

CHARACTERIZATION OF PEEK (POLYARYLETHETHERKETONE) POLYMERS BY SOLID-STATE NMR SPECTROSCOPY

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BIOGRAPHICAL NOTE



Dr. Janet Blümel is a Professor in the Department of Chemistry at Texas A&M University in College Station.

Dr. Blümel obtained her Ph.D. in Chemistry at the Technical University (TU) of Munich in 1989, and then worked as a postdoctoral fellow in the Chemistry Department of the University of California, Berkeley. In 1991 she started her own research program as an Assistant Professor at TU Munich, which she continued as an Associate Professor at the University of Heidelberg from 1997 to 2007. Subsequently, she joined Texas A&M University as a Full Professor. Her main research interests are the characterization of materials by solid-state NMR spectroscopy, catalysis, and organometallic chemistry.

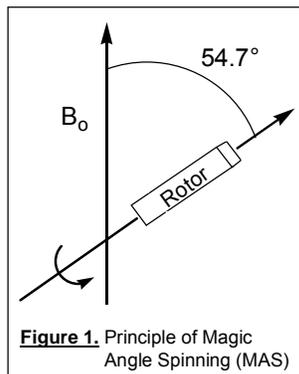
ABSTRACT

The family of poly(aryletherketone) or PAEK polymers are of great interest for extreme service environments in the oil and gas industry. These materials (PEEK's, PEK's, PEKEKK's etc) are often used in environments of high pressures and temperatures, while being exposed to steam, water based drilling fluids or brines, or other corrosive chemical cocktails that are highly acidic, oxidizing or caustic. The longevity of PAEK based devices or components used in such environments is of paramount importance from both a cost/benefit perspective, as well as a safety perspective when such materials are used in critical service devices. An understanding of the mechanisms of degradation and deleterious interaction with the chemical environment that these materials are exposed to is critical in developing more robust and longer lived polymer structures. To enable such understanding, molecular level chemical reaction mechanisms must be understood. NMR spectroscopy is a powerful technique that allows one to study polymers on a molecular level.

In this contribution, we will show that ^{13}C solid-state NMR spectra can be obtained routinely, and all signals can be assigned to the corresponding carbon atoms. Furthermore, contrasts between PAEK materials from different polymerization technologies and material providers can be observed in the NMR spectra, helping to fingerprint or verify specific compositions, stoichiometry and monomer isomerism. By measuring ^{13}C relaxation times, which probe the local segmental motion of monomer sequences in the solid state, it is possible to estimate the ratios between rigid and mobile, crystalline and amorphous domains. Solid-state NMR can also be applied to investigate polymer blends, and therefore the method supports the study of existing and design of new, improved blends of PAEK containing products. New methods development for structural and morphological characterization utilizing an array of NMR spectroscopy techniques is one of the many areas of research within the APPEAL Consortium today.

INTRODUCTION

PAEK (polyaryletherketone) polymers, and PEEK (polyetheretherketone) polymers [1] in particular are of growing importance for the oil and gas industry. They display many advantageous properties for their use under extreme service environments, such as high pressures and temperatures [1]. They have high melting points and glass transition temperatures, and are mechanically and chemically rather robust. In order to further improve the performance of PAEK polymers and prolong their lifetimes, a better understanding of their composition down to the molecular level is necessary. Hereby, their ratio of rigid versus amorphous, and crystalline versus mobile domains are key characteristics. Furthermore, their change before and after application on a molecular level needs to be investigated in order to gain more insight into decomposition processes under realistic conditions.



Solid-state NMR spectroscopy is a powerful analytical tool that allows a multitude of diverse measurements of crystalline and amorphous materials. Polymers represent the most prominent and the classic materials for solid-state NMR investigations [2]. The basic principle of a solid-state NMR measurement consists of packing a finely ground powder densely into a ZrO_2 rotor as the sample vessel. The rotor is placed into the strong magnetic field B_0 of the NMR spectrometer and tilted with respect to the direction of B_0 with the so-called Magic Angle of 54.7° (Figure 1). Then the rotor is spun around its axis with rotational speeds v_{rot} of up to 15 kHz for polymer applications. This Magic Angle Spinning (**MAS**) reduces anisotropic interactions that prevail in the solid state, and would, without the rotation, lead to very broad signals. Cross polarization (**CP**) of magnetization from the abundant protons in the sample to the measured nuclei improves the obtained signal to noise (S/N) ratio [3]. The most important nucleus for measurements of polymers is ^{13}C , and it will be used throughout this contribution.

