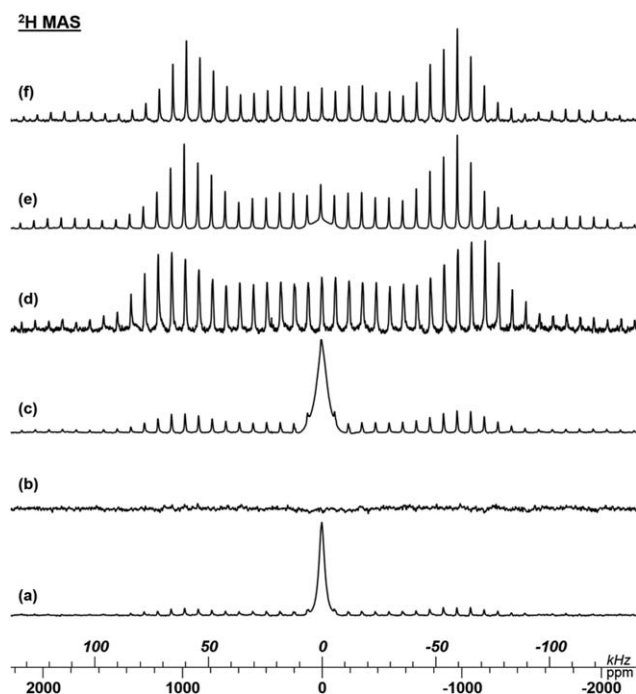


Figure 7. ^2H MAS spectra of rigorously dried PBI stirred as a powder in D_2O at RT for 48 h (a), and after redrying this sample at 110°C *in vacuo* for 48 h (b). ^2H MAS spectra of dry PBI exposed to D_2O at 150°C for 48 h (c), and after redrying at 110°C for 48 h (d). ^2H MAS spectra of pre-dried PBI exposed to D_2O at 315°C for 72 h (e), and after redrying at 110°C for 48 h (f). The Pake patterns are split into rotational sidebands (spinning frequency 6 kHz for all samples). The Q_{cc} values for (a) and (c–f) are given in Table I.

leads to the PBI becoming brittle (Supporting Information Fig. S13).

To gain a more differentiated picture about the various sorts of protons and water present in the PBI, as well as their mobilities, ^2H MAS has been applied. Measuring ^2H instead of ^1H NMR also allows to eliminate any signals from the polymer backbone. Information about the mobilities of the ^2H -containing species can be obtained, because ^2H has a nuclear spin of 1 and is therefore quadrupolar. The Pake patterns^{9,19,22,27–31} 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} . When the sample is rotated, the Pake pattern is split 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.³⁴ The quadrupolar coupling constant can be correlated with the mobility, or more precisely, the reorientation time of the species or functional groups containing the measured ^2H nucleus.^{27–31,39} This correlation between reorientation times and appearances of the corresponding Pake patterns has been described in detail for long alkyl chains.³⁹ ^2H MAS spectroscopy has previously been applied by us to quantify the mobilities of metallocenes adsorbed on silica surfaces.¹⁹ But there are also examples for applications in the field of polymers in the literature, and recently ^2H solid-state NMR has been used to obtain more quantitative insight into various dynamic scenarios.^{27–31} For

example, the segmental mobilities of polymer chains²⁹ and the plasticization of poly(vinyl acetate) adsorbed on silica have been investigated using ^2H solid-state NMR.²⁸

