# Calibration of $^1$H NMR Spin Diffusion Coefficients for Mobile Polymers through Transverse Relaxation Measurements

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ABSTRACT: Solid-state $^1$H NMR spin diffusion experiments are useful tools for the elucidation of domain sizes of heterogeneous polymers. For quantitative determination of domain sizes, however, reliable values of the spin diffusion coefficients are required. In this paper, spin diffusion coefficients are calibrated for mobile polymers through the transverse relaxation rate $T_2^{-1}$ of $^1$H magnetization measured by a Carr−Purcell−Meiboom−Gill sequence. Different regimes were observed for $T_2^{-1}$ below and above 1 kHz.

## Introduction

Solid-state NMR $^1$H spin diffusion experiments[1] have been shown recently to be useful for determining the domain sizes of heterogeneous polymers. In particular, the technique has been applied to study domains in polymer blends,[2,3] of the morphology of latex particles,[4,5] and the water layer surrounding such particles in partially dried films.[6] In a spin diffusion experiment, the magnetization $M$ of one part of the system is selected, while the magnetization of the other part is suppressed. Subsequently, the diffusive flow of magnetization from the first to the second phase is monitored and analyzed using Fick's second law of diffusion:[7]

$$\partial M(r,t)/\partial t = \nabla(D(r,t)\,\nabla M(r,t)) \qquad (1)$$

where $D$ is the spin diffusion coefficient. Using solutions of this partial differential equation, domain sizes in a range of 1−100 nm[8,9] can be determined from the spin diffusion data. However, the determination of length scales by application of eq 1 requires the knowledge of the spin diffusion coefficients of the sample. For rigid phases below $T_g$, there exist already reliable spin diffusion coefficient values. For example, Clauss et al.[10] investigated well-characterized block copolymers of poly(methyl methacrylate) (PMMA) and polystyrene (PS), where the domain sizes could be determined independently by small-angle X-ray scattering (SAXS). For these samples, a spin diffusion coefficient of $D = 0.8$ nm$^2$/ms for the rigid phase was obtained. The determination of the spin diffusion coefficient for mobile phases is more involved, since it is particularly sensitive to different mobilities and thus very sample dependent. As it is not possible to measure both the spin diffusion coefficient of the mobile phase and its domain size at the same time in a spin diffusion experiment, a different strategy is required. In principle, the spin diffusion constant can be calculated by considering the exchange of magnetization in the presence of molecular motion.[11,12] However, this requires extensive calculations for each complex polymer system studied, and the results may not be reliable enough. A much simpler approach was presented by Spiegel et al.,[13] who sought to establish a dependence of the spin diffusion coefficient on the observed NMR spectral line width, using a polybutadiene−polystyrene block copolymer with known domain sizes, measured by transmission electron microscopy (TEM). In this way, it was hoped that the spin diffusion coefficient of a mobile phase could be reliably calibrated through an easily accessible NMR parameter, thus allowing the direct determination of domain sizes from the NMR spin diffusion experiment. However, as only three points with rather large error margins were measured by Spiegel et al.,[13] interpolations between them are problematic. Therefore, the aim of this work is to present an extended set of data points, obtained, as outlined below, using both a better defined NMR parameter and a more consistent method for determining the domain sizes.