RESULTS AND DISCUSSION

A. Structural differences between PAEK polymer types and sources on a molecular level

First, a selection of pure PEEK polymers has been studied by ^{13}C CP/MAS NMR spectroscopy. Figure 2 displays the spectrum obtained from Victrex 450P. All signals can be assigned unequivocally to the corresponding carbon positions in the structure, in accordance to the literature [4]. Two signal groups overlap, the signals of the carbons in the *ipso*- and *ortho*-positions of the keto group at 132.3 ppm, and the carbon resonances in the *ortho* positions to the ether functionality of the diether and of the ketoether benzene rings at 120.1 ppm.

In order to prove the signal assignments, a Dipolar Dephasing (DD) pulse sequence has been applied [5]. Hereby, a delay is inserted after the CP pulse, so that non-quaternary carbon signals are broadened and relax prior to the recording of the signal, which leads to their diminished signal intensities. In contrast to this, quaternary carbon signals, due to the absence of directly bound protons, are not prone to this signal intensity loss. The top spectrum in Figure 2 shows that the signals of all quaternary carbons at 193.0, 160.0, and 150.9 ppm retain their original signal intensities. The signal at 120.1 ppm is substantially diminished because it stems from non-quaternary carbons. With DD, the resonance at 132.3 ppm is about half its original intensity, in correspondence to its origin, being composed of the signals of one quaternary and one non-quaternary carbon site.

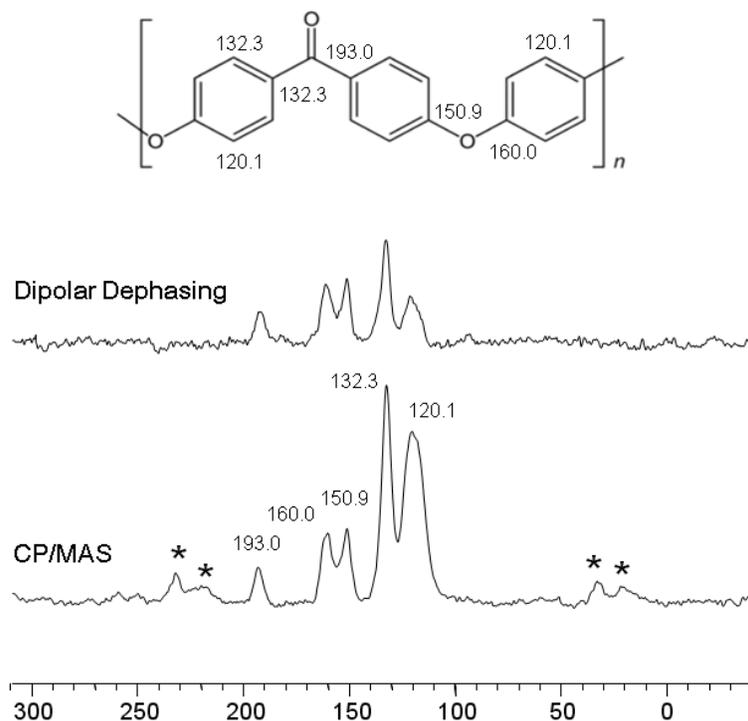


Figure 2. ^{13}C CP/MAS (bottom) and ^{13}C Dipolar Dephasing (top) NMR spectra of Victrex 450P. Rotational speed $v_{\text{rot}} = 10$ kHz. The asterisks denote rotational sidebands.

Next we investigated, whether differences would be visible in the ^{13}C CP/MAS spectra of various PEEK polymers from different vendors. As the ^{13}C CP/MAS spectra in Figure 3 show, subtle differences are clearly visible. Most striking are the signal intensity differences for the quaternary carbons at 160.0 and 150.9 ppm. Taking the above signal assignment into account, this indicates different amounts of ketoether versus etherether segments. The difference in appearance between the spectra of the PEEK brands listed in Figure 3 becomes even more striking, when the ^{13}C DD/MAS spectra are compared.