Figure 7 shows the ^2H MAS spectra after treating PBI with D_2O under different conditions. Stirring PBI in D_2O at ambient temperature results in spectrum (a). There are two signals with very different characteristics discernible in the spectrum. A signal in the center at ca. 5 ppm with a half width of 2.8 kHz is not split into a Pake pattern. This signal is attributed to mobile water present in liquid aqueous domains in the polymer due to a collapsed Pake pattern.^{19,28} The second signal presents as a classic Pake pattern of lower intensity with a Q_{cc} value of 194 kHz (Table I). Due to the sample rotation with 6 kHz, the Pake pattern is split into a manifold of rotational sidebands with residual line widths of about 600 Hz. The origin of this signal must be an immobile species, most probably D_2O strongly hydrogen-bonded to N–H groups of the PBI backbone. This assumption is corroborated by the following experiment: when the PBI sample is redried thoroughly *in vacuo*, there are no longer any ^2H signals emerging in the spectrum [Figure 7(b)], even after prolonged measurement times. Therefore, one can assume that in case PBI is stirred in D_2O at ambient temperature, the merely adsorbed, as well as D_2O residing in liquid domains, can be removed again quantitatively, and there is no chemical exchange of ^1H versus ^2H . This result also corroborates the earlier assumption that the narrow signals in Figure 6 are mostly composed of strongly adsorbed residual H_2O or HDO, and any plasticization that would be visible in the increased mobility of N–D groups in the polymer chains plays a minor role.

After PBI is steam-treated with D_2O at 150°C for 48 h, two signals are again visible in the ^2H MAS spectrum, as shown in Figure 7(c). The only differences as compared with the spectrum in Figure 7(a) are that the Pake pattern shows higher intensity, and that Q_{cc} assumes a slightly larger value of about 195 kHz. When the sample is dried *in vacuo*, a Pake pattern with a larger Q_{cc} of about 201 kHz remains, while the broad resonance in the center is gone [Figure 7(d)]. The latter finding corroborates our assumption that the broad center peak belongs to domains of liquid D_2O , which are removed during the drying procedure. The persistent Pake pattern can be assigned to N–D groups in

Table I. Q_{cc} (Quadrupolar Coupling Constant) Values (kHz) of Samples Treated with D_2O as Liquid and Steam at 150 and 315°C

Q_{cc} of polymers	RT	150°C	315°C
PBI ^a	194	195	184
Redried PBI ^a	b	201	184
PEEK-PBI ^c	b	197	184
PEKK-PBI ^c	b	195	183
PEKK-PBI ^{c,d}	b	198	184

^a Samples exposed as powders.

^b Indicates that no Pake pattern has been observed.

^c Exposed as melt-blended tensile specimens.

^d Sample has been exposed to atmosphere for 1 month after being steam-treated at 315°C . Error margins of the Q_{cc} values are ± 0.5 kHz.

the polymer backbone that come into existence by deuterium exchange of the N—H groups with hydrogen-bonded D₂O.

After PBI is steam-treated with D₂O at 315°C for 72 h, again two signals are visible in the ²H MAS spectrum, as shown in Figure 7(e). When this sample is dried, only the Pake pattern with a Q_{cc} value of 184 kHz remains (7f). The differences as compared with the spectra (a) and (c) in Figure 7 are that the Pake patterns show higher intensities and Q_{cc} assumes a value of 184 kHz for both spectra (e) and (f).

Regarding the Q_{cc} values obtained from the spectra in Figure 7 and compiled in Table I, one should mention that the simulations as described in the experimental section³⁴ are quite accurate. An example that shows the quality of the fit is displayed in Supporting Information Figure S14.

The chemical shift for D₂O 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 linewidth and the huge chemical shift range of ²H in the solid state into account, even the rotational sidebands of the MAS signals of these species overlap. 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 hydrogen-bonded D₂O molecules undergo fast exchange with the D₂O molecules in contiguous liquid domains. This means that the Q_{cc} values are variable in the presence of liquid domains. In the absence of liquid D₂O [Figures 7(d,f)] there is no longer any exchange, and only the signal for N-D groups with maximal Q_{cc} should be present. The Q_{cc} values of PBI redried after steam-treatment at 150 and 315°C, however, are 201 and 184 kHz, a difference that is visible to the bare eye when looking at the spectra in Figure 7. Therefore, one can assume that the steam-treatment at 315°C does not only lead to an exchange of N—H protons, but also to a morphological change influencing the overall polymer chain mobility. The change of the quadrupolar coupling constants to slightly smaller values with harsher treatment conditions underlines the earlier results that the broad wide-line ¹H signals become narrower with increased temperatures and prolonged times of exposure. This suggests a general change of polymer morphology, which is also in accordance with the sample becoming more brittle after this treatment (Supporting Information Figure S13), and with earlier ¹³C T_1 relaxation time measurements.²

