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# Self-Diffusion of Water in Block Copoly(ether−ester) Polymers: An NMR Study

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ABSTRACT: Water diffusion in four hard−soft block copolymer systems, based on poly(butylene terephthalate) as the hard segment and a copolymer with poly(ethylene oxide) (PEO) as the soft block, has been investigated by pulsed field gradient echo NMR. The water absorption and the water diffusion coefficient depend on the composition of the copolymer and the amount of water absorbed in the system. The higher the fraction PEO in the polymer, the higher the amount of absorbed water and the faster the water diffusion. The diffusion experimental results further indicate an interaction between water molecules and the PEO units in the soft segments. For all investigated systems it is found that water molecules reside near PEO units within a distance of less than 0.5 nm for a time of the order of or longer than 1 ns. The higher the amount of PEO in the soft blocks, the shorter the residence time of the water molecules near the PEO units.

## 1. Introduction

Water permeability is a technologically important property of polymer materials. The permeation of water through polymers involves at least two processes:[1] water sorption at the entering face of the material and transport through the material by diffusion.

The amount of water absorbed in a polymer can be experimentally investigated by several methods, e.g. gravimetric methods or NMR,[2] and theoretically described with thermodynamic models.[3,4] The transport of water molecules through polymers by diffusion can be driven by a gradient of the chemical potential or the water molecules can translate through self-diffusion. The (self-) diffusion coefficient of water in polymers represents the ease with which water molecules can move through the polymer matrix and will depend on the mobility of the polymer chain.

The diffusion of a molecule like water in a matrix can be investigated by pulsed field gradient spin−echo NMR spectroscopy experiments.[5] Here we report the results of such a study on the diffusion of water in some block copoly(ether−ester) polymers as a function of the amount of absorbed water (the degree of swelling). We show that the self-diffusion of water strongly depends on the chemical composition of the copolymers and the degree of swelling. In addition we find that the diffusion experiments provide information about the interaction between water protons and protons in the polymer. The presence of these interactions, probably due to hydrogen bonding of water to ether groups in the PEO segments, shows that a significant fraction of the water molecules reside a significantly long time near the polymer chains. This leads to an exchange of nuclear spin magnetization between water and polymer protons which affects the apparent self-diffusion coefficients. Similar effects, but detected via two-dimensional NOE experiments, have been reported for proteins in aqueous solutions (protein hydration).[6,7] In proteins and also for polyamides water molecules interact with amide groups.[8] For the systems studied here the water molecules must interact with the ether groups. We show that the residence time of the water molecules near the ether groups depends on the mobility of the soft segments and on the amount of absorbed water.

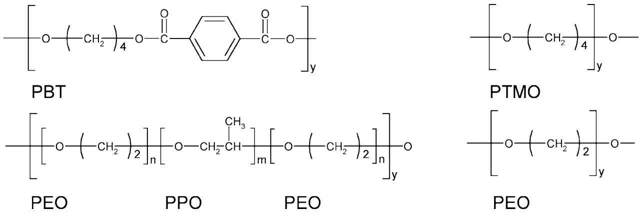

**Figure 1.** Chemical structure of the hard segments PBT and the soft segments PTMO, PEO−PPO−PEO, and PEO.

## 2. Experimental Section

The self-diffusion of water in four hard/soft-segment block copolymers was investigated. The hard segment of the copolymer always consists of the polyester poly(butylene terephthalate) (PBT), and the soft segment is 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); 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; $y$ = mass fraction of the soft segment in percent.

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.[9]

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 vapor pressure for a time long enough (at least 3 weeks) to obtain equilibrium. The used salt solutions and the corresponding relative humidity are shown in Table 1.

With each sample exposed to six different relative humidities RH we obtained 24 samples, which were immediately

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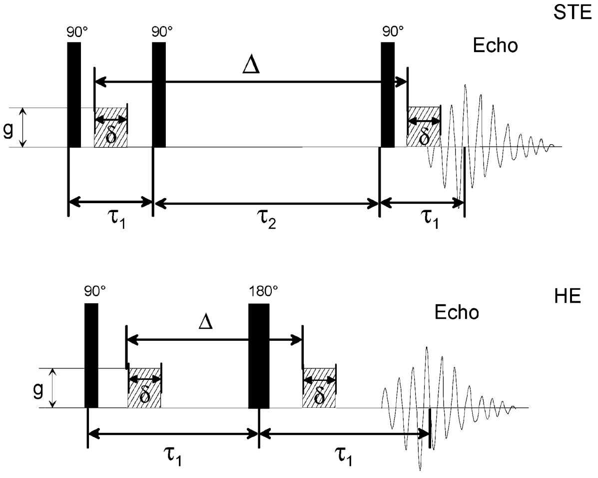

**Figure 2.** Pulse sequences for a pulsed field gradient echo diffusion experiment with a two-pulse (Hahn echo) or a three-pulse echo (stimulated echo).

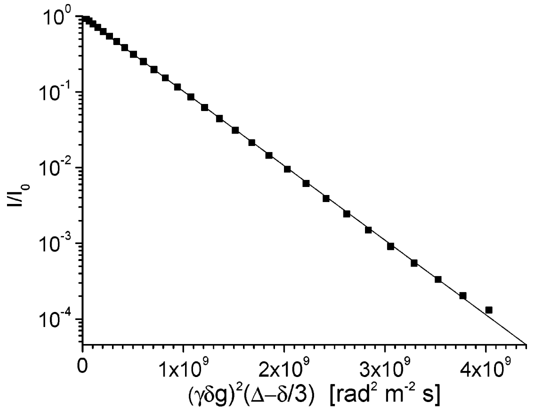

**Figure 3.** Proton-stimulated echo intensity $\ln(I/I_0)$ as a function of the gradient intensity $\gamma^2\delta^2g^2(\Delta - (1/3)\delta)$ for pure water at 298 K.

**Table 1. Relative Humidity of Water and Saturated Salt Solutions**

| rel humidity RH (%) | soln | rel humidity RH (%) | soln |
|---|---|---|---|
| 100 | pure water | 66 | $Mg(CH_3COO)_2$ |
| 90 | $ZnSO_4 \cdot 7H_2O$ | 52 | $NaHSO_4 \cdot H_2O$ |
| 79 | $NH_4Cl$ | 32 | $CaCl_2 \cdot 6H_2O$ |

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

In the PFGE experiment both a Hahn spin−echo sequence (90°−$\tau_1$−180°−$\tau_1$−echo) and a stimulated spin−echo pulse sequence (90°−$\tau_1$−90°−$\tau_2$−90°−$\tau_1$−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 Δ, 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[10]

$$I(g) = I(0)\exp[-\gamma^2\delta^2g^2D(\Delta - (1/3)\delta)] \qquad (1)$$

Figure 3 shows, as an example, the proton-stimulated echo intensity of pure water as a function of $\gamma^2\delta^2g^2(\Delta - (1/3)\delta)$. From the slope of the straight line the self-diffusion coefficient of pure water at 298 K is determined to be $2.28 \times 10^{-9}$ m²/s.