To sum up this paragraph, it is possible to obtain all ^{13}C signals of PEEK polymers with reasonable linewidths, and to assign all signals unequivocally. Different PEEK brands can be distinguished, and some impurities in the polymer can be identified. The extension of this technique of course is to a differentiation of the various ether / keto ratios that exist in commercial products. Furthermore, coupled with relaxational spectroscopic measurements, relative molecular motions of these differentiable species can be assessed. This becomes important in the interaction of the bulk polymer with small molecule diffusion and the accessibility of specific functional groups to reactive small molecule species (ie. diffusion into highly mobile, predominantly amorphous phases is obviously more favourable than into rigid, predominantly crystalline or highly ordered phases).

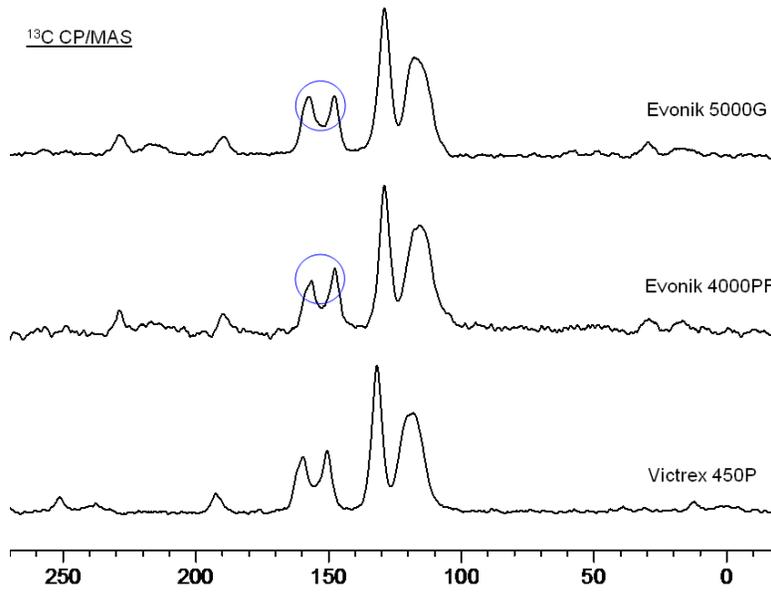
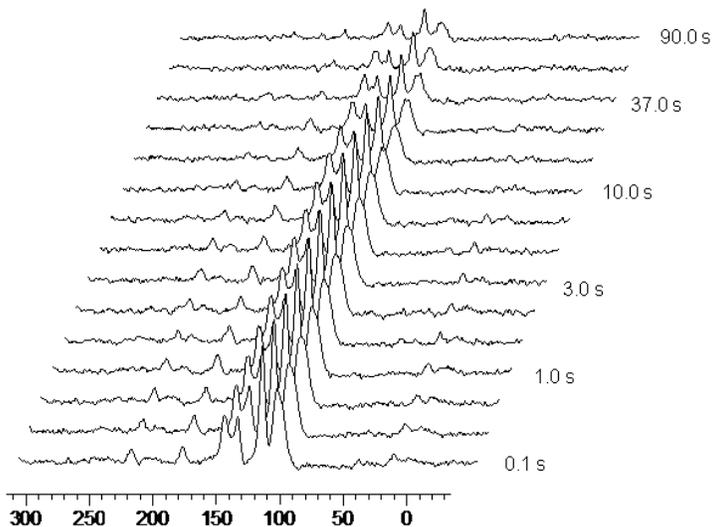


Figure 3. ^{13}C CP/MAS NMR spectra of different PEEK samples. Rotational speed $v_{\text{rot}} = 10$ kHz. Signals outside the region of 100 to 200 ppm are rotational sidebands.

B. Rigid and mobile domains of PEEK polymers

One key element in the characterization of polymers is the ratio between crystalline and amorphous domains in the material, as well as the dimensional scale of such domains in the bulk material. This ratio is one of the most important factors influencing the mechanical properties of PAEK polymers. The solid-state NMR analysis can provide valuable insights with respect to the mobility of these different domains. Crystalline sections of the polymers are always rigid in nature, as are amorphous domains in close proximity to the crystalline domains, in a region often referred to as the crystalline interphase. But the major part of the amorphous regions consists of a non-rigid phase that is rather mobile even in the solid state. The non-mobile and mobile domains can be distinguished and quantified by solid-state NMR spectroscopy via the different relaxation times T_1 of the ^{13}C nuclei. Typically, non-mobile, such as crystalline domains, feature much longer relaxation times than mobile domains.

