

# polymer communications

## $^1\text{H}$ spin diffusion coefficients of highly mobile polymers

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Advanced solid-state n.m.r. techniques using  $^1\text{H}$  spin diffusion are useful tools for the non-destructive investigation of polymer morphologies and domain sizes. Calibration measurements of the spin diffusion coefficients are reported in this communication, combining  $^1\text{H}$  spin diffusion with  $^{13}\text{C}$  detection and electron microscopic measurements on a diblock copolymer of known morphology. The spin diffusion coefficients thus determined can now be used for quantitative determination of domain sizes in systems containing both rigid and mobile components.

(Keywords: n.m.r. spectroscopy; diblock copolymers; phase separation)

### Introduction

Tailor-made polymer materials with adjustable property profiles can be obtained through combining the different properties of individual components in polymer blends and copolymers. These properties are often a linear function of the composition, but synergistic or anti-synergistic effects can result depending on the polymer-polymer interaction. Dynamic and mechanical properties are highly dependent on the compatibility of the components, which determines their morphology<sup>1</sup>. This polymer morphology is also influenced by heat treatment and ageing. Therefore, the characterization of the microphases and morphologies is important for an understanding of the relation between microscopic structures and macroscopic behaviour.

Common tools for examining microscopic structures are techniques such as electron microscopy, X-ray, neutron and light scattering<sup>2</sup>. The microphase structure can also be investigated in a non-destructive manner by solid-state n.m.r., exploiting  $^1\text{H}$  spin diffusion<sup>3-5</sup>.  $^1\text{H}$  spin diffusion experiments make use of the homonuclear dipolar interaction of the abundant  $^1\text{H}$  nuclei. In contrast to scattering techniques, n.m.r. does not rely on periodic structures in the sample. Furthermore, no particular sample preparation for contrast enhancement is needed, as the selection or suppression of certain components depends only on their n.m.r. spectroscopic parameters.

A prerequisite for the quantitative determination of domain sizes from  $^1\text{H}$  spin diffusion experiments is a knowledge of the  $^1\text{H}$  spin diffusion coefficient. By advanced solid-state n.m.r. techniques, i.e.  $^1\text{H}$  spin diffusion with high resolution  $^{13}\text{C}$  magic angle spinning (MAS) detection<sup>6,7</sup>, spin diffusion coefficients of rigid polymers have recently been determined<sup>8</sup>. It is even more desirable to exploit these techniques for systems where one of the components is much more mobile than the other, since n.m.r. yields detailed information about molecular dynamics<sup>6</sup>, which through spin diffusion can be related to the microphase structure<sup>9-11</sup>. Therefore, this communication presents the calibration of the spin diffusion coefficient for mobile systems, using

polystyrene-polybutadiene diblock copolymer samples of known domain dimensions, as determined by electron microscopy.

### Description of the spin diffusion techniques

As described in detail elsewhere<sup>6-8</sup>,  $^1\text{H}$  spin diffusion experiments consist of three steps, namely selection of the magnetization of one component, magnetization transfer during a mixing time  $t_m$ , and the subsequent detection of the resulting distribution of magnetization in the n.m.r. spectrum. In the first step of the experiment, a non-equilibrium state of the  $^1\text{H}$  magnetization is prepared by  $^1\text{H}$  multiple pulse techniques, selecting the magnetization of one component within the investigated sample. The components can be distinguished by differences in their mobilities, as well as by differences in their  $^1\text{H}$  chemical shifts, which result from differences in the chemical structures. In the next step, the equilibration of the magnetization occurs by magnetization transfer between the different components during a mixing time  $t_m$ . The magnetization transfer can be described by a diffusion equation:

$$dM(\vec{r}, t)/dt = \nabla[D(\vec{r})\nabla M(\vec{r}, t)] \quad (1)$$

where  $M(\vec{r}, t)$  is the time-dependent and spatially dependent  $^1\text{H}$  magnetization. The diffusion coefficient  $D(\vec{r})$  is generally also a function of the position since the properties of a sample are spatially dependent, e.g. in the different phases in block copolymers. In the final step, the resulting distribution of  $^1\text{H}$  magnetization after different mixing times  $t_m$  is detected in the n.m.r. spectrum.