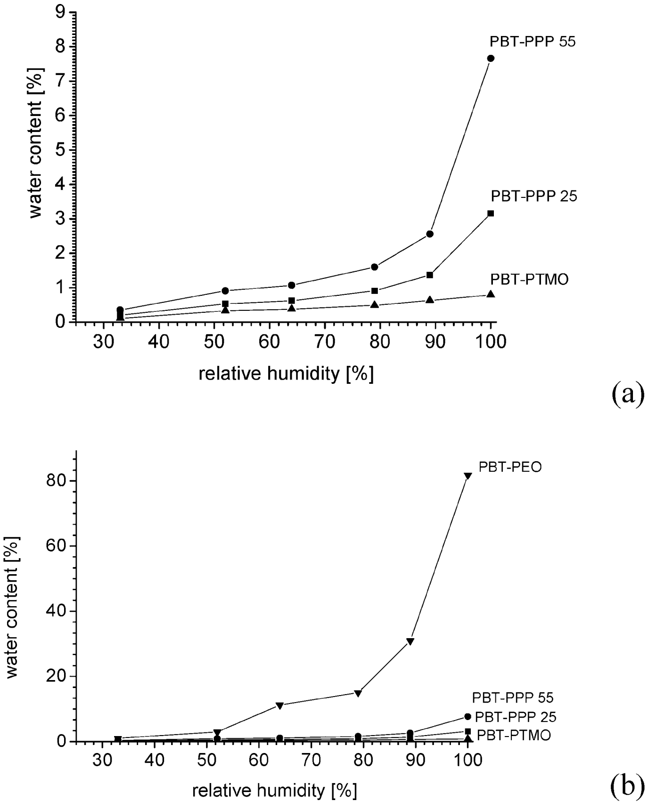

**Figure 4.** Amount of water absorbed by the four polymer systems as a function of the relative humidity to which the samples are exposed. Notice the change of scale in (b).

The phase-sensitive two-dimensional exchange experiment (NOESY) we used is described in the literature;[11] the mixing time was 400 ms.

## 3. Results and Discussion

**3.1. Amount of Absorbed Water.** For each sample the amount of absorbed water as a function of the relative humidity RH is determined gravimetrically; the results are shown in Figure 4.

These diagrams show that (a) the higher the fraction PEO in the polymer the higher the amount of absorbed water and (b) the amount increases more or less exponentially with increasing RH.

The water swells the polymer network; a thermodynamic interpretation has been published elsewhere.[4]

**3.2. Diffusion of Water.** Figure 5 shows the stimulated echo $^1$H NMR spectra of PBT−PPP-55 as a function of the gradient strength $g$ and the relative humidity to which the samples have been exposed.

The line shapes in the spectra change with the relative humidity. First we note that, due to the fact that the NMR spectra are detected with the NMR spectrometer in the “high-resolution mode” (no solid-state high-resolution techniques are applied), only protons in segments that have an appreciable reorientational freedom are detected. That rules out a contribution to the spectra of the protons in the crystalline PBT domains; only protons in the soft segments are detected.

At RH = 32%, corresponding to a water content of less than 0.5 wt %, only one broad resonance is detected, the amplitude of which is practically independent of the gradient strength (Figure 5a). This shows that the spectral contribution of the water molecules is indistinguishable from the polymer proton contribution. The

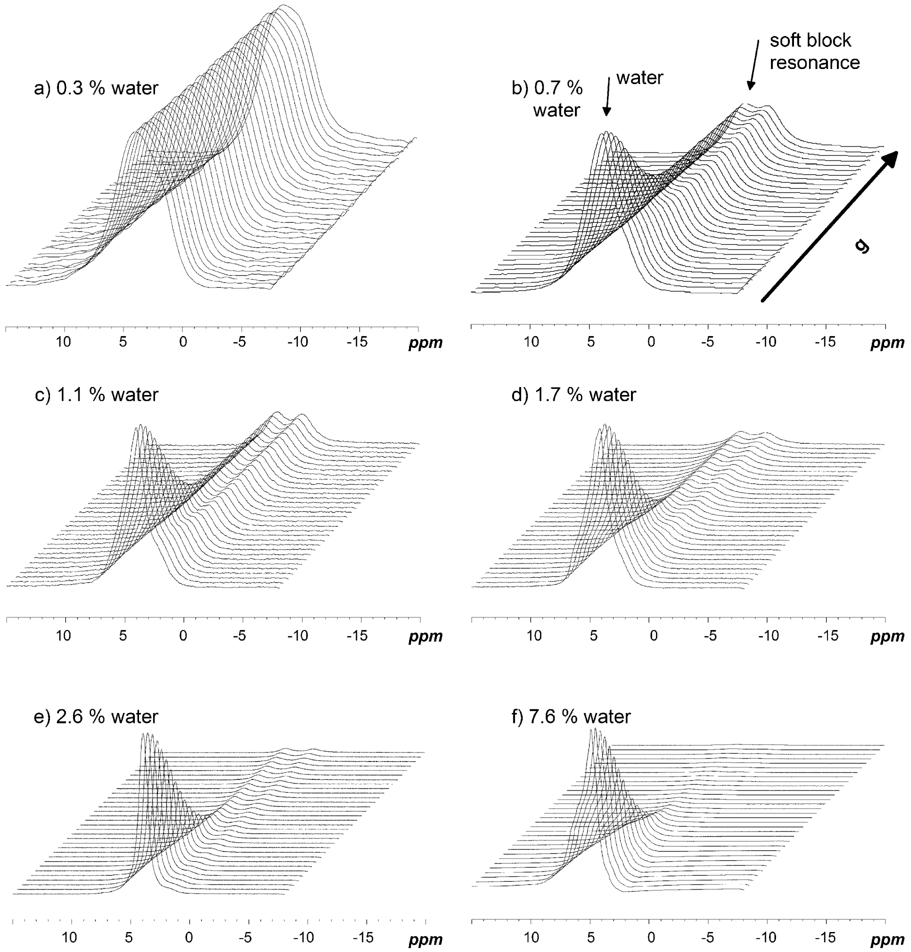

**Figure 5.** Proton NMR spectra for PBT−PPP-55 obtained with the stimulated spin−echo sequence as a function of the gradient strength $g$ (0−8 T/m) and the relative humidity RH to which the samples were exposed: (a) RH = 32%; (b) RH = 52%; (c) RH = 66%; (d) RH = 79%; (e) RH = 90%; (f) RH = 100%. Also indicated are the absorbed water weight fractions. The gradient pulse length $\delta = 2$ ms, and diffusion time $\Delta = 15$ ms. The line intensities for $g = 0$ at each relative humidity are normalized. This means, for instance, that in reality the first spectrum in (f) is at least 1 order of magnitude stronger than the spectra in (a), as can be judged from the fact that in (f) at high gradients the polymer signal seems absent.

independence of the signal from the gradient strength $g$ shows that the polymer molecules and/or water molecules have a diffusion coefficient $D$ smaller than ca. $10^{-14}$ m$^2$/s. This is as can be expected for protons in a polymer network, but also the water molecules are practically immobile.