The $^1$H NMR spin diffusion coefficient in a polymer phase is directly proportional to the dipolar induced transition probability between neighboring spins and thus to the through-space dipolar coupling of protons in the sample.[14,15] Therefore, in principle, spectroscopic parameters such as the line width of a proton NMR signal as used by Spiegel et al.[13] are indeed promising candidates as indirect probes for the spin diffusion coefficient. However, the line width, as measured directly from the $^1$H solid-state NMR spectrum of the sample, has the disadvantage that, in complex polymers, there is a dispersion of isotropic chemical shifts, and thus the measured line width overestimates the residual dipolar coupling in highly mobile systems. Additionally, if the spectral resolution is low, contributions from the shoulders of neighboring signals distort the measured line width. A more reliable means of probing polymer dynamics, especially in mobile phases, is to measure the transverse relaxation time $T_2$. Indeed, for a PEO sample (described below) the line width, $\nu_{fwhm}$, obtained from the $^1$H solid-state NMR spectrum was found to be 10 times greater than the transverse relaxation rate $T_2^{-1}$. For a Lorentzian, a factor of $\pi$ would be expected. This discrepancy is presumably a consequence of additional broadening due to a distribution of isotropic chemical shifts in such an amorphous system. In this paper, therefore, the dependence of the spin diffusion coefficient of mobile phases on the transverse relaxation rate $T_2^{-1}$, rather than the directly measured $\nu_{fwhm}$, is investigated.

## Experimental Section

**A. Samples.** The properties of the samples used in this investigation, namely three block copolymers and a blend

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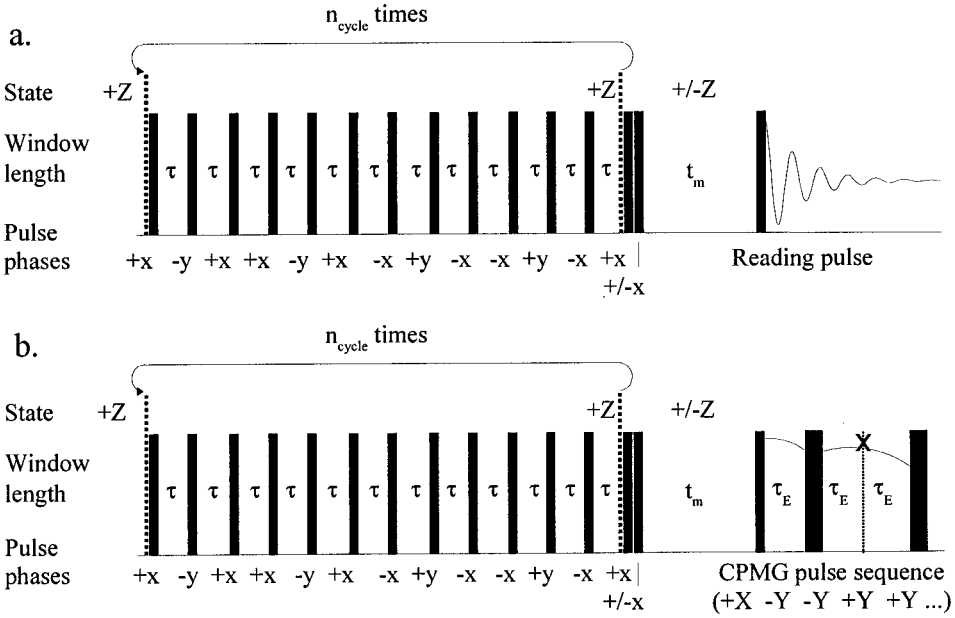


**Figure 1.** Pulse program and NMR phase cycles for (a) spin diffusion experiment and (b) an experiment to determine the transverse relaxation rate $T_2^{-1}$ of the mobile phase in heterogeneous polymers. Both experiments involve the application of a dipolar filter that selects the magnetization of the mobile phases.

sample, are summarized in Table 1. The lamellar block copolymers consisted of a mobile polyisoprene (PI) and a rigid polystyrene (PS) phase. Two chemically different PI polymers were used, with the 1,4-PI and the 1,2,3,4-PI (with olefinic side chains) having a $T_g$ of −60 and 0 °C, respectively. By altering the molecular weights of both phases, the PI and the PS phase, three different block copolymer samples were prepared. The polystyrene (PS) phase possessed $T_g$'s between 70 and 80 °C. The blend sample consisted of poly(ethylene oxide) (PEO) cylinders in a cross-linked poly(hydroxyethyl-methyl acrylate) (PHEMA) matrix. For all samples, the temperature was varied between 0 and 50 °C in order to obtain different $T_2$ relaxation times in the mobile phase.

