# NMR Study of Water Bound to Soft Segments in Thermoplastic Elastomers

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**Summary:** The interaction between water absorbed in four hard-soft segment block-copolymers and the polymer chains is investigated by pulsed field gradient echo NMR spectroscopy and Nuclear Overhauser NMR spectroscopy. The results show, depending on the structure and mass fraction of the soft segments, a strong interaction between water and the soft segments. Most likely this is due to a hydrogen bond between water and the ether groups. The self-diffusion of water has been determined and is described as a jumping process between the ether sites with a residence time $\tau$ and a time between sites t. It is found that the residence time is of the order of a few ns and also that the ratio $t/\tau$ decreases with increasing soft segment rigidity.

**Keywords:** NMR; self-diffusion; swelling; thermoplastic elastomers; water

## Introduction

Recently the self-diffusion of water in some hard-soft segment copolymer systems has been investigated by pulsed field gradient echo NMR spectroscopy[1]. From these experiments it was found that, depending on the chemical composition of the soft segment, the water molecules can interact with the polymer chains in the soft segment for such a long time that a magnetization exchange (cross-relaxation) between the water proton spins and the polymer proton spins can occur. It appeared that pulsed field gradient echo NMR technique is a very sensitive method to detect such a magnetization exchange, because it leads to an apparent increase of the polymer self-diffusion rate and a decrease of the apparent water self-diffusion coefficient. Because magnetization transfer by cross-relaxation between water and polymer protons is caused by the relatively weak magnetic dipolar interaction between the two spins involved, the observation of such a transfer implies that the water molecules stay near enough the polymer chains for a long enough time to have the magnetic dipole-dipole induced magnetization transfer to happen.

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Similar water-macromolecule interactions have been observed for proteins, using NOESY NMR spectroscopy and this has lead to the notion of hydration water of proteins[2].

In this paper we want to discuss in somewhat more detail than in the first paper[1] the conclusions from our experiments with regard to the interaction between the water molecules and the polymer.

## The investigated copolymers

The absorption and the self-diffusion of water in four hard/soft-segment block copolymers has been investigated. The hard segment of the copolymers always consists of the polyester poly-(butylene terephthalate) (PBT), the soft segment can be the triblock copolymer poly (ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO), poly(tetramethylene oxide) (PTMO) or poly(ethylene oxide) (PEO) (Figure 1) The samples were obtained from DSM, Geleen (the Netherlands) and are designated as follows: PBT-(PEO-PPO-PEO) 2200/25 (short notation PBT-PPP-25), PBT-(PEO-PPO-PEO) 2200/55 (PBT-PPP-55), PBT-PTMO 2000/60 (PBT-PTMO) and PBT-PEO 4000/66 (PBT-PEO). Here the numbers x/y behind the polymer notation mean: x = molar mass in g/mol of the soft segment and y = mass fraction of the soft segment in percent.

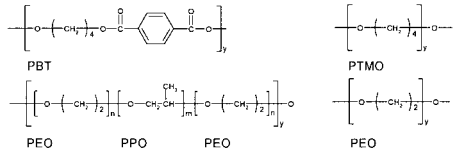



Figure 1. The chemical structure of the hard segments PBT and the soft segments PTMO, PEO-PPO-PEO and PEO.

It is known that the PBT segments form crystalline domains which act as cross-links in the network of the soft segments. The soft segments have a much higher degree of motional freedom than the hard crystalline segments[3].

These samples were swollen with water in exsiccators containing saturated salt solutions, which maintain in the exsiccator a constant relative humidity (rh). The samples were therefore exposed

to a constant water vapour pressure for a time long enough (at least three weeks) to obtain equilibrium. In this way 24 samples were prepared at a relative humidity ranging from 32% to 100%.

## Experimental

The pulsed field gradient echo NMR (PFGE NMR) experiments were performed with a Bruker Avance 400 MHz NMR spectrometer, supplied with a B-AFBA-40 gradient unit and corresponding probe head.

