

## High-Temperature Steam-Treatment of PBI, PEKK, and a PEKK-PBI Blend: A Solid-State NMR and IR Spectroscopic Study

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**ABSTRACT:** Blends of polyaryletherketones (PAEK) with polybenzimidazole (PBI) are of commercial interest due to their improved upper service temperatures and wear properties when compared with the PAEK analogs examined to date. The retention of properties of the PBI component generally thought to be disadvantageous in more thermally or chemically aggressive environments is not well understood, nor are the specifics of interactions between the PBI and PAEK components in a melt or dry blend systems. In this initial investigation, focus is placed on the behavior and mechanism of polyetherketoneketone (PEKK)/PBI systems in contact with steam or condensed phase water. The goal is to understand the chemistry of the reaction, if any, upon exposure to steam as well as to examine the reversibility of moisture uptake of this material when exposed to liquid water or saturated steam. In this contribution, the pure polymer components and the PEKK-PBI (60 : 40 wt %) blend are steam-treated at 149°C (300°F) and 316°C (600°F). IR and solid-state NMR spectroscopy are used to study chemical or morphological transformations of the polymers. All changes detectable by <sup>13</sup>C cross-polarization with magic angle spinning (CP/MAS) upon steam-treatment are reversible, and not of a chemical nature, indicating that under the conditions of exposure used here no detectable chemical degradation occurs during steam exposure and with moisture uptake. The temporary water uptake of the samples, as studied by <sup>1</sup>H wideline NMR and <sup>13</sup>C T<sub>1</sub> time measurements, leads to a change in the ratio of rigid versus mobile domains of the materials. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4395–4404, 2013

**KEYWORDS:** high-performance thermoplastics; PAEK polymers; PBI; PEKK; PEKK-PBI blends; solid-state NMR

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### INTRODUCTION

The polyaryletherketone (PAEK) family of thermoplastic polymers<sup>1</sup> 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 elevated temperatures. One such application, for example, involves the use of such materials as pressure seals or antiextrusion back-up rings in the oil and gas drilling industry, where demands for materials that will perform well in high pressure, high temperature service are steadily increasing, and PAEK polymers are ideally suited. Although the various PAEK grades that are commercially available are of benefit to the end users, demand for even higher temperature applications continues to grow, as does a desire for improved tribological performance. One response to these demands has come forward in the provision of blends of PAEK polymers with polybenzimidazole (PBI) resins, which takes advantage of the increased service temperatures and some

improvement in wear properties afforded by the PBI component. Polyetherketoneketone (PEKK)-PBI blends are manufactured primarily to elevate the service temperature of the PEKK polymer alone as well as to achieve some improvement in wear performance compared with the PEKK homolog. A potential negative feature of this combination is the comparatively poor chemical stability associated with the PBI component. In this study, the traditional Celazole-type PBI (poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole]) is applied.

Solid-state NMR spectroscopy is one of the most powerful methods for studying polymers on a molecular level.<sup>2</sup> Chemical changes during the exposure to adverse conditions can be studied by <sup>13</sup>C cross-polarization with magic angle spinning (CP/MAS) NMR,<sup>2–5</sup> while morphological changes, involving the ratio of rigid versus mobile domains in the polymer, can be investigated by the <sup>13</sup>C T<sub>1</sub> relaxation time characteristics.<sup>6–9</sup> The prerequisite for any chemical change of the polymer due to the

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exposure to water at room temperature or steam at elevated temperatures is that water penetrates into the polymer network.<sup>10</sup> Especially for mostly amorphous materials like PBI<sup>11</sup> this scenario can be studied by <sup>1</sup>H wideline NMR, where proton measurements of the solid samples are recorded without sample spinning.<sup>12–15</sup> Additionally, the  $\nu(\text{O—H})$  stretching band indicates the presence of water in IR spectra.<sup>16,17</sup> PAEK polymers in general are also amenable to IR spectroscopy, as changes of the carbonyl stretching band and modifications in the fingerprint area are indicators for both chemical and morphological transformations.<sup>18</sup> In this contribution, PEKK and PBI polymers as well as their 60% : 40% PEKK-PBI blend are exposed to water at ambient temperature. Additionally, all pure components and the PEKK-PBI blend are exposed to steam at 149°C (300°F) and 316°C (600°F) for a prolonged time to simulate real-life conditions, which these materials are likely to encounter in the oil and gas industry when recovering heavy oil- or tar sands-based hydrocarbons, where direct steam injection is a standard practice. It is shown that all changes are reversible and that any deterioration of the mechanical properties of the pure polymers and blend is not based on any chemical decomposition, but is due to changes of their morphology.

## EXPERIMENTAL

All polymer samples used in this study were provided by Hoerliger Corporation of America. The blend samples have been manufactured by melt-mixing and subsequent injection molding. In the following, PBI stands for Celazole PBI with the product code M51050 and PEKK for materials with the code K7500. The PEKK-PBI blend (60 : 40 wt % PEKK to PBI) with the trade name Arylmax K7500/PBI has been used in this study. Differential scanning calorimetry (DSC) data (Supporting Information Table S1 and Figures S6–S8) of all samples discussed in this contribution have been recorded and are in accord with the NMR and IR results.

### Sample Preparation

Exposing the dry materials to water at room temperature included an initial 30 min of sonication to achieve a homogeneous suspension of the polymer powder in the water prior to letting the mixture stand for 24 h. Then the polymer powder was filtered off and dried in an air stream. The steam-treatment of all samples was undertaken using a Parr pressure reactor Model 4913. Dogbone-shaped samples of the polymers were placed on grids in the reactor together with 150 mL of distilled water and heated to 149°C (300°F) and 316°C (600°F). The resulting pressures in the closed vessels amounted to 5 bar (72 psi) and 110 bar (1600 psi), respectively. The redrying procedure consisted of removing the water at 120°C under vacuum for 3 days.

### <sup>13</sup>C CP/MAS NMR Spectroscopy

The solid-state NMR spectra were measured on a Bruker AVANCE 400 spectrometer operating at 400.1 MHz for <sup>1</sup>H and 100.6 MHz for <sup>13</sup>C. The <sup>13</sup>C CP/MAS (cross polarization with magic angle spinning)<sup>2–5</sup> experiments were performed at rotational frequencies of 10, 12, and 13 kHz using densely packed powders of the polymers in 4 mm ZrO<sub>2</sub> rotors. The <sup>1</sup>H  $\pi/2$  pulse was 2.5  $\mu\text{s}$  and two pulse phase modulation (TPPM) decoupling was applied during the <sup>13</sup>C CP/MAS acquisition. The Hartmann–

Hahn matching condition was optimized using the polymer Vic-trex 450PF at a rotational speed of 10 kHz. Adamantane served as the external chemical shift standard. All spectra were measured with a contact time of 1.5 ms and a relaxation delay of 5.0 s, and typically 1024 free induction decays (FIDs) were accumulated. Line-broadening factors of less than 100 Hz were applied for the processing of the FIDs. The dipolar dephasing delay for the spectra used for signal assignment was 40  $\mu\text{s}$ .