Figure 4. Illustration of the decay of the ^{13}C CP/MAS NMR signal intensities of Victrex 450P with increasing relaxation delay times within the Torchia pulse sequence [6].



T_1 relaxation times can be obtained by a measurement method developed by Torchia [6]. Hereby, a relaxation delay within the CP pulse sequence is incremented between typically 100 ms and 100 s, while the corresponding spectra are recorded. This process is illustrated for the sample Victrex 450P in Figure 4. The longer the relaxation delay becomes, the more the nuclei are relaxed, and the smaller the obtained signals are. The signals of carbons with longer relaxation times persist over longer delay times, while the signal intensities of nuclei with shorter relaxation times deteriorate more quickly. We checked the obtained data carefully to make sure that evaluating the height of the signals, the signal intensities, leads to the same results as the integration over the areas of the signals, the signal integrals. For the following analyses we used the signal intensities.

Due to its large intensity, we chose the signal of the non-quaternary carbons at 120.1 ppm for analyzing the spectra in Figure 4 in order to obtain the T_1 relaxation times. For this purpose, the relative signal intensities are plotted versus the applied relaxation delays for the various PEEK samples (Figure 5). Then, assuming that the signal at 120.1 ppm stems from both mobile and rigid phases, a double-exponential fit [7] is used to determine the shorter relaxation time of the mobile phase. Hereby, the longest relaxation time for the purely crystalline and rigid domain had been determined to be 73 s. From the curve fitting process, the short T_1 time for the mobile amorphous domain, as well as the percentages of mobile (A) versus non-mobile (B) phases, can be obtained. Table 1 summarizes all data for the indicated PEEK samples.