For the same PBT−PPP-55 system exposed to a relative humidity of 52%, resulting in a water content of 0.7%, the situation has clearly changed. The NMR signal shows a structure, and the main part is narrower than in Figure 5a. The intensity of this main part decreases fast with increasing gradient strength. At the highest gradient a doublet remains of which the intensity is more or less independent of the gradient strength. The narrow gradient-dependent part of the resonance line is due to the water molecules which diffuse relatively fast; the remaining doublet is due to the translationally immobile methyl and methylene protons of the soft PEO−PPO−PEO segments.

When more water is absorbed the contribution of the water to the NMR signal becomes stronger, but always as a function of the gradient strength the water peak decays much faster than the polymer peaks.

More or less the same behavior is found for the other samples, except for differences in the relative intensity of the water contribution. Instead of reproducing all the spectra, Figures 6−9 show the integrated intensity of the resonances as a function of the gradient strength $g^2$ for the samples treated at a different humidity.

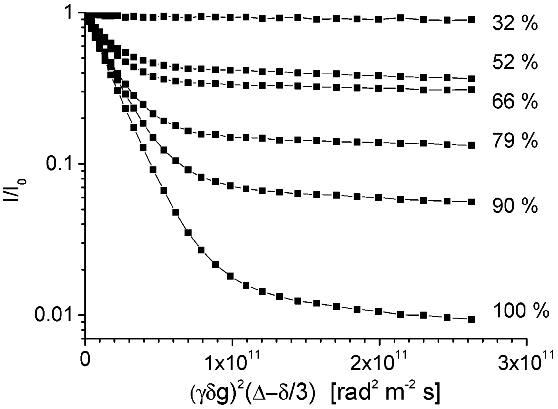

**Figure 6.** Integrated intensity of the resonance of Figure 5 for PBT−PPP-55 as a function of $\gamma^2\delta^2g^2(\Delta - (1/3)\delta)$ and the relative humidity ("diffusion curves").

For the PBT−PPP-55 sample the data in Figure 6 are taken from the spectra in Figure 5 and clearly show that for humidity higher than 32% two components with different diffusion coefficients exist, water with a relatively high diffusion coefficient and polymer protons with a small coefficient. It is remarkable that the slope of the slow decaying part of the diffusion curves, which

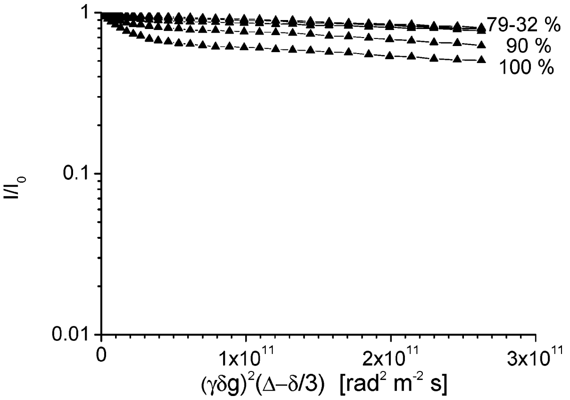

**Figure 7.** Diffusion curves for PBT−PTMO.

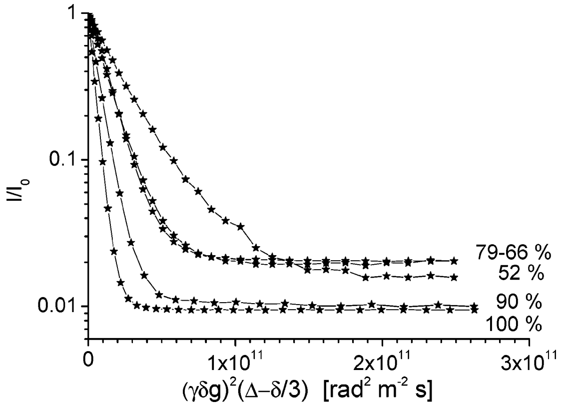

**Figure 8.** Diffusion curves for PBT−PEO.

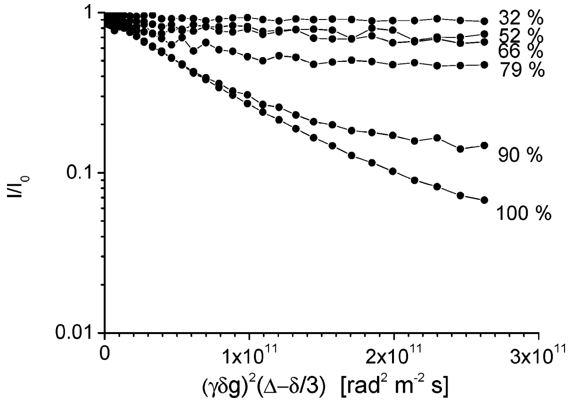

**Figure 9.** Diffusion curves for PBT−PPP-25.

represents the diffusion of the polymer protons, clearly becomes more negative with increasing humidity. At first sight this would mean that the diffusion coefficient of the polymer protons increases with the amount of absorbed water. Although it is clear that by swelling of the polymer network the mobility of the soft segments will increase, the increased translational freedom of these segments cannot be responsible for the change of the slope of the slow decaying part of the curves in Figure 6.

To show this we calculated the apparent polymer diffusion coefficients corresponding to the slow decaying parts of the curves in Figure 6 (Table 2). With these values and the Einstein−Smoluchowsky relation

$$\langle r^2 \rangle = 6D\Delta$$

the apparent root-mean-square displacement during the diffusion time $\Delta = 15$ ms of the protons in the soft segments as a function of the relative humidity can be calculated (also Table 2).