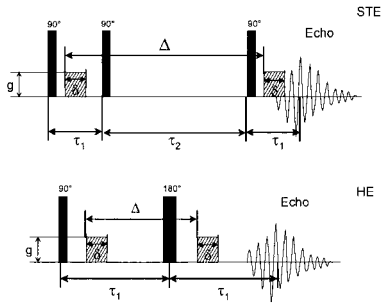



Figure 2. The pulse sequences for a pulsed field gradient echo diffusion experiment with a two-pulse (Hahn echo) or a three-pulse echo (stimulated echo).

In the PFGE experiment both a Hahn spin echo sequence ($90^0$-$\tau_1$-$180^o$-$\tau_1$-echo) and a stimulated spin echo pulse sequence ($90^0$-$\tau_1$-$90^o$-$\tau_2$-$90^o$-$\tau_1$-echo) were used with gradient pulses of duration $\delta$ and strength g applied during both $\tau_1$ times (see Figure 2). The time between the gradient pulses, the diffusion time $\Delta$, was set to 15 ms and the gradient pulse length $\delta$= 2 ms. In a typical experiment the gradient strength $g$ is varied between 0 and 8 T/m. For free diffusion of the molecules containing the observed spins the echo intensity as a function of the gradient strength $g$ is given by[4]:

$$I(g) = I(0)\exp\left[-\gamma^2\delta^2 g^2 D(\Delta - \tfrac{1}{3}\delta)\right] \qquad (1)$$

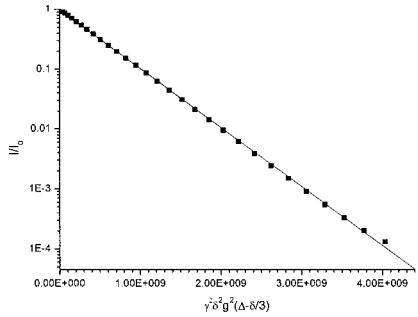



Figure 3. The proton stimulated echo intensity $\ln(I/I_0)$ as a function of the gradient intensity $\gamma^2\delta^2 g^2\left(\Delta - \frac{1}{3}\delta\right)$ for pure water at 298 K.

Figure 3 shows, as an example, the proton stimulated echo intensity of pure water as a function of $\gamma^2\delta^2 g^2(\Delta - \frac{1}{3}\delta)$. From the slope of the straight line the self-diffusion coefficient of pure water at 298 K is determined to be 2.28 x $10^{-9}$m$^2$/s, showing that the gradient strength versus current diagram, supplied with the gradient probe head, is accurate.

The phase-sensitive two-dimensional exchange experiment (NOESY) is described in the literature[5]; the mixing time varied, depending on the material, between 100 and 800 ms.

## The absorption of water

The amount of absorbed water as a function of the relative humidity rh is determined gravimetrically, as shown in fig. 4.

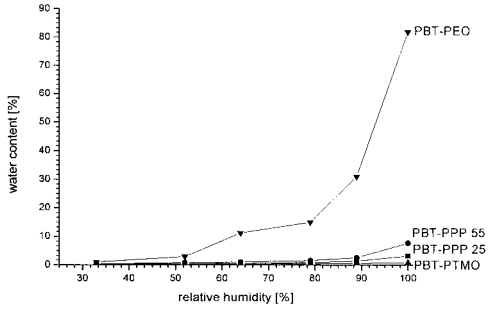



Figure 4. The amount of water absorbed by the four polymer systems as a function of the relative humidity to which the samples were exposed.

These diagrams show that the higher the fraction PEO in the polymer the higher the amount of absorbed water. Also the amount increases more or less exponentially with increasing rh, at least for PBT-PEO and PBT-PPP 55.

## Results from pulsed field gradient echo spectroscopy

The main results from the PFGE experiments[1] can be summarized with a few figures.

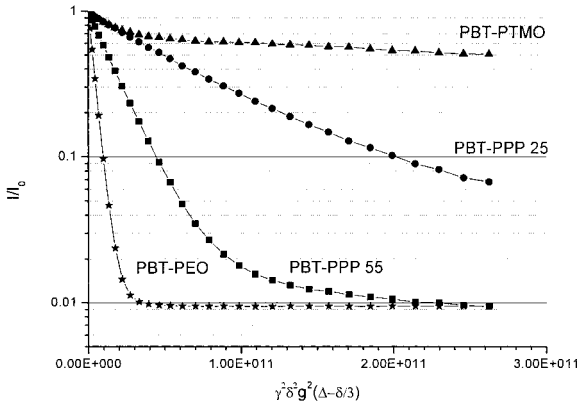



Figure 5. The stimulated echo diffusion curves for all four investigated copolymers treated at a relative humidity of 100%; the intensities represent the integrated intensity of the water NMR signal and of rotationally mobile soft segment polymer protons. The diffusion time Δ=15 ms, δ=2 ms and g is varied between 0 and 8 T/m.