### <sup>1</sup>H Wideline NMR Spectroscopy

The <sup>1</sup>H wideline NMR spectra were recorded in the MAS probehead without sample spinning. H<sub>2</sub>O was used as the external chemical shift standard, but it should be noted that with the obtained broad signals the chemical shifts determined are very sensitive to miniscule changes in the phase correction of the signals. No background <sup>1</sup>H NMR signal of the probehead equipped with an empty rotor was obtained when a spectrum was recorded with the measurement parameters applied for the polymers. 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. The signals in the <sup>1</sup>H NMR spectra were deconvoluted using the program MestRe-C<sup>®</sup>. The broad signal of the polymer backbone was fitted using mainly a Gaussian lineshape, while the narrower signal sitting on top of the broad one was best emulated by a Lorentzian fit.

### <sup>13</sup>C T<sub>1</sub> Relaxation Time Determination

The <sup>13</sup>C T<sub>1</sub> relaxation times were obtained by the method reported by Torchia.<sup>6</sup> Typically 30 spectra with incremented relaxation delays ranging from 100 ms to 30 s were recorded. The decay of the signal intensity over time was plotted and the curves were fitted to a double-exponential decay using the software program TableCurve 2D 4.0.<sup>7</sup>

### IR Spectroscopy

The IR spectra were recorded on the instrument Shimadzu IRAffinity-1 FTIR by placing the powdered polymers on top of a Pike Technologies MIRacle ATR diamond plate. One hundred scans were typically recorded for optimal spectrum quality.

## RESULTS AND DISCUSSION

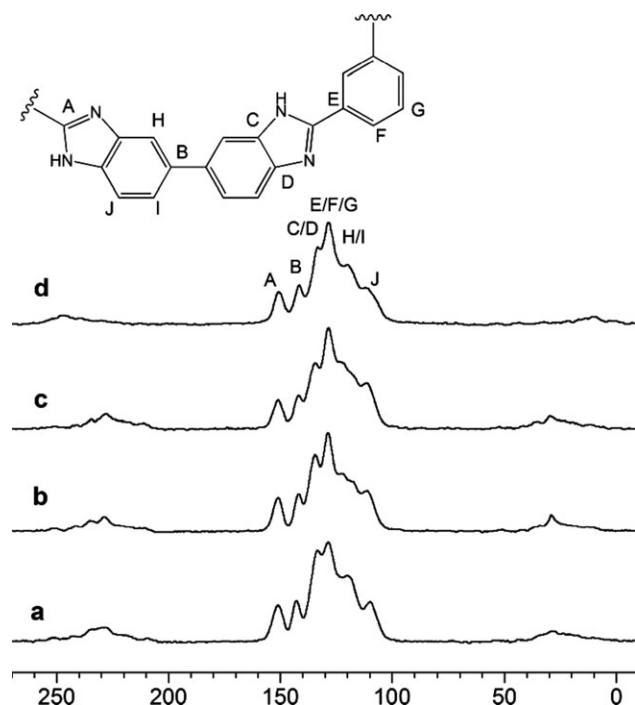
### <sup>13</sup>C Solid-State NMR Spectroscopy of Original Samples

Polymers in general are the classical field of application for solid-state NMR spectroscopy.<sup>2,3</sup> Therefore, according to expectation, the pure PEKK and PBI components as well as the PEKK-PBI blend give well-resolved <sup>13</sup>C CP/MAS<sup>2–5</sup> NMR signals (Figure S1). The signal assignments have been made using dipolar dephasing techniques,<sup>4,19</sup> and short contact times,<sup>4</sup> and they are in accord with literature values for PEKK<sup>20</sup> and PBI<sup>18,21</sup> polymers. The <sup>13</sup>C CP/MAS spectrum of the PEKK-PBI blend (Figure S1) represents approximately a weighted 60 : 40 sum of the spectra of pure PEKK and PBI.

### Steam-Treated PBI

<sup>13</sup>C CP/MAS NMR Spectroscopy. Figure 1 compares the <sup>13</sup>C CP/MAS spectra of PBI (a) with those of PBI exposed to water at ambient temperature (b) and samples treated with steam at 149°C for 48 h (c) and 316°C for 72 h (d).

As expected, an obvious change of the signals in the region from 110 to 135 ppm already occurs when PBI is allowed to



**Figure 1.**  $^{13}\text{C}$  CP/MAS NMR spectra of (a) PBI ( $\nu_{\text{rot}} = 10$  kHz), (b) PBI exposed to water at RT (10 kHz), (c) PBI steam-treated at  $149^\circ\text{C}$  for 48 h (10 kHz), and (d) PBI steam-treated at  $316^\circ\text{C}$  for 72 h (13 kHz). Signals outside the region from 100 to 200 ppm are rotational sidebands.<sup>3,19</sup>

take up water at room temperature. As it can best be seen in the expansion in Figure 2, the signal at 133.5 ppm loses intensity while the resonance at 120.2 ppm splits into two signals at 122.0 and 117.1 ppm. Because of the overlap of multiple signals at 128.6 ppm, it is not possible to judge on any intensity loss or gain. However, the chemical shift anisotropy<sup>3,19</sup> of this signal changes. This can be deduced from the shape change of the rotational sideband at 28 ppm (Figure 1, traces a and b). Steam-treatment of PBI at  $149^\circ\text{C}$  enhances these effects.

Interestingly, however, when treating the sample with steam at  $316^\circ\text{C}$  for a prolonged time, the  $^{13}\text{C}$  CP/MAS spectrum resumes its original appearance. Most probably, at this higher temperature, the equilibrium dominating the water content within the polymer matrix allows only a smaller amount of incorporated water, making spectrum (d) resemble trace (a) in Figure 2.

Most importantly, the  $^{13}\text{C}$  CP/MAS spectra in Figure 1 do not indicate any chemical changes of the PBI on a molecular level. In particular, no carboxylic acid carbon signal in the region from 160 to 180 ppm, which would be expected in case the imidazole ring is hydrolyzed, can be detected. The digitizer with a high resolution of 16-bit used for recording the spectra and the sensitivity of the  $^{13}\text{C}$  measurement would in principle allow the detection of isolated signals on the 0.1% intensity level.