As stated in the Introduction, the determination of spin diffusion coefficients requires the independent measurement of the domain sizes of the samples. In this study, the domain sizes were measured by SAXS, which has the advantage of yielding an average domain size for the whole sample. It should be noted that SAXS yields long periods in our case only for the lamellar samples PI20 to PI25. For sample PEO10, an average distance between cylinders is obtained that is defined by the inverse Fourier transform of the respective scattering curve. However, in contrast to SAXS measurements, where the whole sample contributes to the averaging, in transmission electron microscopy (TEM) micrographs, used in the previous study,[13] only a very small number of domains are visible. Additionally, TEM sample preparation ($OsO_4$ staining in case of the lamellar block copolymers and the cutting process) can induce artifacts. TEM measurements were nevertheless performed in order to establish that the samples were lamellar or contained cylinder-like mobile domains as expected.

**B. NMR Experiments**. NMR experiments were performed on a Bruker DSX spectrometer, operating at a $^1$H frequency of 300.22 MHz with a commercial *static* Bruker double-resonance probe. Our approach of investigating the dependence of the spin diffusion coefficient on the transverse relaxation rate $T_2^{-1}$ involved carrying out two different NMR experiments, first the actual spin diffusion experiment and second a Carr−Purcell−Meiboom−Gill (CPMG) experiment,[16,17] in order to determine the $T_2$ relaxation time of the mobile phase. In this section, these two experiments are described in detail.

In the spin diffusion experiment (Figure 1a) a dipolar filter[18] was used to achieve a magnetization modulation across the sample. The dipolar filter destroys the magnetization of the rigid phase, i.e., that with the higher $T_g$ in a dynamically heterogeneous multiphase system, in a manner very similar to a classical Goldman−Shen experiment.[19] The magnetization of the mobile phase with low $T_g$ is retained. The radio-frequency (rf) pulse sequence for the dipolar filter is described elsewhere.[18] Ten cycles of the dipolar filter together with window lengths of 10−15 $\mu$s between pulses were used. The 90° pulse length was 4 $\mu$s. After application of the dipolar filter the residual magnetization was stored on the $\pm Z$ axis (parallel to the magnetic field $B_0$) for a mixing time $t_m$, during which spin diffusion occurs and eventually equilibrates the inhomogeneous distribution of magnetization. The intensity of the highest peak (at 2 ppm) in the PI spectra was taken for each mixing time and corrected for longitudinal $T_1$ relaxation by measuring the signal decay for the same mixing time without the application of the dipolar filter. The corrections for $T_1$ are particularly relevant for long mixing times, where the spin diffusion curve showed a plateau at a value reflecting the fractions of both components (compare for example Figure 3a and the respective stoichiometric plateau (end) value in Table 1). This enables us to independently check that our $T_1$ corrections were appropriate (see ref 20, pp 326 and 423).

Using the intensities of the $^1$H solid-state NMR spectrum as data points for the spin diffusion curves, the problem arises that, at longer mixing times, the spectrum consists not only of the narrow line of the mobile component but also of a broad background from the remagnetized rigid phase. The presence of this background signal then leads to errors in the measured intensities. Therefore, to exclude all contributions from the broad background, a dead time delay of 50 $\mu$s together with a spectral width of only 12.5 kHz was used. This assured that, for every mixing time, the detected signal consisted of only that due to the magnetization of the mobile source (see Figure 2).