Analysis of PEEK-PBI After Exposure to D₂O as Liquid and Steam

In the following, it will be analyzed whether the PEEK component in a 50 : 50 wt % melt-blended PEEK-PBI polymer will change the behavior of the PBI towards water and steam. The ¹³C CP/MAS NMR spectra of PEEK-PBI samples before and after exposure to D₂O under the indicated conditions are displayed in Figure 8. After stirring the blend at RT in D₂O (b) and steam-treatment at 150°C (c) no major changes of the signals as compared to the dry sample (a) are visible. However, after steam-treatment with D₂O at 315°C (d), the signals 2 and 10 are no longer present and the peak containing overlapping signals of 8 and 9 is diminished in intensity. This result can again be attributed to the CP phenomenon discussed above for

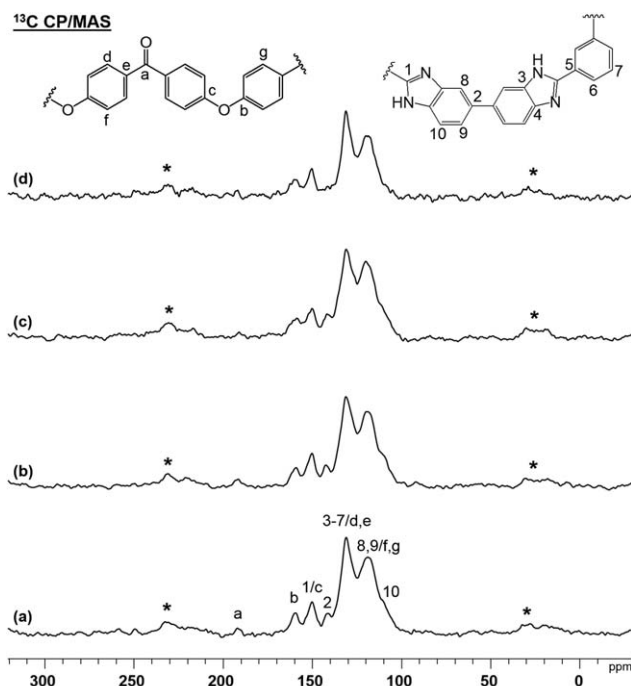


Figure 8. ¹³C CP/MAS NMR spectra of melt-blended PEEK-PBI (50 : 50 wt %) after drying at 110°C for 550 h (a), stirring in D₂O at RT (b), steam-treatment with D₂O at 150°C (c), and immediately after steam-treatment with D₂O at 315°C (d).

pure PBI. Therefore, one can conclude that under these harsh conditions, D₂O penetrates the PBI component of the blend, exchanges N—H by N-D and adsorbed H₂O by D₂O, thus depleting the proton pool close to the benzimidazole unit for magnetization transfer at short contact times. As observed for the noncondensed phenyl ring in the PBI component, the aryl protons of PEEK are not exchanged. Furthermore, since the signal intensities of PEEK are not affected by steam-treatment with D₂O, one can conclude that the PEEK component does not contain adsorbed H₂O that contributes to the magnetization transfer.

The ¹H wide-line NMR spectra of the melt-blended PEEK-PBI samples before and after treatment with liquid D₂O and D₂O steam are displayed in Figure 9. The proton signal with a small line width of about 6.1 kHz on top of the broad resonance with a half width of about 30 kHz in spectrum (a) reveals that even after 550 h of drying *in vacuo*, the tensile specimen still contains adsorbed and mobile H₂O. This result is not surprising taking the drying curve of Supporting Information Figure S5 into account that does not reach a constant weight after 600 h. Stirring the specimen in liquid D₂O leads to slight changes of the linewidths of the broad and narrow signals (29 and 5.8 kHz), but the overall appearance of the spectrum does not change (b). However, after steam-treatment at the higher temperatures of 150 and 315°C (c, d), immobile N—H protons are exchanged and join mobile species. These lead to the narrower proton signals with half widths of 4.9 and 3.5 kHz, respectively.