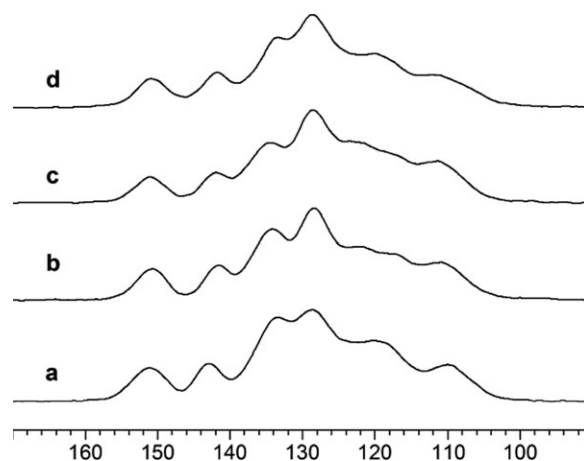
The assertion that there is no chemical transformation of PBI is further corroborated by the fact that the spectral changes visible after water- or steam-treatment at higher temperatures are fully reversible. Supporting Information Figure S2 shows from the bottom to the top the expansion of the  $^{13}\text{C}$  CP/MAS spectra for

the full cycle of original, water-treated, and redried material. The bottom and top trace are practically identical, and therefore we conclude that the water uptake of PBI under the conditions applied here is fully reversible.

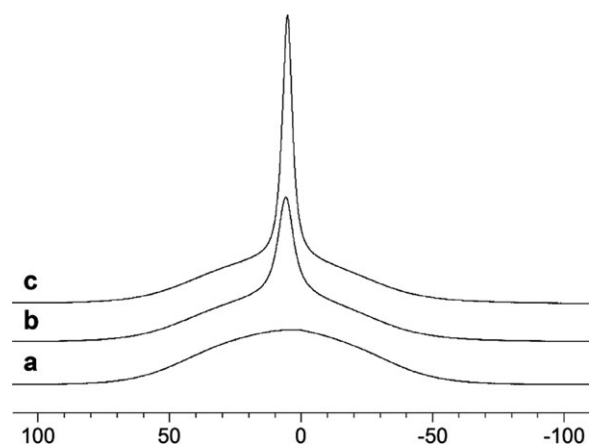
We interpret the reversible change of the aryl signal region in the spectra displayed in Figures 1, 2, S1 and S2 as conformational changes that can be the result of rotational reorientation of the aromatic ring segments. This effect can be quite large, as it has been shown earlier by Tonelli and Gomez<sup>22</sup> in the case of cyclic phenyl sulfides. Typical overall spreads of phenyl  $^{13}\text{C}$  signals of 8 and 18 ppm have been found. For PBI, the maximal chemical shift change, assuming, for example, that one resonance migrates from 134 to 124 ppm (Figures 1, 2 and S2) would result in a signal spread of about 10 ppm, which is well within the described scenario.<sup>22</sup>

The water plays a crucial role in these conformational changes, because PBI, heated to  $300^\circ\text{C}$  for 72 h under a dry nitrogen atmosphere to exclude water, results in a  $^{13}\text{C}$  CP/MAS spectrum that looks practically identical to the one of the original PBI sample.

**$^1\text{H}$  Wideline NMR Spectroscopy.** The  $^1\text{H}$  solid-state NMR spectroscopy of polycrystalline powders or polymers without MAS (wideline spectroscopy) is a very useful tool to study species with different mobilities.<sup>3,12–15</sup> Mobile species typically result in comparatively narrow  $^1\text{H}$  wideline signals while protons bound to a rigid backbone yield signals with up to 100 kHz halfwidth.<sup>3</sup> In the case of rigorously dried PBI, only the protons of the polymer backbone are present, which result in the broad signal with a halfwidth of about 27.4 kHz shown in Figure 3a (see also Table I below). When PBI is steam-treated at  $149^\circ\text{C}$ , a maximal amount of water is incorporated into the polymer network. Because of the mobility of the water molecules in the polymer, a comparatively narrow signal with a halfwidth of about 2.6 kHz is found on top of the polymer backbone signal (Figure 3c, Table I). When this sample is



**Figure 2.** Expansion of the aryl signal region of the  $^{13}\text{C}$  CP/MAS NMR spectra of (a) PBI ( $\nu_{\text{rot}} = 10$  kHz), (b) PBI exposed to water at RT (10 kHz), (c) PBI steam-treated at  $149^\circ\text{C}$  for 48 h (10 kHz), and (d) PBI steam-treated at  $316^\circ\text{C}$  for 72 h (13 kHz).



**Figure 3.**  $^1\text{H}$  wideline NMR spectra of (a) PBI that has been rigorously dried at  $100^\circ\text{C}$  *in vacuo* for 24 h, (b) PBI that has been steam-treated at  $149^\circ\text{C}$  for 48 h, and then left exposed to the atmosphere for 2 months, and (c) PBI measured immediately after steam-treatment at  $149^\circ\text{C}$  for 48 h.

exposed to the atmosphere for 2 months, it loses some of the water and the narrow signal shrinks again (Figure 3b).

The amount of incorporated water after 2 months is about the same as the amount of water found in the polymer after treating the PBI with water at RT for a prolonged period (Figure 4a). This indicates that PBI takes up an equilibrium amount of water at a given temperature and does not eventually dissolve or decompose, in accordance with the findings described above using  $^{13}\text{C}$  CP/MAS. After steam-treatment at  $316^\circ\text{C}$  for a prolonged time (Figure 4c), a smaller amount of water is incorporated into the PBI than at  $149^\circ\text{C}$  (Figure 4b), which is again in correspondence with the  $^{13}\text{C}$  CP/MAS results described above. Therefore, we conclude that the changes visible in the carbon spectra are connected to the water content of the polymer, which is in turn determined by the water uptake equilibrium at a given temperature.

The  $^1\text{H}$  wideline NMR spectra of all polymer samples investigated in this contribution have been subjected to a deconvolution to quantify the halfwidths. One example of a simulated spectrum is shown in Figure 4d, on top of the experimental spectrum (Figure 4c). Table I summarizes all obtained  $^1\text{H}$  wideline NMR data, also for the pure PEKK and the PEKK-PBI blend samples (see below). Although the large linewidths of the polymer backbone signals and the ensuing loss of signal intensity due to the probehead deadtime of  $5.6\ \mu\text{s}$  do not allow a precise quantitative analysis, a useful relative estimate of the amount of water incorporated in the polymers can be obtained. The integrals of the individual signals after deconvolution are given as % contributions to the overall intensity of the overlapping two signals (Table I). The highest amount of incorporated water, 34%, is found when PBI is exposed to it at room temperature. At the higher temperature of  $149^\circ\text{C}$ , which is already nearly  $50^\circ\text{C}$  above the boiling point of water, a slightly smaller amount of 30% is found, and this amount is further diminished to 25% after letting the sample dry in the air for 2 months. The steam-treatment at  $316^\circ\text{C}$  leads to half the amount of incorporated water as compared to the same treatment at  $149^\circ\text{C}$ .