Figure 5 shows the diffusion curves ln [I(g)/I(0)] as a function of $\gamma^2\delta^2 g^2(\Delta - \delta/3)$, resulting from the stimulated echo pulse sequence of fig. 2, for all samples treated at a relative humidity of 100%. In the NMR spectrum only signals from water and mobile parts of the polymer appear, the signals from the rigid parts of the polymer are too broad to be detected in this experiment. Even then the spectral resolution is so low that the points in fig. 5 represent the integrated intensity of the water and the mobile polymer protons.

Under these circumstances one would expect to find a diffusion curve with two slopes, one corresponding to the self-diffusion coefficient $D_W$ of water and the other representing the spatial diffusion coefficient $D_P$ of the polymer soft segments. $D_P$ for polymer chains in a crystalline network should not be larger than $10^{-15}$ $m^2/s$, which means that on the scale of our experiments the diffusion curve corresponding to the polymer protons in fig. 5 should be horizontal. It is clear

that this is the case only for the PBT-PEO sample. For two of the other three samples (PBT-PTMO and PBT-PPP 55) two slopes are recognizable, but the slope of the slow decaying part clearly is far too large for the translationally rather immobile soft segments in the crystalline polymer network. For PBT-PPP 55, for instance, it is found that the self-diffusion coefficient $D_P$ corresponding to the slow decaying part of the diffusion curve in fig. 5 equals 2.7 x $10^{-12}$ $m^2/s$, which, with the Einstein-Smoluchowsky relation:

$$\left\langle r^2 \right\rangle = 6D_p\Delta, \tag{2}$$

can be translated into an apparent root mean square displacement of 0.49 μm during the diffusion time of Δ=15 ms. It seems impossible that the soft segment chains would translate over such a large distance in such a short time.

For PBT-PPP 25, the two slopes practically can not be distinguished.

The reason for all this becomes clear when the stimulated echo diffusion curves (STE) are compared to the curves obtained with the Hahn echo sequence (HE) in fig. 6.

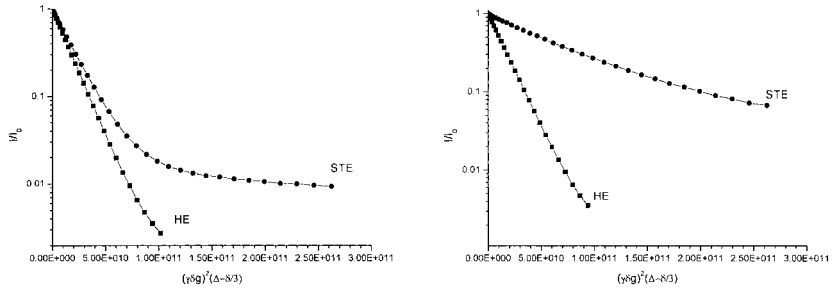



Figure 6. A comparison between the diffusion curves obtained by the Hahn echo sequence (HE) and the stimulated echo sequence (STE) for PBT-PPP 55 (left) and PBT-PPP 25 (right), both treated at a relative humidity of 100%. For all echo experiments Δ=15 ms.

A direct comparison between the STE and HE curves is somewhat complicated by the fact that for an equal diffusion time Δ in both experiments, $\tau_1$ for the Hahn echo has to be longer than for the stimulated echo sequence (see fig. 2) and therefore, due to the shorter polymer proton $T_2$, in the Hahn echo diffusion curve the contribution of the polymer protons has practically