**Table 2. Apparent Diffusion Coefficients and Displacements of the Polymer Protons for PBT−PPP-55 Resulting from a Biexponential Fit of the Diffusion Curves in Figure 6**

| rel humidity (%) | apparent polym self-diffusion coeff (m$^2$/s) | apparent root-mean-square displacement of the polym soft segments during the diffusion time of $\Delta = 15$ ms ($\mu$m) |
|---|---|---|
| 32 | $2.3 \times 10^{-13}$ | 0.14 |
| 52 | $7.6 \times 10^{-13}$ | 0.26 |
| 66 | $4.9 \times 10^{-13}$ | 0.21 |
| 79 | $6.8 \times 10^{-13}$ | 0.25 |
| 90 | $1.1 \times 10^{-12}$ | 0.31 |
| 100 | $2.7 \times 10^{-12}$ | 0.49 |

At the highest humidity this would imply that the polymer soft segment would translate in 15 ms over a distance of 500 nm. This is hard to believe for a polymer network and means that the diffusion coefficients for the soft segments cannot be as large as determined from the slowly decaying parts of the diffusion curves. The polymer segmental translational mobility is expected to be so low that on the time scale of our diffusion experiment and with the applied gradient strengths the echo intensity should be independent of the gradient strength. There must be another explanation why the apparent diffusion coefficient of the soft segments increases with the amount of absorbed water. This will be discussed below.

Figures 7−9 show the stimulated echo diffusion curves for the other three copolymers. The curves for PBT−PTMO in Figure 7 are similar to those of PBT−PPP-55 when taking into account that the maximum amount of water that is absorbed by PBT−PTMO at a relative humidity of 100% is only about 0.7 wt %. Also for the PBT−PTMO system the last part of the curve shows a clear slope. The curves for the PBT−PEO system in Figure 8 show effects opposite to the curves for PBT−PPP-55. First, in this system a much larger amount of water is absorbed (ca. 85 wt %), which causes a clear and strong water component with a high diffusion coefficient to show up. For this case the parts of the curve due to the polymer diffusion are practically horizontal, as they should be. While for PBT−PEO the diffusion of water and polymer can be clearly separated, for the PBT−PPP-25 system in Figure 9 no distinction between the water and polymer contribution to the diffusion curves can be observed.

The comparison between the diffusion curves of the four samples exposed to 100% relative humidity (but different water weight fractions!) in Figure 10 emphasizes the differences between the samples.

Also here it becomes clear that the samples PBT−PPP-25 and PBT−PEO represent two extreme situations, while PBT−PTMO and PBT−PPP-55 are intermediate cases.

For the PBT-PEO sample the situation is most clear. It shows water molecules with a high diffusion coefficient ($D = 2.5 \times 10^{-10}$ m$^2$/s) and soft segments with a very small diffusion coefficient ($D < \sim 10^{-14}$ m$^2$/s), as expected.

In the PBT−PTMO case the amount of absorbed water is very small, but nevertheless the curve clearly shows two components with different slopes due to the water and the polymer protons. The apparent diffusion

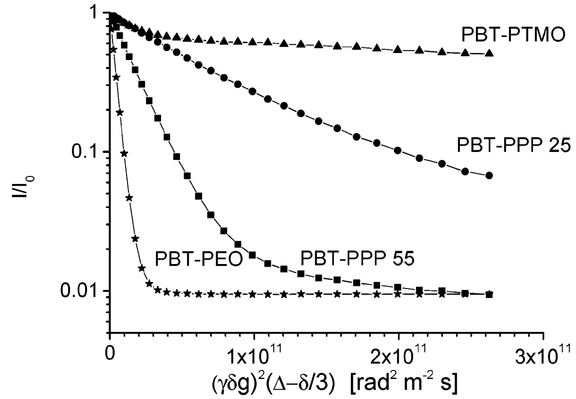

**Figure 10.** Diffusion curves for all four systems at a relative humidity of 100%.

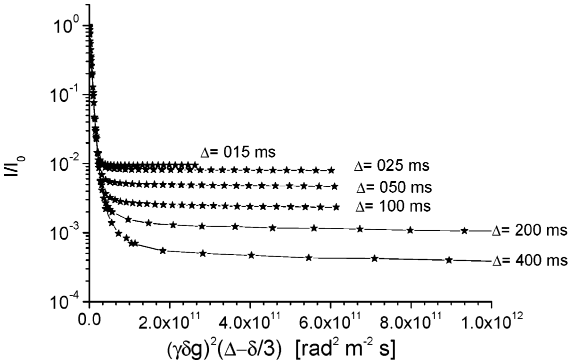

**Figure 11.** Diffusion curves for PBT−PEO at a relative humidity of 100% as a function of the diffusion time Δ.

coefficient of the polymer protons ($D \sim 1.3 \times 10^{-12}$ m$^2$/s) is too high and the water diffusion coefficient ($D \sim 6.4 \times 10^{-11}$ m$^2$/s) is much smaller than for the PBT−PEO system.

For PBT−PPP-25 the water component and the polymer component seem to have the same diffusion coefficient. For PBT−PPP-55 two components are present in the diffusion curves; the apparent water diffusion coefficient is higher than for PBT−PTMO but smaller than for PBT−PEO. Also here the polymer diffusion coefficient is clearly too high.

The fact that for some samples the apparent polymer diffusion coefficient is far too high can be explained by an exchange process between water and polymer protons which averages the diffusion coefficients of the water molecules and the polymer soft segments. Another indication of the existence of such an exchange effect between the polymer protons and the water protons is obtained by varying the diffusion time Δ. In Figure 11 the stimulated echo diffusion curves of PBT−PEO are shown as a function of the diffusion time Δ, increasing from 15 to 400 ms.

For Δ = 15 ms the part of the curve due to the polymer protons is practically horizontal, implying a very small diffusion coefficient. For longer diffusion times, and especially at 400 ms, the apparent polymer diffusion coefficient becomes larger. Apparently, the exchange rate for this system is smaller than $(0.015)^{-1}$ s$^{-1}$ but comparable to or faster than $(0.4)^{-1}$ s$^{-1}$.

So it seems that for all four investigated systems an exchange process is present; only the rate is different for the four samples. The fastest exchange occurs in the sample PBT−PPP-25, and the slowest in PBT−PEO.

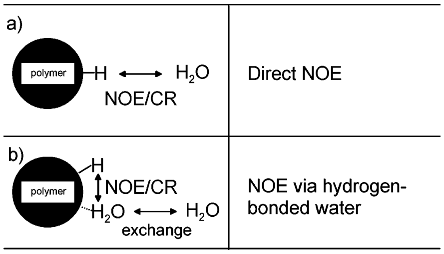

**Figure 12.** Two possible routes for the spin exchange between water protons and polymer protons.

### 3.3. Exchange Effects.

As discussed above, depending on the amount of absorbed water and the type of the soft segment, an averaging process seems to take place between water proton spins and polymer spins which makes the apparent polymer diffusion coefficient higher than expected. An obvious process that would cause such an averaging is direct chemical exchange between a water proton and a polymer proton. Because only aliphatic protons are present in the soft segments, a direct chemical exchange process seems not very probable. We will see below that direct chemical exchange indeed does not contribute to the observed effects.