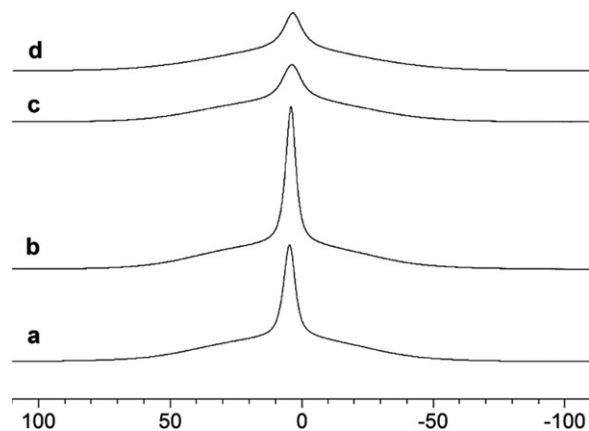
**IR Spectroscopy.** The IR spectra of PBI corroborate the NMR spectroscopic results described above. When the spectra of dry PBI and PBI steam-treated at 149 and  $316^\circ\text{C}$  are compared (Figure 5), the most obvious changes are visible in the region of the OH stretching bands from  $3060$  to  $3400\ \text{cm}^{-1}$ .<sup>9,16</sup> Within this selection of specimen, in accordance with the  $^1\text{H}$  wideline NMR results, the largest amount of incorporated water is found for the sample that has been steam-treated at  $149^\circ\text{C}$ . At  $316^\circ\text{C}$ , the broad absorption in the OH stretching band region<sup>9,16</sup> is slightly smaller.

Other changes in the IR spectra of Figure 5 are visible for the absorptions between  $1531$  and  $1625\ \text{cm}^{-1}$ . This region corresponds to the aryl  $\text{C}=\text{C}$  stretching bands, and differences might again indicate a change in the conformation or crystallinity of

**Table I.**  $^1\text{H}$  Chemical Shifts  $\delta$ , Signal Halfwidths  $\nu_{1/2}$ , and Integrals of the Two Signals After Deconvolution of the Wideline NMR Spectra of the Respective Materials

Sample	$\delta$ (ppm)	$\nu_{1/2}$ (kHz)	Integral <sup>a</sup> (%)	$\delta$ (ppm)	$\nu_{1/2}$ (kHz)	Integral <sup>a</sup> (%)
<b>PBI<sup>b</sup></b>	c	c	c	5.4	27.4	100
PBI <sup>d</sup>	4.6	2.6	34	6.8	27.4	66
PBI $149^\circ\text{C}$	3.9	2.0	30	5.6	27.4	70
PBI $149^\circ\text{C}^e$	4.3	3.0	25	5.5	27.4	75
PBI $316^\circ\text{C}$	3.4	3.3	15	4.4	27.4	85
<b>PEKK</b>	1.0	3.0	3	5.0	24.0	98
PEKK $149^\circ\text{C}$	c	c	c	3.2	24.4	100
PEKK $316^\circ\text{C}$	3.0	3.4	1	5.4	58.7	99
<b>PEKK-PBI<sup>b</sup></b>	c	c	c	4.7	23.2	100
PEKK-PBI <sup>d</sup>	3.5	5.0	13	3.5	23.2	87
PEKK-PBI $149^\circ\text{C}$	3.3	4.0	2	3.2	30.2	98
PEKK-PBI $316^\circ\text{C}$	3.3	3.0	1	3.0	38.0	99

<sup>a</sup>Intensity contribution to the overall intensity of the overlapping two signals, <sup>b</sup>Sample rigorously dried *in vacuo* at  $100^\circ\text{C}$  for 24 h and measured immediately, <sup>c</sup>No signal on top of the broad signal detectable, <sup>d</sup>Samples exposed to water at RT as described in Experimental section, <sup>e</sup>Same sample as in row above, after being exposed to the atmosphere for 2 months.



**Figure 4.**  $^1\text{H}$  wideline NMR spectra of (a) PBI after treatment with water at RT, (b) PBI after steam-treatment at  $149^\circ\text{C}$  for 48 h, (c) PBI after steam-treatment at  $316^\circ\text{C}$  for 72 h, and (d) simulation of the spectrum (c). The spectra are normalized to the height of the broad signal of the polymer protons.

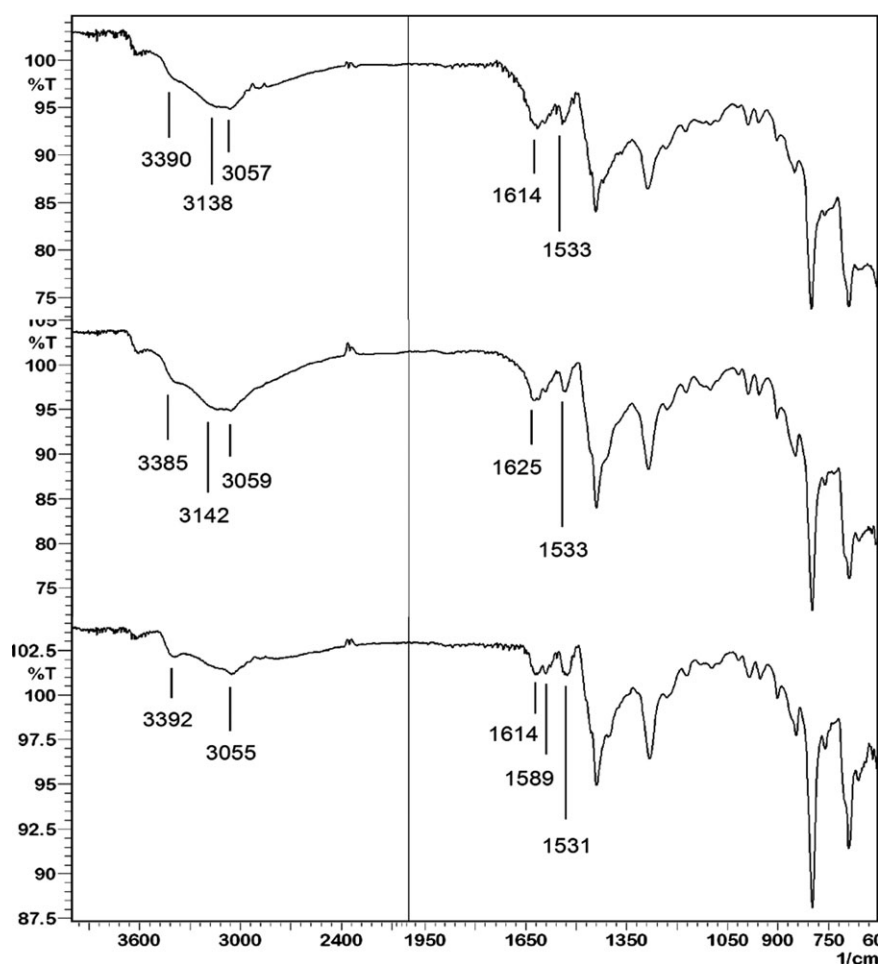
PBI upon steam-treatment, as visible in the  $^{13}\text{C}$  CP/MAS spectra. As the intensity of the band at  $1625\text{ cm}^{-1}$  correlates with the one of the OH absorption of water, it might be assigned to a water overtone band.<sup>16,17</sup> IR spectroscopy also corroborates