disappeared. Nevertheless, the comparison between both curves shows that with the Hahn echo the water self-diffusion coefficient is much higher than the apparent diffusion coefficient determined from the stimulated echo. The reason for this, as extensively discussed in our previous paper[1], is that a significant fraction of the water molecules resides long enough and near enough to polymer protons that via cross-relaxation an exchange of magnetization occurs between the two types of protons. Such a process can affect only the stimulated echo diffusion experiments and not the diffusion curves obtained via the Hahn echo, while in the latter case the magnetization is always perpendicular to the external magnetic field and cross-relaxation can not occur. The cross-relaxation in the stimulated echo experiment causes that the apparent diffusion coefficient of water is lowered by the magnetization exchange with the, on this scale, immobile polymer protons and the measured diffusion coefficient of the polymer protons is enhanced by the exchange with the mobile water molecules. That means that the water self-diffusion coefficient determined from the STE experiments is not correct for the cases that cross-relaxation effects take place. The Hahn echo experiments yield the correct self-diffusion coefficient (Table 1).

Table 1. The water self-diffusion coefficient, determined by the Hahn echo sequence, of water absorbed in the three copolymers, subjected to a relative humidity of 100%.

| Sample | Self-diffusion coefficient of water in samples subjected to 100% rel. humidity, in $m^2/s$ |
|---|---|
| PBT-PPP 25 | $6.6 \times 10^{-11}$ |
| PBT-PPP 55 | $6.7 \times 10^{-11}$ |
| PBT-PEO | $2.5 \times 10^{-10}$ |

Comparing the STE diffusion curves for the four samples in fig. 5 immediately makes clear that the cross-relaxation effect is almost absent for the PPP-PEO system, very strong for the PBT-PPP 25 system and intermediate for the PBT-PPP 55 and PBT-PTMO systems.

## NOESY experiments

The cross-relaxation effects can also be observed by two-dimensional NOE experiments, which is the technique used to detect the hydration water of proteins[2]. The NOE spectra of the three samples, each with two different mixing times, are shown in the figs. 7-9. For all samples the

one-dimensional $^{1}H$ NMR spectrum, shown at the top of the two-dimensional spectrum, consists of a water peak at around 4.0 ppm for PBT-PPP 25, 4.2 ppm for PBT-PPP 55 and 4.5 ppm for PBT-PEO. In addition the one-dimensional spectra show polymer proton lines at 3.5 and 1.0 ppm for PBT-PPP and at 3.7 ppm for PBT-PEO. From the spectra it can be seen that for PBT-PPP 25 already at a mixing time of 100 ms cross-peaks between water and the polymer protons have appeared. For PBT-PPP 55 these cross-peaks show up at a mixing time of 400 ms, at 100 ms they are still absent. For PBT-PEO these cross-peaks are not even there for a mixing time of 400 ms, they first show up for a mixing time of 800 ms.

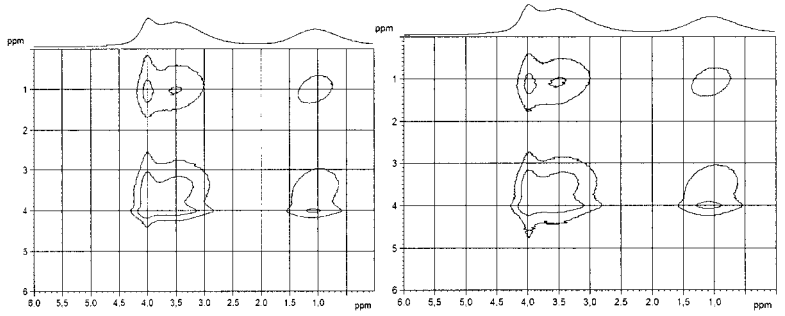



Figure 7. NOESY spectra of PBT-PPP 25, subjected to a 100% relative humidity, with a mixing time of 100 ms (left) and 400 ms (right).

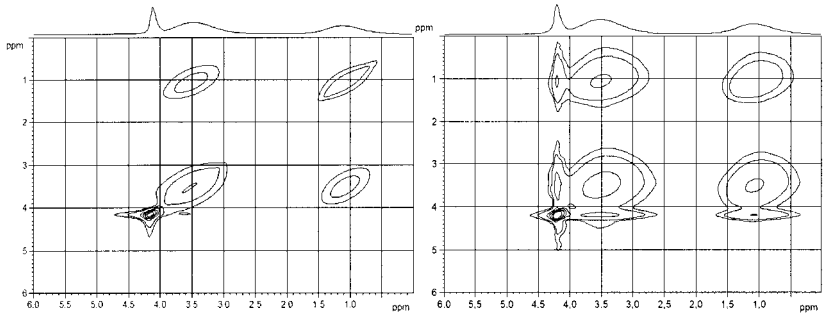



Figure 8. NOESY spectra of PBT-PPP 55, subjected to 100% relative humidity, with a mixing time of 100 ms (left) and 400 ms (right).