The $T_2$ relaxation curves were obtained using a Carr−Purcell−Meiboom−Gill (CPMG)[16,17] sequence which was preceded by a dipolar filter pulse sequence, with the same parameters as used in the corresponding spin diffusion experiment, to measure selectively the $T_2$ relaxation time of the mobile phase in the composite system (see Figure 1b). Besides the expected monoexponential decay, some samples also showed biexponential relaxation, presumably due to different relaxation rates of the different chemical groups within the monomer units of the mobile phases. The $T_2$ relaxation times were thus obtained by fitting the curves to a mono- or biexponential decay function, as appropriate. For biexponential

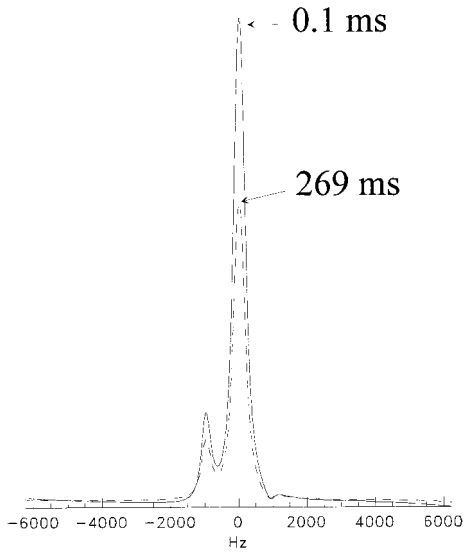


**Figure 2.** Comparison of spectra of PI25 during a spin diffusion experiment for 0.1 and 64 ms. While the magnetization of the rigid PS phase is suppressed in the spectra for 0.1 ms, it will be partly remagnetized after 269 ms. Nevertheless, the appearance of a broad PS background signal in the spectrum at 269 ms could be successfully prevented by using a long dead time of 50 $\mu$s and a spectral width of only 12 500 Hz. The spectrum at 269 ms was magnified approximately by a factor of 2 to allow a better inspection of the baseline.

decays, the relaxation time was computed as the weighted average of the two decay constants. The two relaxation constants were always rather similar, and $T_2$ values obtained from monoexponential and biexponential fits of the same data set agree within 10%.

## Results and Discussion

**A. Spin Diffusion Curves**. First, examples of the spin diffusion curves of the block copolymers are presented. The intensities of the highest peak at ca. 2 ppm of the PI are plotted against the square root of the mixing time, $\sqrt{t_m}$. The peak intensities $I$ are normalized with respect to the intensity at $t_m = 0$, $I_0$. Figure 3a shows a typical spin diffusion curve for a sample PI20 at room temperature (RT), where on account of the additional appearance of multiple quantum coherences for short mixing times,[20] this intensity at $t_m = 0$ cannot be measured directly. However, for small mixing times (1 ms < $t_m$ < 10−20 ms) the spin diffusion curves possess a linear slope (see discussion below), and the intensity at $t_m = 0$ ms can reliably be extrapolated from the first data points of the spin diffusion curve.[20]

The solid line in Figure 3a denotes the plateau (end) value of this spin diffusion curve, corresponding to the ratio of the mobile and rigid phases in the sample. In simple terms, the polymers investigated in this study can be considered to consist of separate mobile and rigid phases corresponding to the two components. However, there will of course exist interfaces between the two regions, in which the definition of the phase is less clear-cut. Thus, it is found that the spin diffusion plateau value varies, if the dipolar filter parameters are changed.[5] In our experiments, we adjusted the filter such that the experimental plateau value for each sample corresponded roughly to their stoichiometric proton ratio of the mobile phases. Those are equivalent to the stoichiometric plateau values which are listed in Table 1.