the results obtained by  $^{13}\text{C}$  and  $^1\text{H}$  solid-state NMR with respect to the reversibility of the effects of steam-treatment. As shown in Figure 6, top, the spectrum of the redried material displays an absorption band in the OH stretching frequency range that is reduced in intensity as compared to the one of the sample steam-treated at  $149^\circ\text{C}$  (Figure 6, bottom), and it resembles the IR spectrum of the pristine PBI shown in Figure 5.

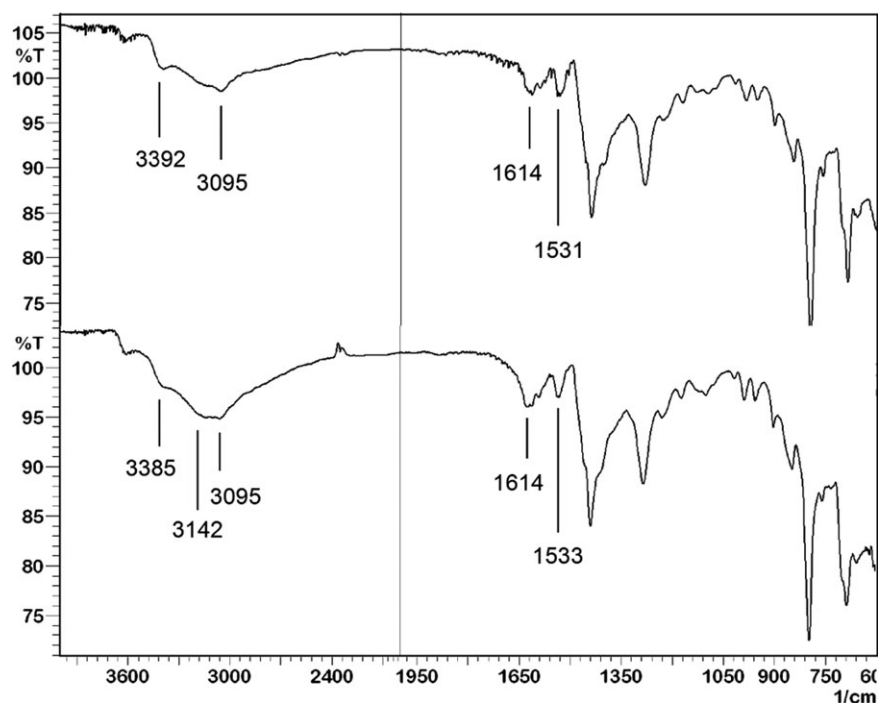
#### Steam-Treated PEKK

$^{13}\text{C}$  CP/MAS NMR. The  $^{13}\text{C}$  CP/MAS spectra shown in Figure 7 suggest that the signals of PEKK do not undergo detectable changes in chemical shift or linewidth that could be ascribed to interactions of the polymer with water at room temperature.

However, changes in the spectra do manifest themselves after steam-treatment of PEKK at  $149^\circ\text{C}$  (Figure 7c). All signals become broader, but especially in the region of the signals assigned to carbons labeled 3–7 some resonances also undergo changes in their chemical shifts. As in the case of PBI, the spectrum of the sample steam-treated at  $316^\circ\text{C}$  resembles more the one of the original material. According to the  $^1\text{H}$  wideline measurements, only a tiny amount of water is incorporated into the PEKK polymer, no matter how it was treated (Table I). As for PBI, no chemical changes of the polymer can be identified, so the different signal shapes must be solely based on



**Figure 5.** IR spectra of original PBI (bottom) and PBI after steam-treatment at  $149^\circ\text{C}$  for 48 h (middle) and  $316^\circ\text{C}$  for 72 h (top).



**Figure 6.** IR spectra of PBI after steam-treatment at 149°C for 48 h (bottom) and subsequent redrying *in vacuo* at 120°C (top).

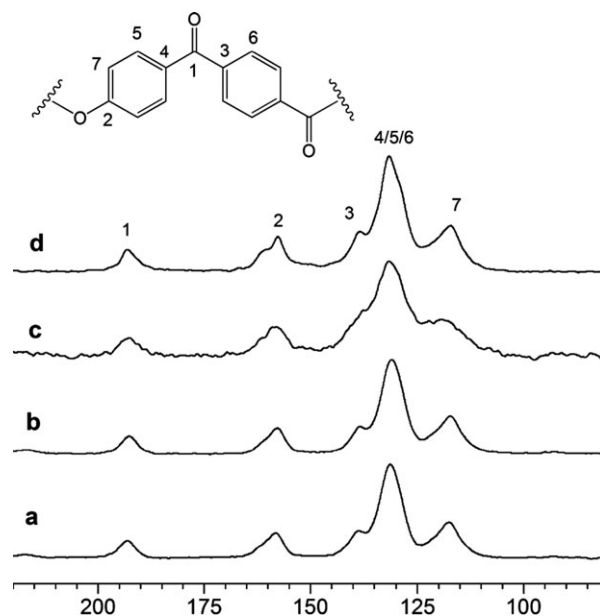
conformational or crystallinity changes. Analogous to the scenario described for PBI, the water plays a crucial role in these changes, because PEKK heated to 300°C for 72 h under a dry nitrogen atmosphere to exclude water results in a  $^{13}\text{C}$  CP/MAS spectrum that looks practically identical to the one of the original PEKK sample.