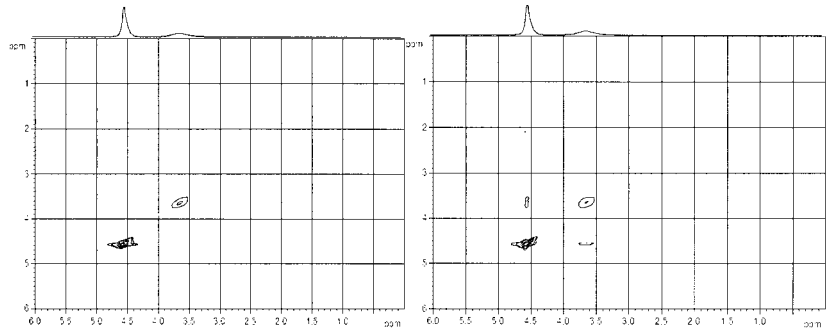


Figure 9. NOESY spectra of PBT-PEO, subjected to 100% relative humidity, with a mixing time of 400 ms (left) and 800 ms (right).

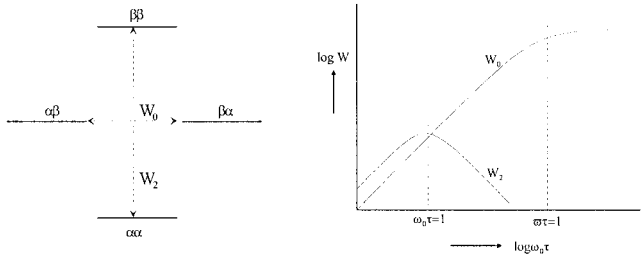
This proofs again that the cross-relaxation or NOE effect increases in the order PBT-PEO → PBT-PPP 55 → PBT-PPP 25, as we concluded already from the diffusion curves in fig. 5. While the water uptake of the PBT-PTMO system is very small, NOE spectra for this system were not taken.

## Polymer-water interaction

From the diffusion curve and the NOESY spectra it has become clear that for a certain time the water molecule has to be within circa 0.5 nm of some of the protons of the polymer. The questions we want to address here are near to which proton and for how long?

The $^1$H spectra of PBT-PPP 55 and PBT-PPP 25 show two polymer proton lines, the resonance at ~ 3.5 ppm originates from (–$OCH_2$) groups of PEO and PPO groups in the soft segment, the resonance at ~ 1.0 ppm from (–CH-$CH_3$) protons of PPO. With the values n=7.5 and m=26.5 (fig. 1) both lines have approximately the same integrated intensity. Although the water peak in figs. 7 and 8 has cross-peaks with both polymer proton lines (*intermolecular* cross-peaks), this does not prove that water molecules necessarily interact with both proton containing groups in the polymer. From the cross-peaks between the two polymer lines (*intramolecular* cross-peaks) we know that there also is a relatively fast magnetization exchange between the two polymer proton types due to spin diffusion inside the polymer soft segment. Therefore we can not decide from the NOESY spectra with which group, or possibly with both groups, the water molecules interact

in the polymer. It seems logic, however, to assume that the water molecules interact primarily with the ether groups in the soft segment. With a hydrogen bond between water and the ether group the distance between water protons and the protons in the soft segments is then 0.2-0.3 nm. The next question is how long does one water molecule stay with one ether group. When we assume for simplicity that during this stay one water proton is near to one of the polymer protons, the two protons form a proton pair with four spin states (fig. 10 a ).




(a) (b)

Figure 10. Zero- and double-quantum relaxation rates in a system of two coupled like spins; $\omega_0$ is the Larmor frequency of the spins, $\varpi$ the frequency corresponding to the rigid dipolar line width and $\tau$ the correlation time characterizing the fluctuation rate of the motion (see text).