As the ²H MAS NMR spectra displayed in Figure 10 show, it takes steam-treatment at elevated temperatures of 150 and

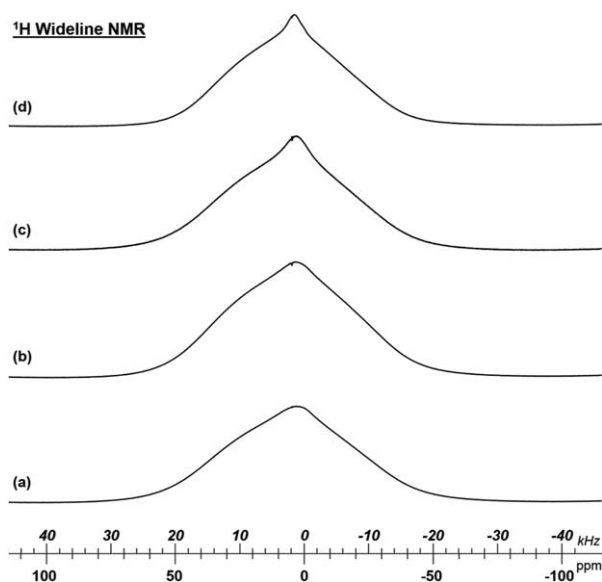


Figure 9. ^1H Wideline NMR spectra of melt-blended PEEK-PBI after drying at 110°C for 550 h (a), stirring in liquid D_2O at RT (b), steam-treatment with D_2O at 150°C (c), and immediately after steam-treatment with D_2O at 315°C (d).

315°C to bring substantial amounts of D_2O into the PEEK-PBI melt-blended samples. However, even after stirring the sample in liquid D_2O at room temperature, a Pake pattern with low intensity emerges. This demonstrates that even under mild conditions D_2O migrates into the polymer, most probably along the PBI backbone. After 150 and 315°C steam-treatment with D_2O , two signals are visible in each spectrum (b, c). A central signal attributable to mobile D_2O , adsorbed or in liquid domains in the polymer, and Pake patterns. The Q_{cc} values of 197 and 184 kHz are matching those of PBI (195, 184 kHz) after being subjected to the same D_2O -treatment conditions (Table I). This indicates once more that the PBI component in the blend is dominating the interaction of the blend with water.

^2H MAS

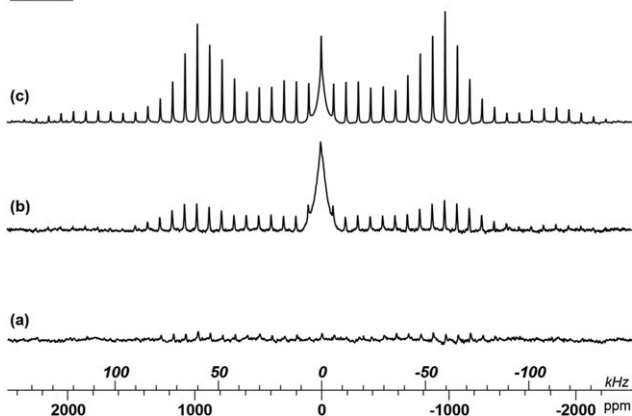


Figure 10. ^2H MAS NMR spectra of melt-blended PEEK-PBI after stirring in liquid D_2O at RT (a), steam-treatment with D_2O at 150°C (b), and immediately after steam-treatment with D_2O at 315°C (c). The Q_{cc} values of the Pake patterns are given in Table I. The Pake patterns are split into rotational sidebands (spinning frequency 6 kHz for all spectra).