**IR Spectroscopy.** The  $^{13}\text{C}$  CP/MAS and  $^1\text{H}$  wideline NMR results described above indicate that water is not incorporated in large amounts into the PEKK polymer. This is confirmed by the IR spectra of the original and steam-treated samples. There is practically no change in the wavenumbers of the C=O stretching band at  $1651\text{ cm}^{-1}$ , which would indicate hydrogen bridges of the water with the oxygen of the carbonyl group, or in the aryl C—H absorption at  $3064\text{ cm}^{-1}$  (Supporting Information Figure S3). Therefore, the slight changes visible in the  $^{13}\text{C}$  CP/MAS spectra discussed above can only be due to changes in the conformation of sections of the polymer or the morphology of the samples upon steam-treatment.

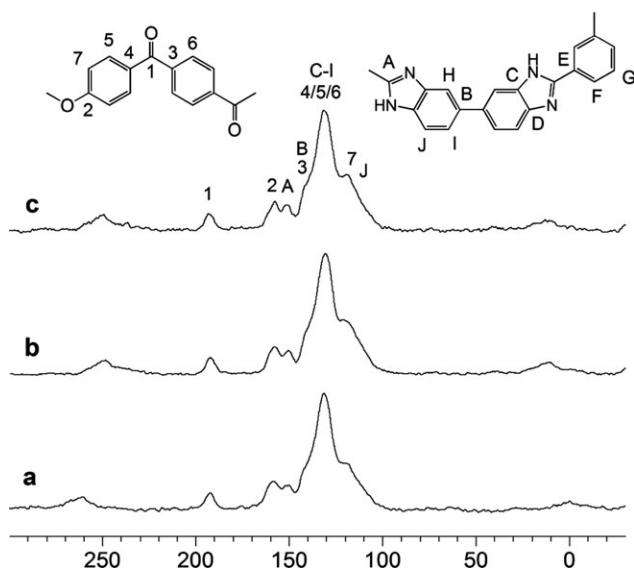
#### PEKK-PBI Blend

**$^{13}\text{C}$  CP/MAS NMR.** The change in the  $^{13}\text{C}$  CP/MAS spectra of the PEKK-PBI blend after steam-treatment follows the trend observed for the pure components PEKK and PBI. Again, the largest change is visible for the sample steam-treated at 149°C for 48 h (Figure 8). Comparing the spectra in Figure 8 with those of the pure PBI component (Figure 1) confirms that the changes are mostly due to the PBI signals at about 120 and 134 ppm. Overall, at higher temperatures, the PEKK component prevents water from being incorporated into the blend, whereas at room temperature, as expected, it is mostly the PBI part of the blend that interacts with the water.

**$^1\text{H}$  Wideline NMR Spectroscopy.** The  $^1\text{H}$  wideline NMR spectra confirm the assumption that water is incorporated into the PEKK-PBI blend (Figure 9), as there is a signal with smaller halfwidth sitting on top of the broad polymer backbone proton resonance (see also Table I above). As in the case of pure PBI, the amount of water is largest, when the sample is exposed to



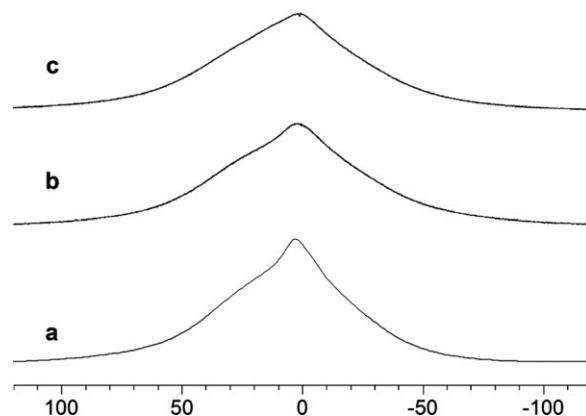
**Figure 7.**  $^{13}\text{C}$  CP/MAS NMR spectra of (a) original PEKK ( $\nu_{\text{rot}} = 10\text{ kHz}$ ), (b) PEKK treated with water at RT (10 kHz), (c) PEKK steam-treated at 149°C for 48 h (10 kHz), and (d) PEKK steam-treated at 316°C for 72 h (13 kHz).



**Figure 8.**  $^{13}\text{C}$  CP/MAS NMR spectra of (a) original PEKK-PBI blend ( $\nu_{\text{rot}} = 13$  kHz), (b) PEKK-PBI blend steam-treated at  $149^\circ\text{C}$  for 48 h (12 kHz), and (c) PEKK-PBI blend steam-treated at  $316^\circ\text{C}$  for 72 h (12 kHz). Peaks outside the region from 100 to 200 ppm are rotational sidebands.

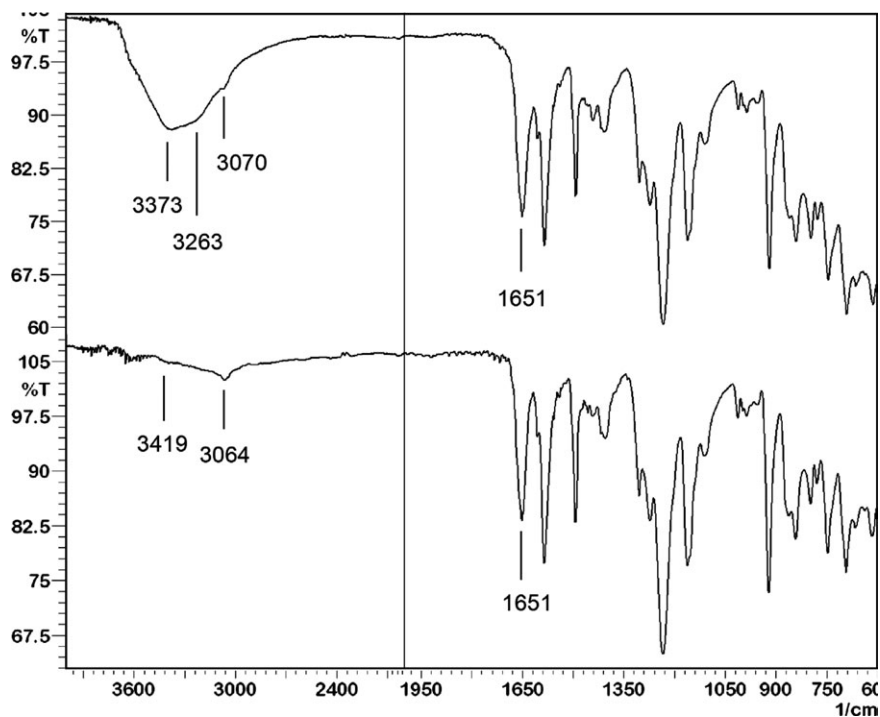
water at room temperature (Figure 9a). At higher temperatures, the water is not incorporated as readily, again following the trend for pure PBI. With the PEKK-PBI blend we find, as expected, a lower water content, as the PEKK component is less susceptible to water uptake than the pure PBI.<sup>10</sup>