The relaxation rate $W_0$ for the transition $|\alpha\beta\rangle \leftrightarrow |\beta\alpha\rangle$ and the rate $W_2$ for the relaxation transition $|\alpha\alpha\rangle \leftrightarrow |\beta\beta\rangle$ determine the NOE cross-peak intensity and sign[5]. The signs of the NOE cross-peaks relative to the diagonal peaks depend on the relative sizes of $W_2$ and $W_0$. For $W_2 > W_0$ the cross-peaks are negative and positive for the opposite case. Around $\omega_0\tau$=1 and $W_2 \approx W_0$ the cross-peak intensity is zero. $W_0$ alone is responsible for the cross-relaxation effects on the diffusion curves. Both relaxation rates are a function of the motional correlation time $\tau_c$ which describes the rate of the motional processes in which the two spins are involved and which make the dipolar interaction between these two spins time dependent.

In the most simple picture of random, isotropic motions the dependence of the relaxation rates $W_0$ and $W_2$ on $\tau_c$ can be calculated[5]. Fig. 10b shows that the sign of the NOE cross-peaks changes around a value for $\tau_c$ for which $\omega_0\tau_c = 1$. From the positive cross-peaks in our 400 MHz

NOE spectra we conclude that $\tau_c$ must be longer than ~ 0.5 ns. Fig. 10b also shows that $W_0$, responsible for the cross-relaxation effects in the diffusion curves, reaches a maximum for values of $\tau_c$ approaching or larger than $10^{-4}$ s, the inverse of the dipolar strength $\varpi$ for two proton spins at about 0.25 nm distance. We know that during the characteristic time of the diffusion experiments, $\Delta$=15 ms, the water molecules do not stay with one ether group all the time. If that were the case then the self-diffusion coefficient of water would have been equal to the self-diffusion coefficient of the polymer protons, $D \sim 10^{-15}$ $m^2/s$. Therefore two motional processes contribute to $\tau_c$: the motion of the water molecule to and from the hydrogen bonding sites on the soft segment and the collective rotational motion of the soft segment - hydrogen bonded water complex.

The intramolecular NOE is affected by the collective rotational motion of the water-polymer complex alone, the intermolecular NOE by both motional processes. From the dependence of the cross-peak intensities in the NOESY spectra on the mixing time we know that the intramolecular magnetization exchange (spin diffusion) in the polymer is significantly faster than the water-polymer magnetization exchange, at least for PBT-PPP 55 (fig. 11).

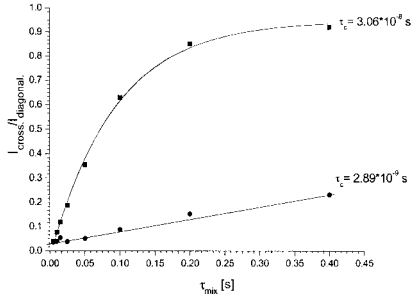



Figure 11. The cross-peak intensities from the NOESY spectra of PBT-PPP 55 as a function of the mixing time; the top curve represents the polymer-polymer cross-peak intensity, the lower curve the water-polymer cross-peak. The experimental points are fitted with the theory for dipolar relaxation for random isotropic motion[6], the resulting correlation times are indicated.

By fitting the curves in fig. 11 with the formulas which result from dipolar relaxation theory for two spins at a distance of 0.25 nm assuming random isotropic motions[6], the correlation times which describe these motions, can be determined. When one keeps in mind that the theory may

not be exactly applicable because the motions of the soft segments most likely are not isotropic, the following values for the correlation time are found. The polymer proton-proton cross-peaks (intramolecular NOE) arise from a dipolar interaction which is modulated by motions with a correlation time of $\tau_c=3*10^{-8}$ s. The motional process that modulates the dipolar interaction between the water and the polymer protons (intermolecular NOE) is found to be described by a correlation time of $\tau_c=2.9*10^{-8}$ s (fig. 11). The longest correlation time corresponds most likely to the chain motions of the soft segments, the shorter correlation time must correspond to the residence time of the water molecules near the ether groups.