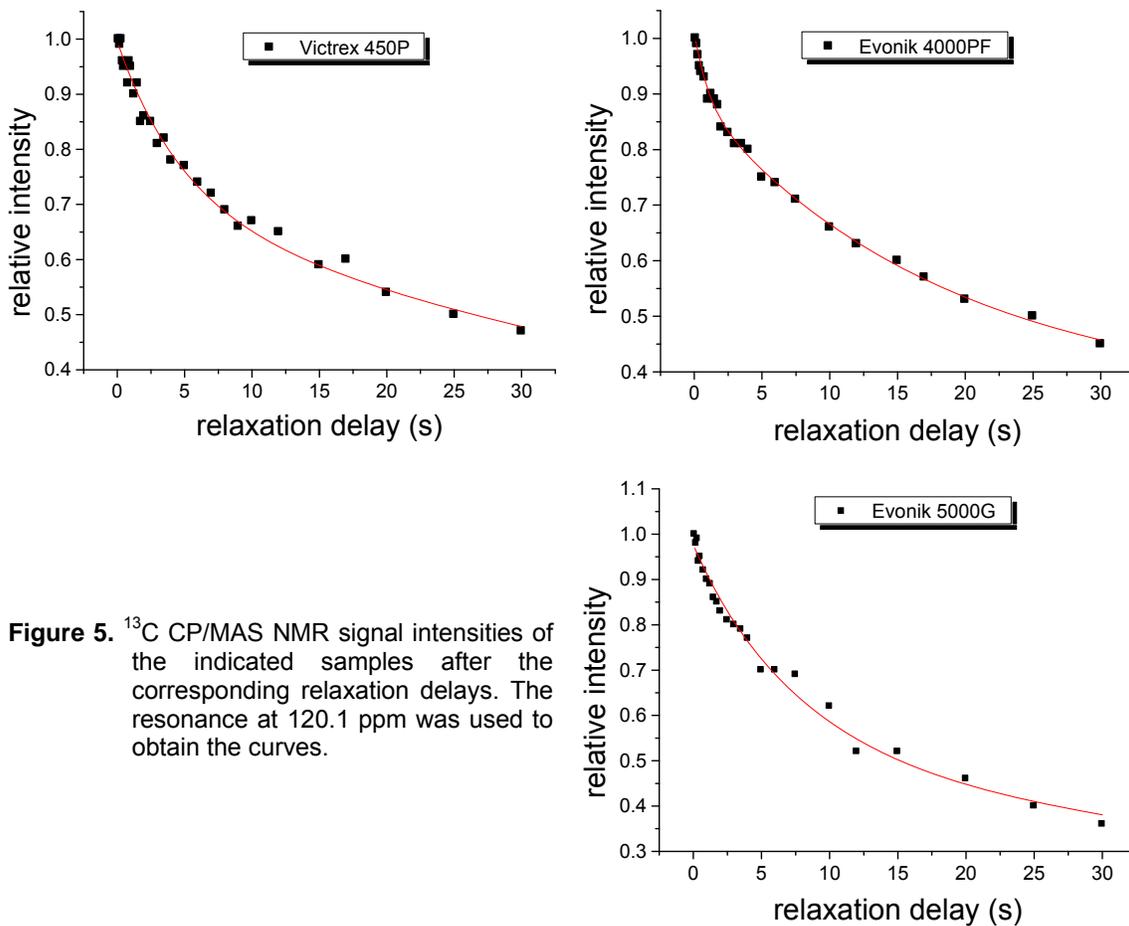


Figure 5. ^{13}C CP/MAS NMR signal intensities of the indicated samples after the corresponding relaxation delays. The resonance at 120.1 ppm was used to obtain the curves.

As Table 1 shows, the PEEK samples Victrex 450P and Evonik 4000PF are very similar. The T_1 times of the mobile region are in the same range from about 4.0 to 4.5 s, and the percent amount of amorphous domain is the same with 27% for both materials. The T_1 time is longer for the sample Evonik 5000G. The amount of mobile matter **A** is, with 41%, more than 10% larger as compared to the previous two samples. This difference is of interest in the context of structure/property model development, in that substantial differences in the melt processing characteristics and physical property attributes of the Evonik 4000PF and Evonik 5000G are noted in recent conference presentations and within substantial characterization work completed by the APPEAL Consortium group.

Table 1. ^{13}C T_1 relaxation times of the mobile domain **A** and the rigid domain **B** of the indicated samples. **A** and **B** are given in the percent amounts of the mobile and rigid domains after the curve fitting process with a goodness of fit r^2 .

Table 1 ^{13}C T_1 relaxation times					
Sample	A (%)	$T_1(\text{A})$ (s)	B (%)	$T_1(\text{B})$ (s)	r^2
Victrex 450P	27	4.02	72	73	0.989
Evonik 4000PF	27	4.54	71	73	0.987
Evonik 5000G	41	6.69	56	73	0.992

C. Examination of blend systems: A PAEK blend with polybenzimidazole (PBI)

There is interest and value in utilizing blends of other high temperature polymers with PAEK grades to achieve a more diverse range of property balance, or in some cases an economic benefit of lower material cost without substantial sacrifice of physical properties. Commercially, the combination of PEEK or PEKK with PBI, PEEK with PPS, and PEEK with polyphenylsulphone are available to those who desire the traits achieved in such systems. As above, the complexity of such systems is not well understood, including the creation of the mechanical blend and domain size distribution, the long term compatibility of the two polymer species as a thermodynamically stable blend, and the potential for changes in the chemistries of molecular association and reaction.

The utility of NMR spectroscopic techniques in examining blend systems is well documented in the literature, and has proven a valuable tool in probing such systems at both ambient and elevated temperatures. In the following, we investigate a PEKK blend with polybenzimidazole, PBI-PEKK. The initial interest in this blend system arises from the susceptibility of PBI to adsorption of moisture, and a desire to determine whether careful blending of PBI with a PAEK material would alter the equilibrium moisture uptake and the actual location of the chemical association of water on the polymer backbone. Understanding the chemistry of such processes might allow the determination of schemes to substantially reduce the impact of moisture induced degradation and physical property deterioration in this high temperature blend system. Data presented below is preliminary, but promising.

Figure 6 shows the ^{13}C CP/MAS spectra of the pure components, as well as the signal assignments for PEKK [8] and PBI [9], and their blend. There is more substantial overlapping of the signals than for the PEEK polymer discussed in the previous section, especially for PBI. Nevertheless, we could get interesting insights regarding the mobilities of the polymers and the blend via the T_1 relaxation times of the pure compounds.