**IR Spectroscopy.** The IR spectra of the PEKK-PBI blend shown in Figure 10 corroborate the findings obtained by the  $^1\text{H}$  wide-line spectra (Table I, Figure 9), namely that some water is incor-

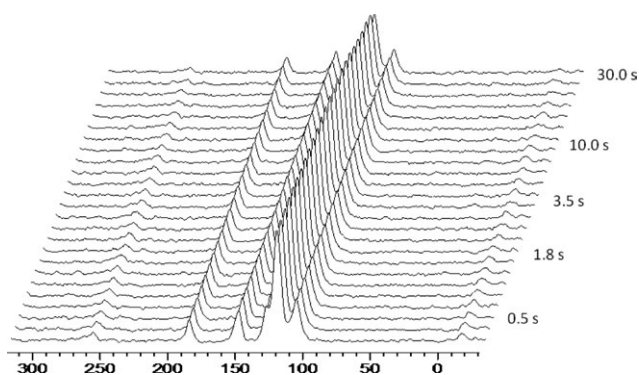


**Figure 9.**  $^1\text{H}$  wide-line NMR spectra of PEKK-PBI blend after (a) treatment with water at RT, (b) steam-treatment at  $149^\circ\text{C}$  for 48 h, and (c) steam-treatment at  $316^\circ\text{C}$  for 72 h.

porated into the polymer network at room temperature despite the presence of the PEKK component. Treatment of the PEKK-PBI blend with water at ambient temperature leads to a large  $\nu(\text{O—H})$  stretching band between  $3000$  and  $4000\text{ cm}^{-1}$ . The  $\nu(\text{C=O})$  band of the PEKK component remains unchanged at  $1651\text{ cm}^{-1}$ , excluding strong hydrogen bonding to incorporated water, which would result in a weakened  $\text{C=O}$  bond and therefore lower wavenumber. The IR spectra of the steam-treated samples (not shown) display much smaller  $\nu(\text{O—H})$  bands. It should be pointed out that there was no free water attached to the surface of any of the polymer samples. After the steam-treatment, all samples felt dry to the touch and did not have any wetness luster.



**Figure 10.** IR spectra of original PEKK-PBI blend (bottom) and after being exposed to water at RT for 48 h (top).

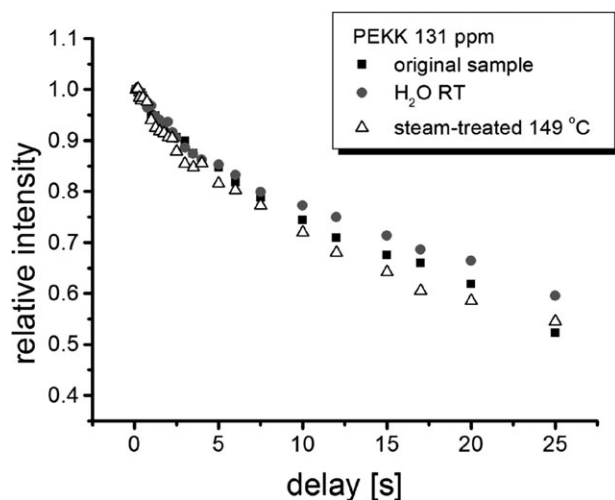


**Figure 11.** Decay of the  $^{13}\text{C}$  CP/MAS NMR signal intensities of PEKK with the indicated increasing delay times within the Torchia pulse sequence.<sup>6</sup> The most intensive signal at 131 ppm was used for the  $T_1$  characteristics determination in the following.

### $^{13}\text{C}$ $T_1$ Relaxation Time Measurements

A key element for characterizing polymers is the ratio between crystalline and amorphous domains in the material. This ratio is one of the most important factors influencing the mechanical properties and longevity of PAEK polymers.<sup>1</sup> The  $^{13}\text{C}$  CP/MAS NMR analysis can provide valuable insights with respect to the mobility of these different domains.<sup>2</sup> Crystalline sections of a polymer are always rigid in nature, and this is also the case for amorphous domains adjacent to the crystalline domains. This region is often called the crystalline interphase. However, the major part of amorphous regions consists of a nonrigid phase that is rather mobile even in the solid state. These nonmobile and mobile domains can be distinguished and quantified by  $^{13}\text{C}$  solid-state NMR spectroscopy via the different relaxation times  $T_1$  of the nuclei.<sup>2–4,8,9</sup> Typically, nonmobile, such as crystalline domains, feature much longer relaxation times than mobile domains.<sup>2–4,8,9</sup>

$T_1$  relaxation times can be obtained by a measurement method developed by Torchia.<sup>6</sup> Figure S4 shows the applied pulse sequence, which is based on the conventional CP pulse



**Figure 12.**  $^{13}\text{C}$   $T_1$  relaxation time characteristics of PEKK samples, treated as indicated and described in the Experimental section.

**Table II.**  $^{13}\text{C}$   $T_1$  Relaxation Times of the Mobile Domain A and the Rigid Domain B of the Indicated Water-Containing and Dry Samples

Sample		A (%)	$T_1(\text{A})$ (s)	B (%)	$T_1(\text{B})$ (s)
PBI	Original	25	2.5	76	39.6
	H <sub>2</sub> O RT	6	3.0	91	41.2
	149°C <sup>a</sup>	b	b	99	53.7
PEKK	Original	19	4.0	79	81.8
	H <sub>2</sub> O RT	12	3.4	87	79.8
	149°C	14	3.1	86	52.1
PEKK-PBI Blend	Original	18	4.0	80	45.8
	H <sub>2</sub> O RT	12	3.3	88	79.3
	149°C	24	9.7	74	63.5
	316°C	11	2.8	87	70.0

<sup>a</sup>Best fit was found for a monoexponential decay, <sup>b</sup>No fast relaxing component could be identified. **A** and **B** are given in the percent amounts of the mobile and rigid domains after the curve fitting process.