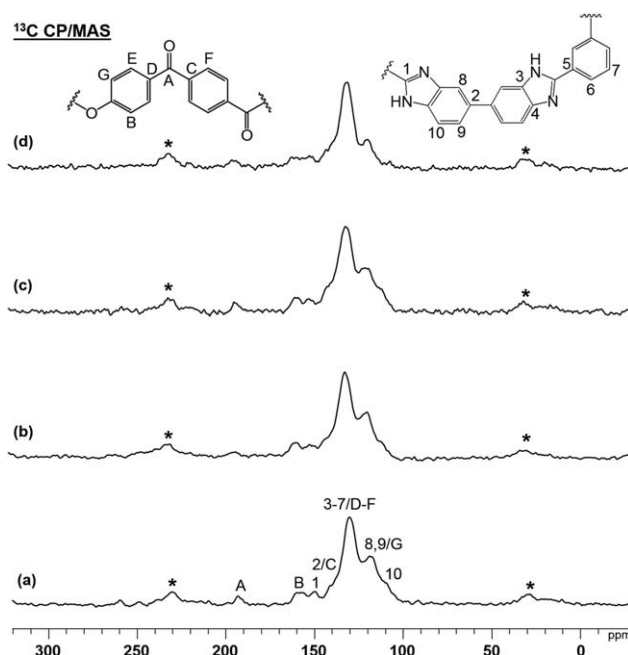


Figure 11. ^{13}C CP/MAS NMR spectra of melt-blended PEKK-PBI after drying at 110°C for 550 h (a), stirring with liquid D_2O at RT (b), steam-treatment with D_2O at 150°C (c), and immediately after steam-treatment with D_2O at 315°C (d).

Analysis of PEKK-PBI After Exposure to D_2O as Liquid and Steam

The ^{13}C CP/MAS NMR spectra of melt-blended PEKK-PBI samples (Figure 11) follow the same trends as observed for pure PBI and PEEK-PBI, when treated with D_2O at ambient and elevated temperatures. After treatment at RT (b) and 150°C (c) there are no major changes in the signals as compared to the starting material (a). However, steam-treatment with D_2O at 315°C again leads to a disadvantage for the benzimidazole signals of the PBI component at the short CP time of 1.5 ms. This phenomenon has been observed and discussed for pure PBI and PEEK-PBI. It can be concluded that in the case of PEKK-PBI, too, D_2O is more readily incorporated into the PBI- than the PEKK component.

In contrast to the PEEK-PBI, in the case of PEKK-PBI steam-treatment at 150°C is needed to bring substantial amounts of D_2O into the polymer, as the ^2H MAS spectra in Figure 12 show. Even at this elevated temperature most of the D_2O is included in the blend in the form of liquid domains, as the unstructured center signal with a half width of 4.3 kHz implies. However, steam-treatment at 150°C also leads to the formation of less mobile ^2H -containing species (b), whose Q_{cc} value of 195 kHz matches the one of PBI after exposure to D_2O under the same conditions (Table I). After steam-treatment at 315°C , the polymer contains more of the less mobile ^2H species as indicated by the increase in intensity of the Pake pattern with a Q_{cc} value of 183 kHz. The same phenomena and similar Q_{cc} values of 184 kHz are observed after the treatment of PEEK-PBI and pure PBI with D_2O under identical conditions. Therefore, we conclude that in the case of PEKK-PBI, too, the PBI component is mainly responsible for the interactions with D_2O . As