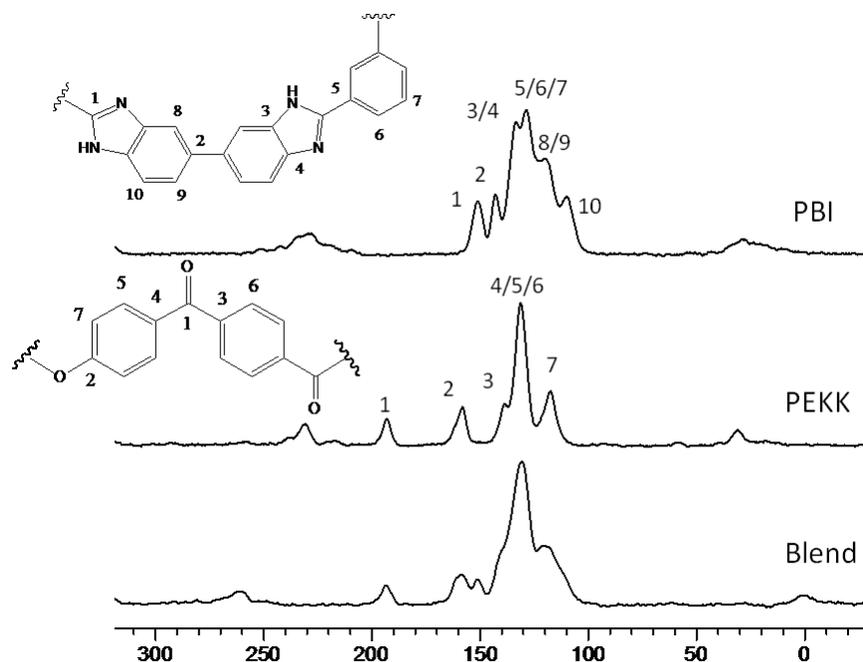


Figure 6. ^{13}C CP/MAS NMR spectra of the PBI blend (bottom, 13 kHz), neat PEKK (middle, $\nu_{\text{rot}} = 10$ kHz), and neat PBI (top, $\nu_{\text{rot}} = 10$ kHz). Signals outside the region from 100 to 200 ppm are rotational sidebands.

Figure 7 (left) shows the relative intensities of the ^{13}C CP/MAS signal at 130.0 ppm depending on the relaxation delay in the Torchia pulse sequence [6]. Three data sets have been obtained for the pure PEKK and PBI components, as well as the blend. Then, the samples were treated with an excess of water for a prolonged period of time, and three more curves have been sampled for these wet materials (Figure 7, left). After applying a double exponential fit [7] without further entry assumptions, the data with the smallest error have been obtained. The T_1 times of the mobile (A) and non-mobile (B) domains and their percent amounts are given in Table 2.

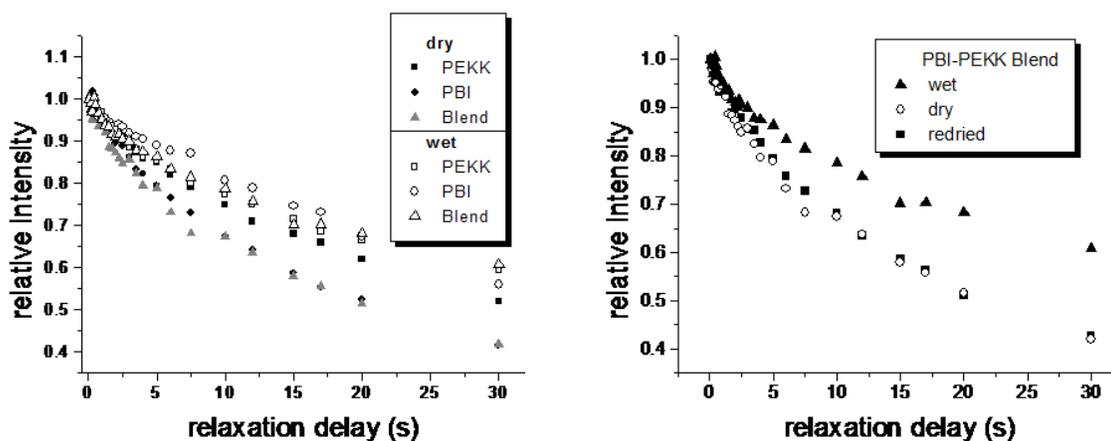


Figure 7. ^{13}C CP/MAS signal intensities depending on the relaxation delays for dry and wet PEKK, PBI, and their blend (left), and comparison of the signal intensities of dry, wet, and redried blend (right) depending on the relaxation delays.