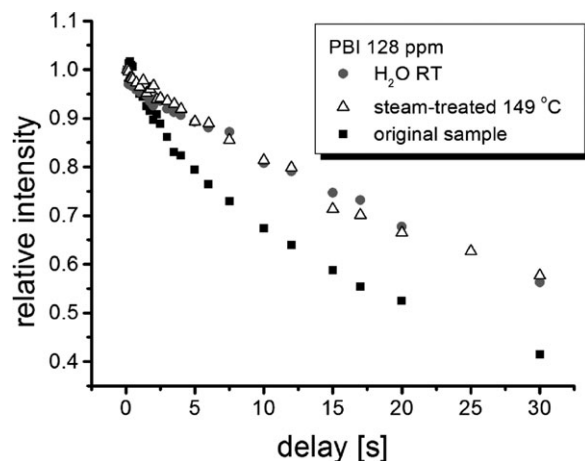
sequence.<sup>3–5</sup> In the Torchia sequence, a relaxation delay  $\tau$  is inserted and incremented between typically 100 ms and 30 s while the corresponding spectra are recorded. This process is illustrated for the PEKK sample in Figure 11. The longer the relaxation delay applied, the smaller the obtained signals are, because their corresponding nuclei have relaxed during  $\tau$ . The  $^{13}\text{C}$  signals with longer relaxation times persist over prolonged  $\tau$  times, whereas the signal intensities of nuclei with shorter relaxation times decrease more quickly. The obtained data have been checked carefully to ascertain that evaluating the height of the signals, the signal intensities, results in the same data as the integration over the areas of the signals, the signal integrals. In the following, we used the signal intensities.

Because of its large intensity, we chose the signal of the nonquaternary carbons at 131 ppm for analyzing the spectra in Figure 11 to obtain the  $T_1$  relaxation times. For this purpose, the relative signal intensities are plotted versus the applied relaxation delays for the various polymer samples (Figure 12). Then, assuming that the signal at 120.1 ppm stems from both mobile and rigid phases, a double-exponential fit<sup>6</sup> is used to determine the relaxation times of the rigid and mobile phases. From the curve fitting process, the short  $T_1$  time for the mobile amorphous domain and the percentages of mobile (**A**) versus nonmobile (**B**) phases can be obtained. Table II summarizes all data for the indicated polymer samples.

Interestingly, the  $T_1$  time for PEKK is longest, when it has been exposed to water at ambient temperature (Figure 12). The  $T_1$  time characteristics for PEKK steam-treated at 149°C are similar to those of the sample treated with water at room temperature. This means that with water uptake the polymer network becomes slightly more rigid in nature, as the rigid phase **B** increases to 87% (Table II).

The same phenomenon, but much more pronounced, is observed for the  $T_1$  characteristics of the resonance at 128 ppm of the PBI samples (Figure 13). The more water PBI incorporates, the longer the  $T_1$  relaxation times become, and the percentage of rigid domain **B** increases from 76 for the original

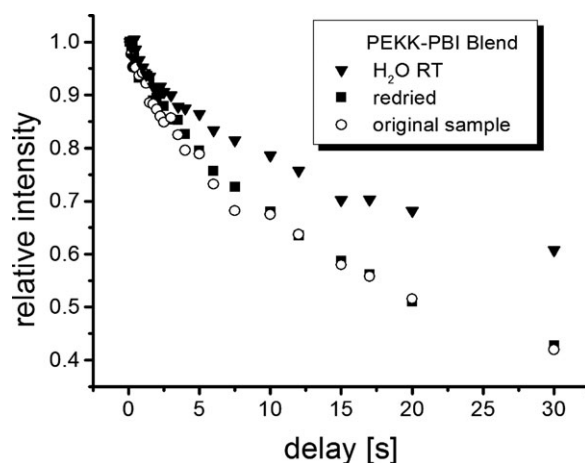




**Figure 13.**  $^{13}\text{C}$   $T_1$  relaxation time characteristics of the indicated PBI samples.

sample to 91% for the water-treated, and to 99% for the sample steam-treated at 149°C (Table II). In accordance with the previous  $^{13}\text{C}$  CP/MAS,  $^1\text{H}$  wideline NMR, and IR measurements there is only a small difference in the  $T_1$  characteristics between the material treated with water at ambient temperature and the steam-treated PBI (Figure 13). The original sample with significantly lower water content shows the fastest relaxation and is therefore most mobile. This effect might be due to the formation of hydrogen bridges between the imidazole nitrogen atoms and the water protons in the polymer network, which leads to an immobilization of the polymer chains and a more rigid structure. Although this might at first sight seem counterintuitive, the structure-giving effect due to the relatively strong hydrogen bridges in biological material such as proteins is well known. So, water could act as a binder, holding the polymer chains of PBI together and in this way reducing their mobility.

According to the expectation based on the measurements in the previous chapters, the  $T_1$  time characteristics of the PEKK-PBI blend show the reversibility of the water treatments (Figure 14). The original dry sample can be exposed to water at ambient



**Figure 14.**  $^{13}\text{C}$   $T_1$  relaxation time characteristics of the indicated PEKK-PBI blend samples obtained from the  $^{13}\text{C}$ -NMR signal at 128 ppm.

temperature over a prolonged time, and then redried *in vacuo*. The  $T_1$  time curve for the original sample is practically identical to the one of the redried sample while the signal intensities for the blends incorporating water are much higher, thus again indicating a more rigid polymer network.

For easy comparisons, Figure S5 summarizes all  $T_1$  time characteristics of the studied samples. All dry samples display faster  $^{13}\text{C}$   $T_1$  relaxation than water-containing polymers. Although for the dry samples the PBI component of the blend seems to dominate the  $T_1$  time characteristics, the water-treated blends resemble more the PEKK component. So, the  $T_1$  time characteristics of the PEKK-PBI blend do not contradict the general assumption that PEKK makes PBI more water resistant while PBI improves the stability of PEKK.

## CONCLUSIONS

Three materials, PEKK, PBI, and a PEKK-PBI blend (60% : 40%) have been exposed to water at room temperature and subjected to steam-treatment at 149°C and 316°C. Using  $^{13}\text{C}$  CP/MAS and  $^1\text{H}$  solid-state NMR as well as  $^{13}\text{C}$   $T_1$  relaxation time and IR measurements, it could be concluded that all polymers take up a maximal amount of water at ambient temperature or 149°C, whereas at 316°C, the equilibrium water content within the polymer network is lower. Most importantly, no chemical changes on a molecular basis have been detected. All changes appear to be reversible and due to changes in conformation of sections of the polymers, or the morphology of the materials. The presence of water is crucial for these changes, as samples heated in dry inert gas atmospheres result in  $^{13}\text{C}$  CP/MAS NMR spectra that are practically identical to the spectra of the original samples. For the PEKK-PBI blend, it has been demonstrated that less water is incorporated than potentially possible, based on the 40 wt % amount of PBI in the blend. Therefore, it is concluded that the PEKK component of the PEKK-PBI blend prevents the PBI component from excessive incorporation of water in the polymer network.

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