It was shown[12] that spin exchange between protons of two components without exchange of the proton itself, via cross-relaxation or in general nuclear Overhauser effects (NOE), can also cause an averaging of the diffusion coefficients of the two components. In protein solutions it has been found that under the right conditions NOE effects between the protein protons and hydration water can occur.[6,7] There is no reason similar effects in polymer−water systems could not occur.

Figure 12 schematically shows that spin exchange, which can also lead to averaging of the diffusion coefficient of water and polymer, can result from a direct process and an indirect process:[7] (a) direct spin exchange via dipolar coupling between a water proton spin and a polymer proton spin (cross-relaxation,[13] Figure 12a); (b) chemical exchange between bulk water and hydrogen bonded water followed by cross-relaxation between a polymer proton and the hydrogen bonded water molecule (Figure 12b).

The cross-relaxation in the mechanisms a and b only affects the $z$-component of the magnetization; therefore, cross-relaxation will influence diffusion curves obtained with a stimulated echo but not when they are obtained with a Hahn spin−echo experiment. Direct chemical exchange will show up, when fast enough, with both types of experiment.

Figures 13 and 14 show a comparison of the diffusion curves for PBT−PPP-25 and PBT−PPP-55, both at 100% relative humidity, obtained by a Hahn echo and a stimulated echo experiment.

The comparison between these two curves is somewhat complicated by the fact that although both curves were taken with a diffusion time Δ = 15 ms, the $\tau_1$- time of the Hahn echo experiment is longer than that of the stimulated echo (see Figure 2), which causes that in the Hahn echo experiment the polymer proton signal due to its shorter $T_2$-value is almost absent; only the water signal remains. Nevertheless it can be seen that, especially for PBT−PPP-25, the initial decays of the Hahn and stimulated echo diffusion curves, which are both due to water, are very different. The decay in the

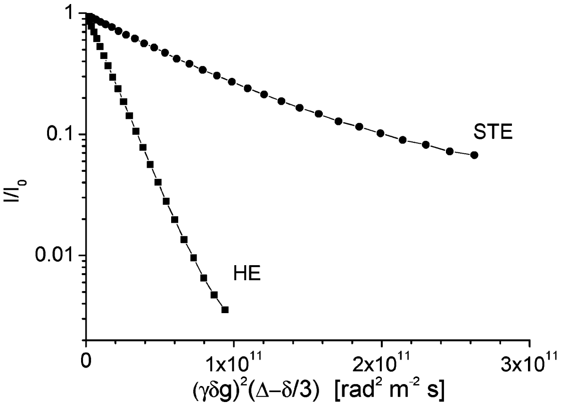

**Figure 13.** Diffusion curves for PBT−PPP-25 at a relative humidity of 100%, obtained by the Hahn echo sequence (HE) and the stimulated echo sequence (STE).

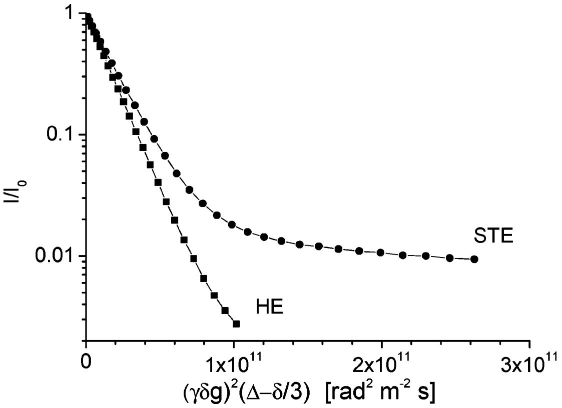

**Figure 14.** Diffusion curves for PBT−PPP-55 at a relative humidity of 100%, obtained by the Hahn echo sequence (HE) and the stimulated echo sequence (STE).

**Table 3. Water Self-Diffusion Coefficient in Three Samples That Were Exposed to 100% Relative Humidity**

| sample | type echo expt | diffusion coeff (m$^2$/s) |
|---|---|---|
| PBT−PPP-25 | Hahn echo | $6.6 \times 10^{-11}$ |
| PBT−PPP-55 | Hahn echo | $6.7 \times 10^{-11}$ |
| PBT−PEO | Hahn echo | $2.5 \times 10^{-10}$ |
| PBT−PEO | stimulated echo | $2.5 \times 10^{-10}$ |

stimulated curve has been slowed due to cross-relaxation. Chemical exchange would affect the results of both experiments.

Therefore, in general the water diffusion coefficient determined from the Hahn echo curves is closer to the true water diffusion coefficient than the apparent diffusion coefficient from the stimulated echo experiment. The Hahn echo water diffusion coefficient increases when going from PBT−PPP-25/55 to PBT−PEO (see Table 3). For PBT−PEO at 100% RH the diffusion coefficient determined from both types of diffusion curves are the same.

**3.4. Cross-Relaxation.** In the previous section we concluded that the stimulated echo diffusion curves can be influenced by cross-relaxation between water protons and polymer protons. Since this cross-relaxation can only occur when the two types of protons stay close enough (within ca. 0.5 nm) for a long enough time, the residence time, the stimulated echo experiments yield information regarding the interaction between water and the polymer. This will be investigated in this section.

The exchange mechanisms a and b, which cause an exchange of spin magnetization between the water and polymer protons, affect the stimulated echo diffusion curves in the same way and can therefore be described within the same mathematical formalism.

When we characterize the exchange rates by $k_w$ and $k_p$ with

$$n_w k_w = n_p k_p$$

where $n_w$ and $n_p$ represent the number of water and polymer protons that are involved in the exchange process. We can write two coupled differential equations that describe the time dependence of the water (subscript w) and polymer (subscript p) spin magnetization components parallel to the $z$-axis (the axis of the static external magnetic field) between $t = 0$ (the time of the first field gradient pulse) and $t = \Delta$ (the instant of the second gradient pulse):[12]

$$\frac{\partial M_w(z,t)}{\partial t} = -R_{1w}[M_w(z,t) - M_w^{\,e}] - k_w M_w(z,t) + k_p M_p(z,t) + D_w \frac{\partial^2}{\partial z^2}\{M_w(z,t)\}$$

$$\frac{\partial M_p(z,t)}{\partial t} = -R_{1p}[M_p(z,t) - M_p^{\,e}] - k_p M_p(z,t) + k_w M_w(z,t) + D_p \frac{\partial^2}{\partial z^2}\{M_p(z,t)\} \quad (2)$$

Here $R_{1w}$ and $R_{1p}$ represent the spin−lattice relaxation rates, $D_w$ and $D_p$ the self-diffusion coefficients, and $M_w^{\,e}$ and $M_p^{\,e}$ the equilibrium $z$ magnetizations for water and polymer. For this equation it has been assumed that all water protons are equally involved in the exchange process. For the polymer protons this is probably not the case, since it seems that the water is absorbed mainly in domains containing PEO segments. Therefore, water molecules probably interact mainly with PEO protons. How large the reservoir of polymer protons is will depend on the spin diffusion rate between the PEO protons and the protons of other segments. Without any knowledge about the rates and about $n_w$ and $n_p$, $M_w^{\,e}/M_p^{\,e}$ may not be equal to $n_w/n_p$.