**B. Determination of Effective Spin Diffusion Coefficients $D_{eff}$.** A detailed account of spin diffusion

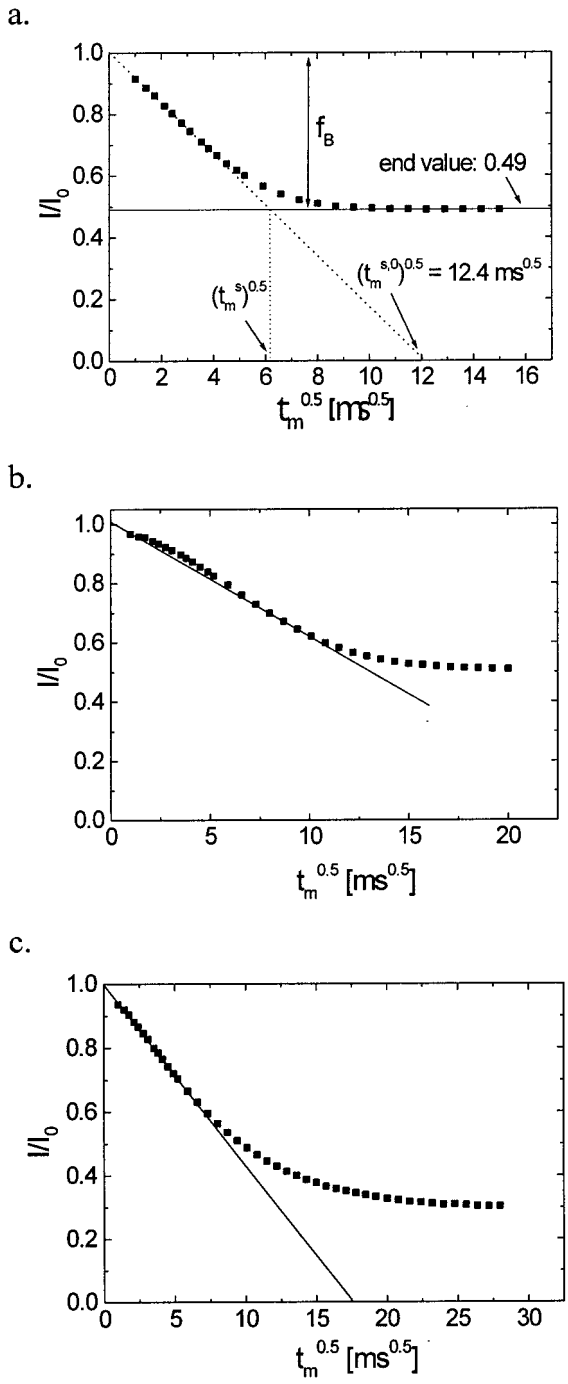


**Figure 3.** Spin diffusion curves, plotted as the normalized intensity $I/I_0$ against the square root of the mixing time for (a) PI20 at 26 °C, (b) PI25 at 70 °C, and (c) PEO10 at 100 °C. These graphs illustrate the following important features: (a) By the extension of the initial slope of the first linear points, the value $\sqrt{t_m}^{s,0}$ is obtained as the intercept of the dotted line with the $X$-axis, from which the desired spin diffusion coefficient is calculated, using eqs 3 and 5. Also shown is the difference between the values $\sqrt{t_m}^{s,0}$, used here, and $\sqrt{t_m}^{s}$, used in ref 20. (b) If the experiment temperature exceeds a certain limit, the initial part of the spin diffusion curve no longer has a linear behavior and thus cannot be used for the determination of the spin diffusion coefficients. The limiting temperature depends on the actual sample; the curve shown here was measured at 70 °C, 10 °C below the $T_g$ of the rigid PS phase. (c) For the PEO10 sample with only one chemical shift, the nonlinear behavior of the initial part of the spin diffusion curve does not appear even for transverse relaxation rates $T_2^{-1}$ as low as 34 Hz.

**Table 1. Sample Names and Composition**

| | PI20 | PI25 | PI24 | PEO10 |
|---|---|---|---|---|
| morphology | lamellar block copolymer | lamellar block copolymer | lamellar block copolymer | PEO cylinders (blend) in PHEMA matrix (cross-linked) |
| composition, wt % | PI(1,4)−PS 50:50 | PI(1,4)−PS 50:50 | PI(1,2;3,4)−PS 50:50 | PEO−PHEMA 20:80 |
| $T_g$(mobile), °C | −60 | −60 | 0 | −60 ($T_g$) +60 ($T_m$) |
| $T_g$(rigid), °C | +60 | +78 | +80 | +110 |
| mol wt | PI: 8900 PS: 10100 | PI: 12500 PS: 12900 | PI: 11300 PS: 12700 | PEO: 10000 PHEMA: ∞ |
| stoich plateau value | 0.54 | 0.57 | 0.54 | 0.21 |
| SAXS, nm (see text) | 17 (long period) | 20 (long period) | 18 (long period) | 18 (av distance between cylinders |