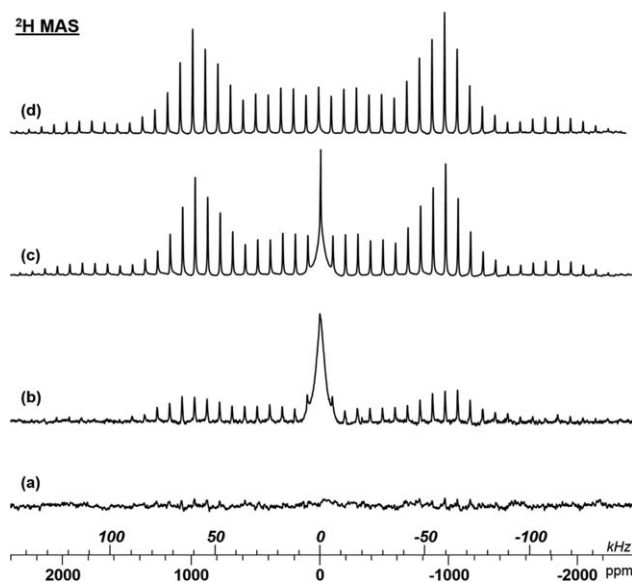


Figure 12. ^2H MAS NMR spectra of melt-blended PEKK-PBI after stirring in liquid D_2O at RT (a) and steam-treatment with D_2O at 150°C (b), immediately after steam-treatment with D_2O at 315°C (c), and one month of exposure to the atmosphere after the latter treatment (d). The Q_{cc} values are listed in Table I. The Pake patterns are split into rotational sidebands (spinning frequency 6 kHz for all spectra).

compared with PEEK-PBI, however, the PEKK component fends off D_2O slightly better, as indicated by the nearly complete lack of a Pake pattern in spectrum 12 (a).

Interestingly, when the PEKK-PBI that has been steam-treated with D_2O at 315°C is exposed to the H_2O -containing ambient atmosphere for one month, the D_2O residing in liquid domains is nearly quantitatively exchanged by H_2O , a process that ultimately removes the broad center ^2H signal in the MAS spectrum [Figure 12(d)]. In contrast to this, the Pake pattern with a Q_{cc} of 184 kHz is fully retained. This means that the N-D groups do not undergo any D/H exchange with H_2O from the atmosphere.

The ^1H wideline NMR spectra of the PEKK-PBI (Figures 13 and 14) provide complementary information and corroborate the conclusions drawn above. The PEKK-PBI sample as received contains only traces of H_2O [Figure 13(a)], which is in accordance with earlier results.² Therefore, only the broad signal for the backbone protons with a line width of about 23 kHz is visible in the spectrum. After steam-treatment with H_2O at 150°C a narrow peak with a half width of 3.7 kHz appears on top of the hump, indicating the presence of mobile H_2O [Figure 13(b)]. When this sample is steam-treated again with D_2O at 150°C , the H_2O from the liquid domains and hydrogen-bonded water is quantitatively replaced by D_2O , and therefore the narrower ^1H NMR signal is gone from the ^1H NMR spectrum in Figure 13(c).

The ^1H wideline NMR spectrum obtained after steam-treatment of PEKK-PBI with H_2O at 315°C shows a 19 kHz broad hump and a narrower signal with a half width of 2 kHz on top of it [Figure 14(a)], representing the backbone protons and the

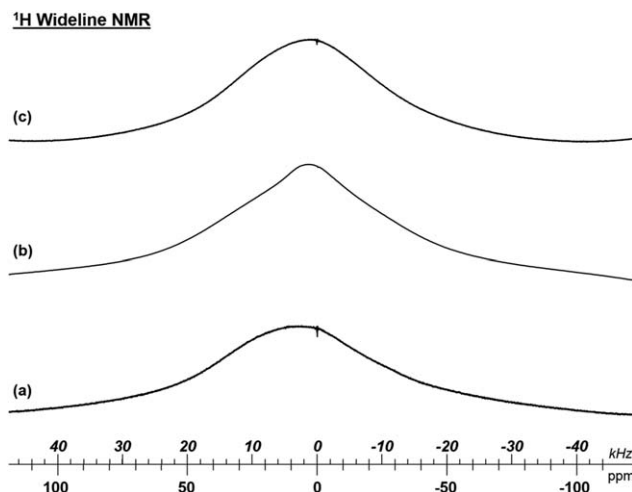


Figure 13. ^1H Wideline NMR spectra of the PEKK-PBI blend as received (a), after steam-treatment with H_2O at 150°C for 48 h (b), and after steam-treating this sample at 150°C with D_2O for 48 h (c).

mobile H_2O in liquid domains. Steam-treating this sample with D_2O at 315°C removes nearly all of the narrow ^1H signal, since now it is mainly D_2O residing in the liquid domains [Figure 14(b)]. Finally, exposing the sample to the ambient atmosphere reinstates the narrow signal on top of the ^1H backbone hump, because the D_2O in the liquid domains has gradually been replaced by atmospheric H_2O .