An additional uncertainty is that due to the high-resolution mode of the spectrometer we may not detect all $n_p$ polymer protons involved in the exchange process.

In the eqs (2) the time development of the water and polymer proton $z$-magnetization $M_w$ and $M_p$ is described after the first magnetic field gradient pulse with length $\delta$ and magnitude $g$ has created a spatial dependence of the initial $z$-magnetization. In our case the magnetic field gradient happens to be in the same direction $z$ as the static external magnetic field. Therefore

$$M_w(z,t=0) = M_w^{\,e}\cos(qz) \quad M_p(z,t=0) = M_p^{\,e}\cos(qz)$$

where the wave vector $q = \gamma\delta g/2\pi$. The second gradient pulse after the diffusion time $t = \Delta$ decodes this $z$-dependence.

The solutions of eq 2 show the magnetization $M$ after the second gradient pulse as a function of the diffusion time $\Delta$ and $q$:[12]

$$M_w(q,\Delta) = [(a_+ - q^2D_p - k_w - k_p - R_{1p})e^{-a_+\Delta} - (a_- - q^2D_p - k_w - k_p - R_{1p})e^{-a_-\Delta}]/(a_+ - a_-)$$

$$M_p(q,\Delta) = [(a_+ - q^2D_w - k_w - k_p - R_{1w})e^{-a_+\Delta} - (a_- - q^2D_w - k_w - k_p - R_{1w})e^{-a_-\Delta}]/(a_+ - a_-) \quad (3)$$

where

$$a_\pm = \frac{1}{2}[q^2(D_w + D_p) + k_w + k_p + R_{1w} + R_{1p} \pm \sqrt{\{q^2(D_w - D_p) + k_w - k_p + R_{1w} - R_{1p}\}^2 + 4k_wk_p}]$$

The solutions (3) are more general than the original formulas of Peschier et al.,[12] for which it was assumed that $D_p = 0$ and $M_p(z,t = 0) = 0$. For the following we also put $D_p = 0$, since, as discussed before, the diffusion of the polymer segments on the scale of our experiments can be neglected. The second approximation, $M_p(z,t = 0) = 0$, was justified by Peschier et al.[12] by a short polymer proton $T_2$. For our experiments this assumption is not correct while we detect some of the polymer proton magnetization.

With the solutions (3) the effect of exchange with rates $k_w$ and $k_p$ can be simulated. Figure 15 shows three diffusion curves, simulated with eq 3.

The parameters used are given in the figure caption. The simulations show exactly the effect observed for the experimental curves: when the exchange rates are sufficiently large the apparent polymer diffusion coefficient is higher than it should be and for high exchange rates, the apparent diffusion coefficients of water and of the polymer become equal.

In principle it must be possible to fit the experimental diffusion curves with the solutions in eq 3. Due to the uncertainty about the number of polymer protons that are involved, as discussed above, we found that fitting does not provide unique answers and therefore was not pursued. Qualitatively, however, the curves can exactly reproduce the experimental curves, as shown in Figure 15 for PBT−PPP-55 at 100% relative humidity. We can conclude from the simulated diffusion curves that cross-relaxation between water and polymer protons is very strong for the PBT−PPP-25 sample, less strong for PBT−PPP-55 and PBT−PTMO, and weak for PBT−PEO.

Another experimental technique to detect the presence of dipolar interactions between spins is the two-dimensional NOESY technique.[11] Here such dipolar interactions cause cross-peaks in the NOESY spectrum. Phase-sensitive proton 2D-NOESY spectra with a mixing time of 400 ms for three samples, PBT−PPP-25, PBT−PPP-55, and PBT−PEO, all treated at 100% relative humidity, are shown in the Figures 16−18.

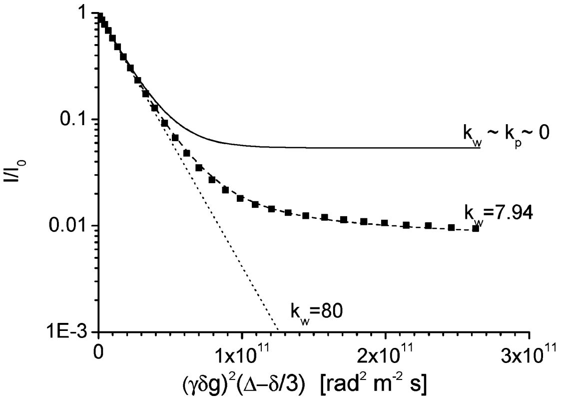

**Figure 15.** Simulated diffusion curves for different exchange rates and the following parameter values: $D_p = 0$, $D_w = 5.6 \times 10^{-11}$ m$^2$/s, $k_w = k_p = 0$, $M_w^e = 0.94$, $M_p^e = 0.06$, $R_{1p} = R_{1w} = 0$; $D_p = 0$, $D_w = 5.6 \times 10^{-11}$ m$^2$/s, $k_w = 7.94$ s$^{-1}$, $k_p = 124.4$ s$^{-1}$, $M_w^e = 0.94$, $M_p^e = 0.06$, $R_{1p} = R_{1w} = 0$; $D_p = 0$, $D_w = 5.6 \times 10^{-11}$ m$^2$/s, $k_w = 80$ s$^{-1}$, $k_p = 1253$ s$^{-1}$, $M_w^e = 0.94$, $M_p^e = 0.06$, $R_{1p} = R_{1w} = 0$. The experimental points are from PTB−PPP-55 at RH = 100%.

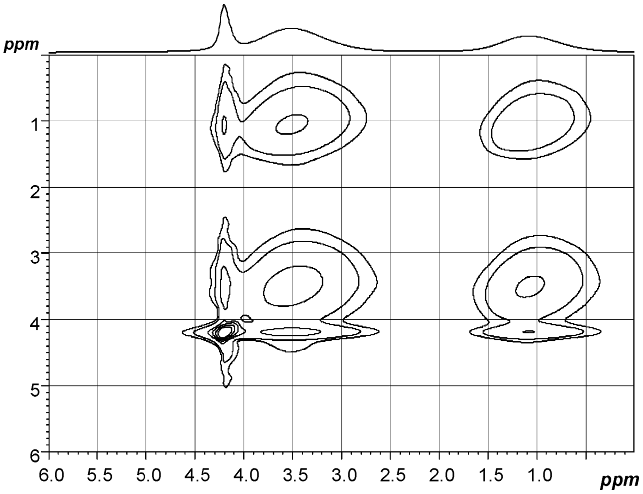

**Figure 16.** Two-dimensional NOE spectrum of PBT−PPP-55 with a mixing time of 400 ms. The cross-peaks have the same sign as the diagonal peaks.