Interestingly, for both, the PBI and PEKK sample, the corresponding ^{13}C relaxation times for the dry and wet samples are in similar ranges. However, both dry materials have a larger degree of mobility than the corresponding wet specimen. For example, for the PBI, which is known to swell substantially in water, the percent amount of mobile domain **A** decreases from 25% in the dry to 6% in the wet sample. At the same time, the rigid domain **B** grows from 76% to 91%. This suggests that rather than the water providing a plasticization effect in this system, we are in fact observing the opposite, suggesting that perhaps a strong associative bond system is being established with the bound water phase adsorbed into the polymer. We assume that the water in the polymer propagates hydrogen bonding between the chains, thus impeding their mobility. Although, due to the overlapping of the signals, the curves of the blend could not easily be fitted in the same way, from Figure 7 it is obvious that the ^{13}C T_1 times of the dry and wet PBI-PEKK blends follow the same trend.

Table 2. ^{13}C T_1 relaxation times of the mobile domain **A** and the rigid domain **B** of the indicated wet and dry samples. **A** and **B** are given in the percent amounts of the mobile and rigid domains after the curve fitting process with a goodness of fit r^2 .

Table 2		^{13}C T_1 relaxation times				
Sample		A (%)	$T_1(\text{A})$ (s)	B (%)	$T_1(\text{B})$ (s)	r^2
PBI	dry	25	2.50	76	39.6	0.988
	wet	6	2.98	91	41.2	0.975
PEKK	dry	19	3.96	79	81.8	0.984
	wet	12	3.39	87	79.8	0.981

Finally, we investigated, whether the water uptake might lead to some decomposition of the PBI polymer, which could, in principle, be responsible for the polymers becoming more rigid. For this purpose, we dried a PBI-PEKK blend sample again, which had been exposed to water for a prolonged period of time. As it can be seen in the graphic of Figure 7 on the right side, the wet sample shows a shorter ^{13}C T_1 relaxation time as compared to the original sample, but the re-dried material yields a T_1 curve that is practically identical to the one of the dry starting material. Therefore, we conclude that the processes leading to an increased rigid domain of the polymer samples upon treatment with water are entirely reversible. This supports the notion of few if any chemical transformations on a molecular level and corroborates our assumption of the "stiffening" of the polymer chains by hydrogen bonding.

CONCLUSIONS

The long-term goal of our work is to enable the polymer community through solid-state NMR spectroscopy and targeted synthetic approaches to characterize, improve, and tailor their polymers according to the specific needs. Existing problems with the materials will be analyzed in order to enhance the understanding of the polymer properties and their possible application ranges. The chemistry and engineering community should profit from a better understanding of the polymer structures, mobilities, and changes thereof upon exposure to water or other solvents, and from elucidation of specific molecular level interactions and degradation mechanisms.

EXPERIMENTAL SECTION

The solid-state NMR spectra were measured on a *Bruker* AVANCE 400 spectrometer operating at 100.6 MHz for ^{13}C . The ^{13}C CP/MAS (Cross Polarization with Magic Angle Spinning) experiments were carried out at MAS rates of 13, 12, and 10 kHz using densely packed powders of the polymers in 4 mm ZrO_2 rotors. The ^1H $\pi/2$ 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 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 FIDs were accumulated. The dipolar dephasing delay for the spectra discussed was 40 μs . The ^{13}C T_1 relaxation times were obtained by the method reported by Torchia [6]. Typically 30 increments with 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 program TableCurve 2D 4.0. Hereby, as a first step, the T_1 relaxation time of the non-mobile domain was determined to be 73 s from measurements with relaxation delays of up to 90 s. Then, in order to fit the relaxation curves presented here the long relaxation time was held constant at 73 s. No entry assumptions regarding the T_1 times of the rigid domains were made for the PEKK, PBI, and PBI-PEKK blend samples. The wet PBI-PEKK blend was prepared by exposing the dry material to water for 24 hours. The re-drying procedure consisted of removing the water at 120°C under vacuum for 3 days.

ACKNOWLEDGEMENTS

This material is based upon work supported by The Welch Foundation (A-1706), the National Science Foundation (CHE-0911207 and CHE-0840464), and the industrial APPEAL Consortium.

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