It must be realized, however, that the residence time of water molecules near the ether group can only be equalled to the correlation time found from the NOE build-up curve if there are during the NMR characteristic time many encounters with ether groups. If only one encounter of length $\tau=\tau_c=2.9*10^{-9}$ s during the NOE mixing time would occur, the probability for a $W_0$ process would be extremely small, since the dipolar interaction is only about 10 kHz.

Setting the residence time equal to the correlation time implies that many water-ether group encounters occur during the NMR characteristic time. The correlation time of $2.9*10^{-9}$ s or the residence time of water near the ether group is longer than the value at which the NOE cross-peaks change sign ($5*10^{-10}$ s), as it should be.

To describe this process a bit more quantitative we assume that each water molecule randomly walks from ether group to ether group with:

- average residence time near an ether group = $\tau \sim 3*10^{-9}$ s
- average distance between ether groups in the soft segments = $\ell$
- average time needed to move from one ether site to another = t
- during $\Delta$=15 ms the water molecule jumps N times.

Then we have the following equation from random walk theory:

$$N\ell^2 = 6D_w N(t+\tau)\,, \tag{3}$$

where $D_w$ is the measured diffusion coefficient of water (table 1) and where

$$N(\tau+t)=\Delta\ . \tag{4}$$

From magic angle spinning experiments on PBT-PEO we know that the chemical shift $\delta$ of water hydrogen bonded to the ether group is 3.2 ppm[1], significantly different from the shift of non-bonded water in the same material. At a relative humidity of rh=100% we find chemical shifts of

water in PBT-PPP 25, PBT PPP 55 and PBT-PEO at 4.0 ppm, 4.2 ppm and 4.5 ppm, respectively. With these values we can estimate the ratio between the time t that the water molecule is not hydrogen-bonded and the time it is bonded, the residence time $\tau$.

The measured chemical shift of water $\delta$ can be written as:

$$\delta = \frac{t}{t+\tau}\delta_w + \frac{\tau}{t+\tau}\delta_{hb} \qquad (5)$$

where $\delta_w$ is the water chemical shift of non-bonded water in the polymer material and taken to be 4.5 ppm, and $\delta_{hb}$ the chemical shift of hydrogen bonded water and equal to 3.2 ppm[1].

Then we find: $\frac{t}{\tau} = 1.6$ for PBT-PPP 25, $\frac{t}{\tau} = 3.3$ for PBT-PPP 55 and $\frac{t}{\tau}$ = large for PBT-PEO.

Using equations (3) and (4) and $\tau = 3*10^{-9}$ s for PBT-PPP 55 this results in t=10 ns, $\ell$=2 nm and N $\approx 10^6$.

The mean jump length $\ell$ between water-bonding ether sites is considerably longer than in PEO solutions[7], where it was found that $\ell$=0.342 nm and $\tau$=16.4 ps. This is a very surprising result and one wonders if equation (3) is too simple. On the other hand the motion and the path of the motion of water molecules in a solid are much more restricted than in a solution. Could it be that the residence time $\tau$ represents the time the water molecule spends in a soft domain and $\ell$ the distance between soft domains? That, however, would be in contrast to the idea of continuous amorphous domains in these materials[8]. Another possibility might be that once a water molecule leaves an ether group, it is absorbed in a water cluster in which it diffuses for a time of the order of t over a considerable length of the order of $\ell$ before it gets trapped again at an ether site. In that case $\ell$ would represent the cluster size.

Although we only fitted the cross-peak intensity versus mixing time for the PBT-PPP 55 sample, the trend seems to be clear. The more rigid the soft segment, the smaller the ratio $t/\tau$

At this moment we can not establish whether the increase of $W_0$ in the order PBT-PEO → PBT-PPP 55 → PBT-PPP 25 is mainly due to a decrease of t or to an increase of $\tau$.

## Conclusions

PFGE and NOESY experiments on four hard-soft segment copolymers show that water molecules can bind to the soft segments for a time longer than ~1 ns. It seems likely that the water

molecules are hydrogen bonded the water and polymer protons can exchange magnetization. The rate of the magnetization exchange depends on the chemical structure and mass fraction of the soft segments, presumably because the residence time of the water near the soft segment depends on the mobility of the soft segment domains. The PBT-PEO system absorbs much more water than the other systems, but the magnetization exchange is the slowest.

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