between two polymer phases has been given in refs 10 and 20, where it is shown that, for small $t_m$, $I/I_0$ is proportional to $\sqrt{t_m}$. As indicated by the dotted line in Figure 3a, the PI20 data fit this behavior, the so-called initial rate approximation, very well. The intercept of this dotted line with the $X$-axis yields the value $\sqrt{t_m^{s,0}}$, which is a measure for the diameter of the mobile phase, $d_{mobile}$:

$$d_{mobile} = \frac{2\epsilon}{\sqrt{\pi}}\sqrt{D_{eff} t_m^{s,0}} \qquad (2)$$

The value $\sqrt{t_m^{s,0}}$ can be considered as a measurable quantity for the magnetization exchange rate between the magnetization source and sink phase. The faster the magnetization exchange, the bigger the ratio between the surface and the volume of the magnetization source.[21] This, in turn, gives information about the diameter of the magnetization source if the morphology of this phase is known.

It should be noted that here the decreasing signal intensity of the magnetization source is detected rather than the increasing sink magnetization as in ref 20. Therefore, under the same mathematical assumptions, a plot of decreasing spin diffusion curves offers the additional possibility of using a differently defined parameter $\sqrt{t_m^{s,0}}$ in contrast to $\sqrt{t_m^{s}}$ of ref 20. $\sqrt{t_m^{s,0}}$ is determined by the intercept of the extrapolated linear initial decay with the $X$-axis (see Figure 3a). Using this parameter $\sqrt{t_m^{s,0}}$, the expression for $d_{mobile}$ does no longer depend on the volume ratio of sink/source, as is the case if $\sqrt{t_m^{s}}$ is used.[20] This feature is easily explained by the geometric relationship between $\sqrt{t_m^{s}}$ and $\sqrt{t_m^{s,0}}$: According to the definition of these two parameters (see Figure 3a), the ratio of $\sqrt{t_m^{s}}$ and $\sqrt{t_m^{s,0}}$ depicts nothing else than the volume ratio of the magnetization sink phase, $f_B$. Therefore, $f_B$, which is contained in eq 13.8 of ref 20, is no longer included in eq 2 (see above). Using $\sqrt{t_m^{s,0}}$, an expression for $D_{eff}$ in terms of measurable quantities is obtained by rearranging eq 2:

$$\sqrt{D_{eff}} = \frac{d_{mobile}\sqrt{\pi}}{2\epsilon\sqrt{t_m^{s,0}}} \qquad (3)$$

where $d_{mobile}$ is derived from the long period of the heterogeneities (as determined by SAXS). In eqs 2 and 3, $\epsilon$ is the number of orthogonal directions relevant for the spin diffusion process. Its value depends on the morphology and is 1 for lamellar block copolymers, 2 for phases with a cylinder-like morphology in a matrix, and 3 for discrete phases, for example spheres in a matrix.[10,20] The so-calculated square root of the effective spin diffusion coefficient, $\sqrt{D_{eff}}$, is defined as the geometric average of $\sqrt{D_{mobile}}$ and $\sqrt{D_{rigid}}$, divided by the arithmetic average of their square roots:[10,20]

$$\sqrt{D_{eff}} = \frac{\sqrt{D_{mobile} D_{rigid}}}{(\sqrt{D_{mobile}} + \sqrt{D_{rigid}})/2} \qquad (4)$$

The spin diffusion coefficient of the mobile phase is thus obtained by

$$\sqrt{D_{mobile}} = \frac{\sqrt{D_{eff}}\sqrt{D_{rigid}}}{2\sqrt{D_{rigid}} - \sqrt{D_{eff}}} \qquad (5)$$

As described in the Introduction, a value for the rigid phase spin diffusion coefficient of $D_{rigid} = 0.8$ nm$^2$/ms has been determined in a previous study;[10] using this value, $D_{mobile}$ can hence be calculated.