^7Li MAS for Investigating Salt Uptake of the PEKK-PBI Blend
During the polymerization process of PAEK polymers typically NaCl is formed, which is extracted subsequently with water. This can be counted as another indication that water can diffuse into the polymer and leave it again, carrying NaCl along. It also corroborates the results above which describe how H_2O can be replaced by D_2O in the polymer and vice versa. But, there are two questions left, (a) whether salts other than NaCl can be

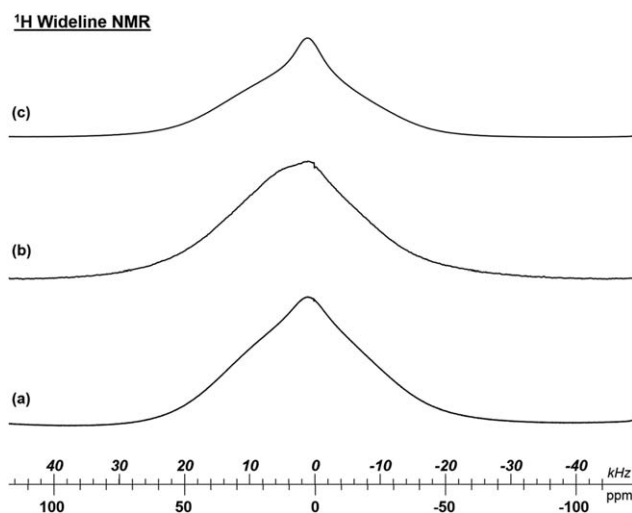


Figure 14. ^1H Wideline NMR spectra of PEKK-PBI after steam-treatment at 315°C with H_2O for 72 h (a), steam-treatment of this sample at 315°C in D_2O for 72 h (b), and after exposure to the atmosphere for one month (c).

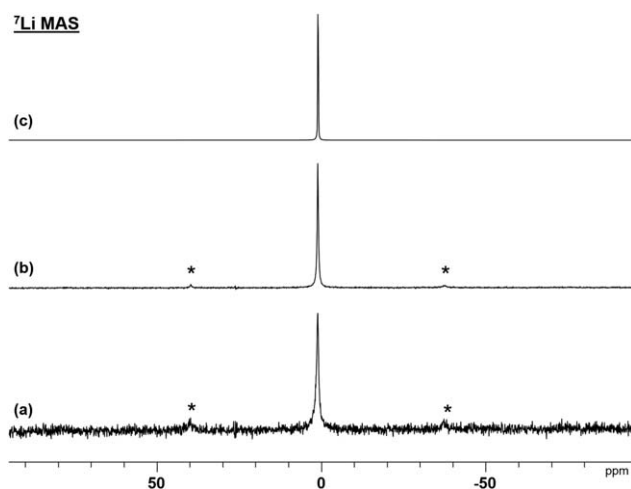


Figure 15. ^7Li MAS NMR spectra of (a) PEKK-PBI after stirring a tensile specimen in a 150 mL solution of 15 g of LiCl (10 wt %) in H_2O at 106°C for 24 h (6 kHz), (b) PEKK-PBI sample described under (a) after stirring it in H_2O at 100°C for 48 h (6 kHz), and (c) aqueous phase after stirring the PEKK-PBI sample (b) with H_2O . Asterisks denote rotational sidebands. The half widths of the signals are 134.3 (a), 85.4 (b), and 61.0 Hz (c).