Figures 16 and 17 clearly show strong positive cross-peaks between the water resonance line (at 4.2 ppm for PBT−PPP-55 and at 4.0 ppm for PBT−PPP-25) and the polymer lines at 3.5 and 1.1 ppm, while for the PBT−PEO system these cross-peaks are too weak to be significant. The absence of cross-peaks in the NOESY spectrum of the PBT−PEO system (Figure 18) agrees with the conclusion reached above that for the PBT−PEO system the magnetization exchange between water and polymer protons is weak. The strong NOE cross-peaks for the PBT−PPP systems agree with the observation of strong cross-relaxation effects in the diffusion curves of these systems.

Since we saw that the amount of absorbed water increases with the fraction PEO in the copolymer and we expect that the water molecules mainly interact with the PEO ether groups, it is a somewhat surprising result that just in the system with the highest PEO fraction the cross-relaxation is the weakest. This can be explained by the effect the amount of absorbed water has on the PEO-segment mobility and on the water diffusion coefficient. From the width of the proton NMR lines in the spectrum of Figure 18 and from the higher diffusion coefficient of water in the PBT−PEO polymer (Table 3), it is clear that the segmental mobility of the PEO segments and the mobility of the water molecules in PBT−PEO is higher than in the other systems. The residence time of a water molecule near a PEO ether site will depend on the relative mobility of the polymer segments and the water molecule. A high mobility like in PBT−PEO may mean a short residence time, too short for effective cross-relaxation. For the two PBT−PPP systems the water diffusion coefficient is lower than for PBT−PEO and the cross-relaxation effect on the diffusion curves stronger, for the PBT−PPP-25

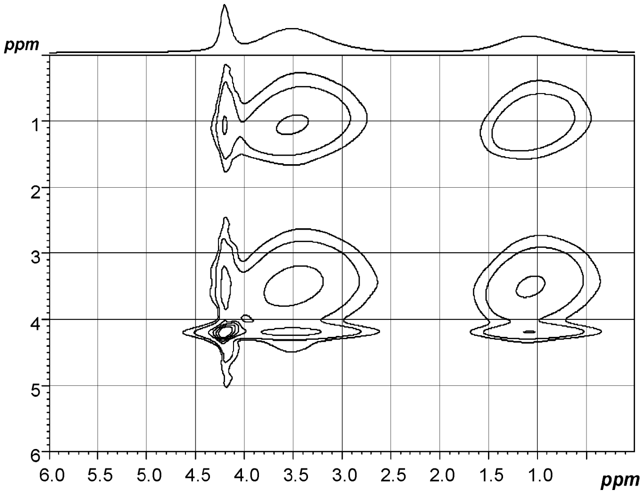

**Figure 17.** Two-dimensional NOE spectrum of PBT−PPP-25 with a mixing time of 400 ms. The cross-peaks have the same sign as the diagonal peaks.

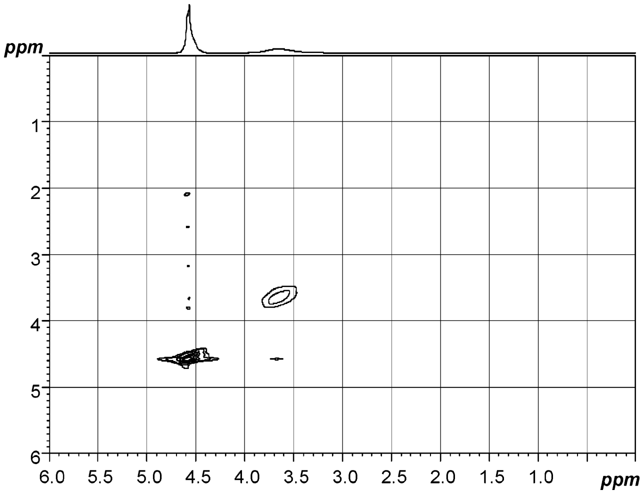

**Figure 18.** Two-dimensional NOE spectrum of PBT−PEO with a mixing time of 400 ms.

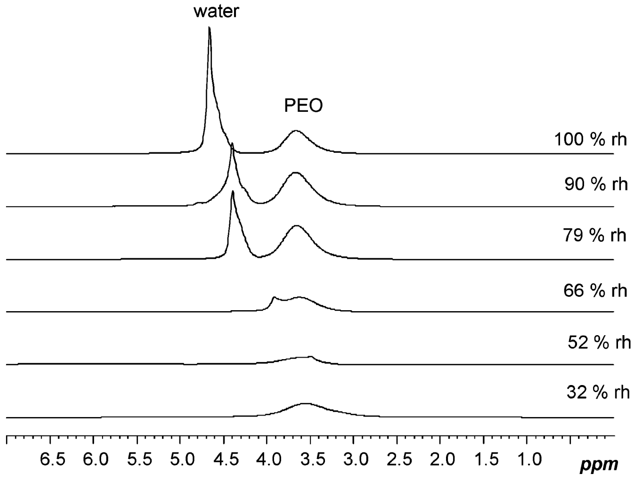

**Figure 19.** MAS NMR proton spectrum of PBT−PEO as a function of the relative humidity.

system more so than for PBT−PPP-55. The effect of the length of the residence time on cross-relaxation will be discussed below.

**3.5. Exchange Mechanism.** In Figure 12 we showed two situations that can lead to exchange effects in the diffusion curves. The difference between the two situations is only gradual; in case a the water molecule remaining near the polymer proton is hydrogen-bonded, while in case b such a formal bond does not exist. For both cases, however, the residence time of the water molecule near the polymer proton (distance < 0.5 nm) must be long enough for cross-relaxation to take place.

The existence of a formal hydrogen bond should affect the chemical shift of the water protons. The system for which it can be hoped to detect such a shift is the PBT−PEO copolymer. Here the water mobility is so high that the water resonance line is reasonably narrow and the resolution can be further enhanced by magic angle spinning (MAS). Figure 19 shows the proton MAS NMR spectra of PBT−PEO treated at different humidity.

Especially at higher humidity the water resonance and the single NMR line of the PEO segments can be resolved. As a function of the amount of absorbed water the water resonance shifts from under 3.5 ppm at RH = 52% to 4.8 ppm at RH = 100%. Apparently the first water molecules absorbed by the dry polymer strongly interact with the polymer. It is known from $^{1}$H and $^{2}$H relaxation studies on $^{17}$O-enriched water in PEO[14,15] that the intramolecular OH bond length of a water molecule near a PEO interface is significantly longer than in bulk water. This corresponds with an upfield shift, as observed in Figure 19. In addition it has been reported that hydration water molecules of PEO show a decreased mobility,[16] which explains why we do not observe a relatively narrow water signal for PBT−PPP-55 at a relative humidity of 32% (Figure 5).