If the temperature is increased above a certain level, the spin diffusion curves of the PI block copolymers show a significant nonlinear behavior for small $t_m$, as illustrated in Figure 3b for PI25 at $T = 70$ °C. Such data then cannot be interpreted by the above method. The reason for this nonlinear behavior at low transverse relaxation rates $T_2^{-1}$ of the mobile phase is not yet clear. It may be related to the increasing resolution of two distinct chemical shifts in the $^1$H NMR spectrum of PI. The deviation from the predicted linear behavior can then be understood by noting that spin diffusion is a process between spins with the same resonance frequency: At high temperatures the two signals in the spectrum of PI do not overlap enough to allow flip-flop processes between aliphatic and olefinic protons. A more detailed discussion of this problem is presented in ref 22.

However, spin diffusion coefficients for very low transverse relaxation rates $T_2^{-1}$ could be obtained by using a blend of poly(ethylene oxide) (PEO) in a rigid cross-linked poly(hydroxyethylmethyl acrylate) matrix (PHEMA). The mobile PEO phase has only one chemical shift and did not show the initial nonlinear spin diffusion behavior even for transverse relaxation rates $T_2^{-1}$ as low as 107 Hz (see Figure 3c).

Figure 4a shows a plot of the spin diffusion coefficients, calculated as described above, against the transverse relaxation rate $T_2^{-1}$, as determined from the spin echo experiments. The measured data points cover a range of $T_2^{-1}$ from 100 to 3500 Hz. Up to 1000 Hz, they can all be described by an empirical curve (see the expanded region in Figure 4b):

$$D(T_2^{-1}) = (8.2 \times 10^{-6} T_2^{-1.5} + 0.007)\ \text{nm}^2/\text{ms}, \quad 0 < T_2^{-1} < 1000\ \text{Hz} \qquad (6)$$

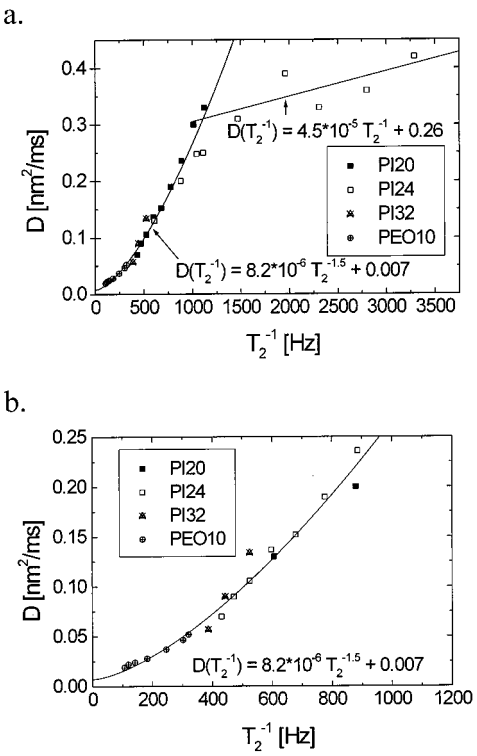


**Figure 4.** Dependence of the spin diffusion coefficients of the investigated samples on the transverse relaxation rate $T_2^{-1}$. From 0 to 1000 Hz, all data points are well described by a dependence $D \propto T_2^{-1.5}$. For values of $T_2^{-1}$ between 1000 and 3500 Hz, the data scattering increases considerably: Thus, it is appropriate to fit the data in this range to a simple linear function. In (b) the region corresponding to $0 < T_2^{-1} < 1000$ Hz is expanded.