extracted by water, and (b) whether salts can also move into the polymers, not only out of them. Therefore, the PEKK-PBI blend has been stirred with an aqueous LiCl solution at 106°C for two days. To qualitatively probe the presence of LiCl, a ^7Li MAS spectrum has been recorded [Figure 15(a)]. Although ^7Li is quadrupolar with a nuclear spin of $3/2$, it behaves nearly like a spin- $1/2$ nucleus and can easily be measured in various materials.³² As the spectrum in Figure 15(a) shows, a substantial amount of ^7Li can be found in the polymer blend after its exposure to an aqueous LiCl solution. When this sample is then stirred with H_2O , the LiCl is only partially extracted, as ^7Li is found both in the aqueous phase [Figure 15(c)], as well as in the polymer [Figure 15(b)]. Interestingly, while spectrum 15a needed 1064 scans, the spectrum of trace (b) only required the accumulation of 64 FIDs. Nevertheless, the signal-to-noise ratio is much better for (b). Additionally, the rotational sidebands of the signal in spectrum (b) have lower intensity. One possible explanation for this phenomenon might be that ^7Li is a quadrupolar nucleus, and the concentration of LiCl is so high in the polymer measured for trace (a) that the dissociation of the ions is not complete, or aggregates form and the local electronic symmetry around the ^7Li nuclei is disturbed. Once most of the LiCl is extracted from the polymer, the Li^+ ions remaining in the polymer network are dilute with a complete hydration shell and therefore they possess electronically symmetric surroundings. This might be why the ^7Li signal in the middle spectrum of Figure 15 is nearly as narrow as in solution (top spectrum). The lower intensity of the rotational sidebands corroborates the assumption that Li^+ ions, fully dissolved in aqueous domains within the polymer network, contribute most to the signal in Figure 15(b).

To test whether the salt uptake is only possible for LiCl or also in the case of other salts, PBI, PEEK-PBI, and PEKK-PBI have been exposed to 5 wt % aqueous ZnBr_2 solution. ^{79}Br is quadrupolar with a nuclear spin of $5/2$, which means that in the

solid state NMR spectrum of a Br nucleus, given that it resides in an electronically symmetric environment, a center transition and a Pake pattern of lower intensity are visible. As a Br^- anion naturally has a symmetric surroundings, spectra are in principle obtainable. The ^{79}Br MAS NMR spectra show (Supporting Information Figure S15) that pure PBI admits the salt readily. Interestingly, no signal can be found after PEEK-PBI is treated with the ZnBr_2 solution, and only traces in the case of PEKK-PBI. Therefore, one can conclude that the PEEK and PEKK components make the PBI more resistant toward uptake of ZnBr_2 . In future work a quantitative measure of the tenacity of the salts in the polymer networks, as well as their impact on the morphologies and reactivities of the polymers will be pursued.

CONCLUSIONS

In this contribution, we have successfully demonstrated that PEEK and PEKK blends with PBI (50 : 50 wt %) can be characterized by ^{13}C CP/MAS and all signals can be assigned due to the favorable signal resolution. While physical mixtures of the components cannot be distinguished from their melt-blended versions based on their ^{13}C CP/MAS spectra, more pronounced differences are visible in the ^{15}N CP/MAS spectra. Furthermore, it is described that the moisture uptake of PEEK-PBI and PEKK-PBI samples is much faster than the reverse process, especially at elevated temperatures. PEEK-PBI incorporates overall more water than PEKK-PBI. With the use of ^2H MAS and ^1H wideline NMR spectroscopy for samples steam-treated with D_2O and H_2O , three different ^2H sites can be distinguished in PBI and in the PEEK- and PEKK-PBI blends. Mobile D_2O can reside in liquid domains in the polymer network. Less mobile D_2O is attached to N—H (or N-D) groups via hydrogen bonds, and they are exchanging with mobile D_2O molecules in contiguous liquid D_2O domains. Potential partial plasticization of PBI with increasing amounts of incorporated water is discussed. Finally, immobile ^2H nuclei, covalently bound in N-D groups are found after steam-treatment at higher temperatures. Furthermore, it has been demonstrated with ^7Li MAS that LiCl is incorporated into PEKK-PBI by treating the blend with an aqueous LiCl solution at elevated temperatures. This LiCl can partially be extracted again with H_2O at elevated temperatures. Finally, it has been shown by ^{79}Br MAS NMR that ZnBr_2 is readily incorporated into pure PBI out of an aqueous solution, while only traces move into the PEEK-PBI and PEKK-PBI blends.

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AUTHOR CONTRIBUTION

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

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