At least for PBT−PEO the following simple model seems to apply. The first water molecules absorbed by the polymer system strongly interact with the polymer. At a higher relative humidity more water is absorbed and not all water molecules can be hydrogen bonded to the polymer; the PEO adsorption sites are saturated. Then two pools of water are built, one fraction of molecules near PEO and the other fraction more or less free. The distance between these two fractions is small so that during the NMR time scale molecules exchange between the two pools. The more water is absorbed the larger the pool of free water becomes and the more the exchange averaged chemical shift resembles the chemical shift of pure water. By comparing the two mechanisms for cross-relaxation depicted in Figure 12, we conclude that at least for PBT−PEO but probably also for the other systems the second mechanism describes the situation well. The water molecules near PEO segments are responsible for the cross-relaxation. This implies that the model we used to calculate the diffusion curves is too simple, while there we considered only one pool of water. This is another reason it is not worthwhile to fit the diffusion curves with the model presented in section 3.4.

**3.6. Residence Time.** The last question we have to answer is how long do water molecules stay near a PEO ether group. The MAS experiments on PBT−PEO suggest that water molecules exchange fast between the pool of free water molecules and molecules hydrogen-bonded to PEO. Nevertheless, the diffusion curves for PBT−PEO do not show a cross-relaxation effect and the two-dimensional NOE spectra for this system show no cross-peaks. This can be explained by a closer look at NOE experiments. The intensity of cross-peaks in two-dimensional NOE experiments is determined by the NOE cross-relaxation rate $\sigma^{\mathrm{NOE}}$, which for two like spins can be written as[7]

$$\sigma^{\mathrm{NOE}} = q\{6J(2\omega_0) - J(0)\} \quad (4)$$

where $J(\omega)$ is the spectral density at the frequency $\omega$ due to the fluctuating dipolar interaction between the two protons involved. This dipolar interaction fluctuates in time while the distance between and the orientation of the vector connecting the two protons is time dependent when the water molecule jumps from the pool of bulk water to the PEO ether group. The shorter the residence time the higher the fluctuation frequency of the dipolar interaction. The proton Larmor frequency is $\omega_0$, $2\omega_0$ represents the frequency of the double quantum transition $\alpha\alpha \leftrightarrow \beta\beta$ of the spin pair, and 0 represents the frequency of the zero-quantum transition $\alpha\beta \leftrightarrow \beta\alpha$; $q$ is a constant that depends among others on the gyromagnetic ratio of the nucleus. The sign and intensity of NOE cross-peaks are caused by the interplay of $J(2\omega_0)$ and $J(0)$, and the cross-relaxation effects in the diffusion curves by $J(0)$ alone.

Equation 4 makes clear that depending on the spectral densities the NOE cross-relaxation rate can be positive or negative; a negative NOE cross-relaxation $\sigma^{\mathrm{NOE}}$ causes a positive NOE cross-peak, as is observed in our spectra for PBT−PPP-25 and -55. In other words, for these two systems the spectral density $J(0)$ is larger than $J(2\omega_0)$, which points to a residence time of the water molecule near PEO longer than about 1 ns.[7]

Longer residence times cause a larger $J(0)$ and larger effects in stimulated echo diffusion curves. Although for PBT−PEO the MAS spectra indicate interactions between water and PEO, the NOE spectra show no cross-peaks and the diffusion curves show a cross relaxation effect only for long diffusion times. This can be explained when the exchange between the pool of free water and of hydrogen-bonded water is so fast that the residence time of water at PEO is shorter than in the other systems. This would make $J(0)$ small and of the same magnitude as $6J(2\omega_0)$. Therefore, the NOE cross-peaks for PBT−PEO will have a much smaller intensity.

From the combination of MAS, diffusion, and NOE experiments we can therefore conclude that the difference between the four systems for the effects we investigated lies in the length of the time the water molecules reside near PEO segments. For PBT−PPP-25 the polymer soft segment is so rigid that the water molecules can only slowly diffuse. Consequently the residence time of water near PEO in this system is relatively long and $J(0)$ large, resulting in strong cross-relaxation effects in the stimulated diffusion curves and strong NOE cross-peaks.

For PBT−PPP-55 the soft segment is less rigid (although this has no effect on the water diffusion coefficient), $J(0)$ is smaller, and the cross-relaxation effect and the NOE cross-peak intensity are smaller. For PBT−PEO the soft segments are so mobile that the water molecules exchange fast between a situation where they are more or less bonded to PEO segments and free water. This makes the residence time of water near PEO too small to be detected by 2D-NOE spectra or diffusion experiments.

## 4. Conclusions

From self-diffusion experiments on water in hard−soft block copoly(ether−ester) polymers, containing PEO units in the copolymer forming the soft segments, we find that the diffusion coefficient of water in such systems depends on the amount of absorbed water and the molecular mobility of the soft segments, which itself is affected by the degree of swelling of the soft segments. The amount of absorbed water increases with the fraction of PEO in the copolymer forming the soft segment.

It is found that the water molecules interact with the PEO unit in the soft segment; most likely a fraction of the water molecules is hydrogen-bonded to the ether group. Due to this interaction water and polymer protons can exchange spin magnetization, causing the water and the polymer self-diffusion coefficients determined by pulsed field gradient stimulated echo experiments to, some degree, be averaged.

From the experiments it has been derived that in all four investigated systems water molecules interact with polymer soft segments and that the amount of absorbed water increases with the fraction of PEO in the soft segment. On the other hand, the residence time of a water molecule near a PEO unit (distance less than 0.5 nm) in the soft segment decreases with increasing fraction of PEO units. The mobility of the soft segment seems to influence the time length of the interaction between water molecules and PEO segments. A decrease of the water residence time near PEO results in an increase of the water self-diffusion coefficient.

The only experimental observation which does not completely fit in this model is the observation that the water diffusion coefficient in PBT−PPP-55 is not faster than in PBT−PPP-25 (Table 3). According to the model described above the weaker cross-relaxation in PBT−PPP-55, relative to PBT−PPP-25, should correlate with faster water diffusion. The reason for this discrepancy is not clear. From the composition of both systems we see that the soft domains must have about the same size, only in PBT−PPP-25 there are less soft domains and more hard domains. A possible cause for the discrepancy may lie in the circumstance that water diffusion may be hindered by the crystalline PBT blocks. The existence of hindered diffusion could be established by changing the diffusion time Δ in the echo experiments. In the case of hindered diffusion the water diffusion coefficient would become dependent on the diffusion time. For the Hahn echo experiments varying Δ is not practical because the time window of such experiments in a solid is very limited. For the stimulated experiments this would be feasible, but here the interpretation will be complicated by the presence of cross-relaxation effects.

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