This empirical correlation is valid for both the chemically different PEO and PI samples, indicating that the data points over this range appear to be sample independent. Instead of the usual diffusion unit $cm^2/s$, the unit $nm^2/ms$ is adapted to the microscopic sizes of heterogeneities in polymers and commonly used for spin diffusion experiments.[20]

Due to the inherent error of the data points, it is, however, not clear, whether the small *Y*-axis intercept of 0.007 $nm^2/ms$ of eq 6 is significant. It might be related to *physical* diffusion of the polymer chains. However, we refrain from a detailed analysis because of the complexity of magnetization transfer due to combined action of spin diffusion and physical diffusion,[11,12] where the translational motion is generally considered to be a minor contribution.[23]

In the range 1000−3500 Hz, both the quality of the correlation (much more scatter is observed) and the slope of the curve differ strongly from the first regime. Therefore, we describe the dependence by a simple linear function:

$$D(T_2^{-1}) = (4.4 \times 10^{-4} T_2^{-1} + 0.26)\ \mathrm{nm^2/ms}, \quad 1000 < T_2^{-1} < 3500\ \mathrm{Hz} \quad (7)$$

It is important to note that, as both eqs 6 and 7 are empirical, only interpolations within the range covered by the measured data points are meaningful. The extrapolation to spin diffusion coefficients beyond the indicated range is not possible by the means presented here. For values of $T_2^{-1} > 3500$ Hz of the mobile phase, the mobility contrast between mobile and rigid phase is rather low, and reliable data are not available.

In the previous study by Spiegel et al.,[13] spin diffusion coefficients were calibrated by correlating TEM measurement with $^1$H NMR line width. However, the chemical shift effects in polybutadiene (ratio aliphatic/olefinic protons: 2:1) are expected to be even larger than in polyisoprene (where the ratio is 7:1). Indeed, the spin diffusion coefficients reported by Spiegel et al.[13] do not correspond to those found here when the proton line widths $\nu_{fwhm}$ are considered.

## Conclusions

$^1$H NMR effective spin diffusion coefficients of PI−PS block copolymers and PEO−PHEMA blend samples have been determined from spin diffusion experiments, using domain sizes obtained from an independent characterization of the sample by SAXS. It has been shown that these spin diffusion coefficients can be correlated with the transverse relaxation rate $T_2^{-1}$, as determined by a Carr−Purcell−Meiboom−Gill (CPMG) experiment. If $T_2^{-1}$ is smaller than 1000 Hz, the dependence of the spin diffusion coefficient on $T_2^{-1}$ can be described by an empirical power law $T_2^{-1.5}$. Within this range, the data points obtained for all samples considered here are described by the same function, and it can be anticipated that eq 6 is also a good approximation for other systems, at least when they are chemically not too different. Previously, the line width of the $^1$H spectrum was used for calibration of the spin diffusion constant. This, however, reflects three contributions: chemical shift dispersions, residual dipolar couplings, and the transverse relaxation rate $T_2^{-1}$. Their relative weights are not always clear. In the CPMG experiment we separately measure $T_2^{-1}$, which depends on the molecular dynamics but is independent of chemical shifts and residual dipolar couplings. Therefore, the calibration is better defined. On the other hand, the relationship between $T_2^{-1}$ and the spin diffusion constant is not a simple one. Indeed, we empirically find a second regime for larger values of $T_2^{-1}$, where in the range between 1000 and 3500 Hz the spin diffusion coefficient scales linearly with $T_2^{-1}$. The quality of the correlation, however, was considerably poorer.

It should be further noted that a closer inspection of eq 3 reveals that only the square root of the spin diffusion coefficients enter the formula for the determination of the domain sizes. Thus, even if there is significant error in the so-calibrated spin diffusion coefficients, the error for the domain sizes so determined by spin diffusion experiments is largely reduced. Therefore, the determination of domain sizes in heterogeneous polymer samples by a combination of $^1$H NMR spin diffusion and $T_2$ relaxation methods represents a promising method for complex systems.

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