Numerical solutions of the diffusion equation (1) are used for the simulation of the magnetization transfer. In this simulation, different model structures<sup>8</sup> can be used, depending on the dimensionality of the diffusion process. The build-up of magnetization as a function of time can then be fitted by such spin diffusion curves. If  $D(\vec{r})$  is known, the fit yields the domain sizes. On the other hand, if the domain sizes in a sample with well-defined morphology are known, the fit yields the spin diffusion coefficient  $D$ . The values of  $D$  determined in this way can then be compared to those expected from the  $^1\text{H}$  linewidths of the corresponding mobile phase  $\Delta\nu_{1/2}$ , since

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both  $D$  and  $\Delta v_{1/2}$  are governed by the dipolar coupling. In fact, for rigid systems one has<sup>8,12</sup>:

$$D \propto \Delta v_{1/2} \langle a^2 \rangle \quad (2)$$

where  $\Delta v_{1/2}$  is the full width at half height of the  $^1\text{H}$  signal and  $\langle a^2 \rangle$  is the average of the square of the nearest distance of the protons. It is by no means obvious that this simple relation is also valid for mobile systems where the dipolar interaction is largely averaged. In this study we show that  $D$  should be calibrated through spin diffusion measurements on well-defined systems with known domain sizes.

### Experimental

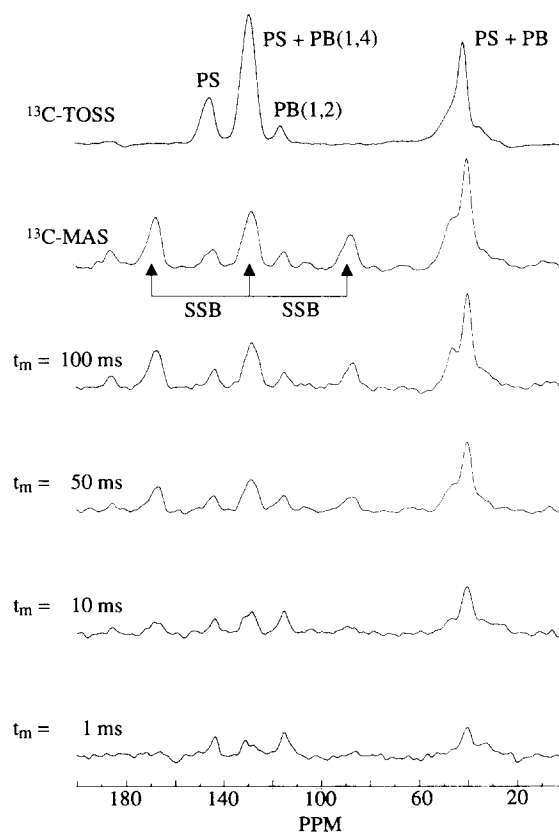
The calibration system used for the measurements is a polystyrene-polybutadiene diblock copolymer, with a molecular weight  $M_w = 20\,000$  for the polystyrene and  $M_w = 40\,000$  for the polybutadiene and a polystyrene volume fraction of 0.30. Since there is a high proportion of 1,2-polybutadiene, the glass transition of the polybutadiene is detected by d.s.c. at about 238 K. Thus, at ambient temperatures the polybutadiene is well above its glass transition and is mobile, whereas the polystyrene is rigid. The  $^1\text{H}$  linewidth of the polybutadiene component depends markedly on temperature. Thus, by performing  $^1\text{H}$  spin diffusion experiments at different temperatures, the relation between  $\Delta v_{1/2}$  and  $D$  can be established. The morphology determined by electron microscopy is cylindrical, as expected for the given volume fraction<sup>1,13</sup>; the polystyrene cylinders have a diameter of 11 nm.

All reported solid-state n.m.r. experiments were carried out on a Bruker MSL-300 spectrometer with a standard Bruker  $^1\text{H}$ - $^{13}\text{C}$  double-resonance MAS probe head, using  $90^\circ$   $^1\text{H}$  and  $^{13}\text{C}$  pulse lengths between 3.5 and 4.0  $\mu\text{s}$  and a MAS spinning rate of 3 kHz. The magnitude of the magnetic field is 7.05 T, which results in resonance frequencies of 300.13 and 75.47 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. The  $^1\text{H}$  magnetization of the highly mobile polybutadiene component is selected by a  $^1\text{H}$  multiple pulse technique, known as the 'dipolar filter'<sup>9,10</sup>, using seven filter cycles each consisting of 12  $90^\circ$   $^1\text{H}$  pulses separated by a delay time of 10  $\mu\text{s}$ . Differences in mobility result in different strengths of the dipolar couplings and therefore allow the selection of the mobile component. The exchange of the  $^1\text{H}$  magnetization is detected by the increasing intensity of the polystyrene signals with increasing mixing times  $t_m$ , here called the 'spin diffusion time'. Because of the higher resolution in the  $^{13}\text{C}$  cross polarization (CP)/MAS n.m.r. spectrum, the  $^1\text{H}$  magnetization is not detected directly in the  $^1\text{H}$  n.m.r. spectrum, but in the  $^{13}\text{C}$  n.m.r. spectrum after polarization transfer by CP. Typically 2000 to 3000 scans were accumulated for every spectrum, with a repetition delay of 3 s and mixing times between 1 and 1000 ms. Thus spin diffusion data can be obtained in a reasonable time; spectra of higher quality are not essential.

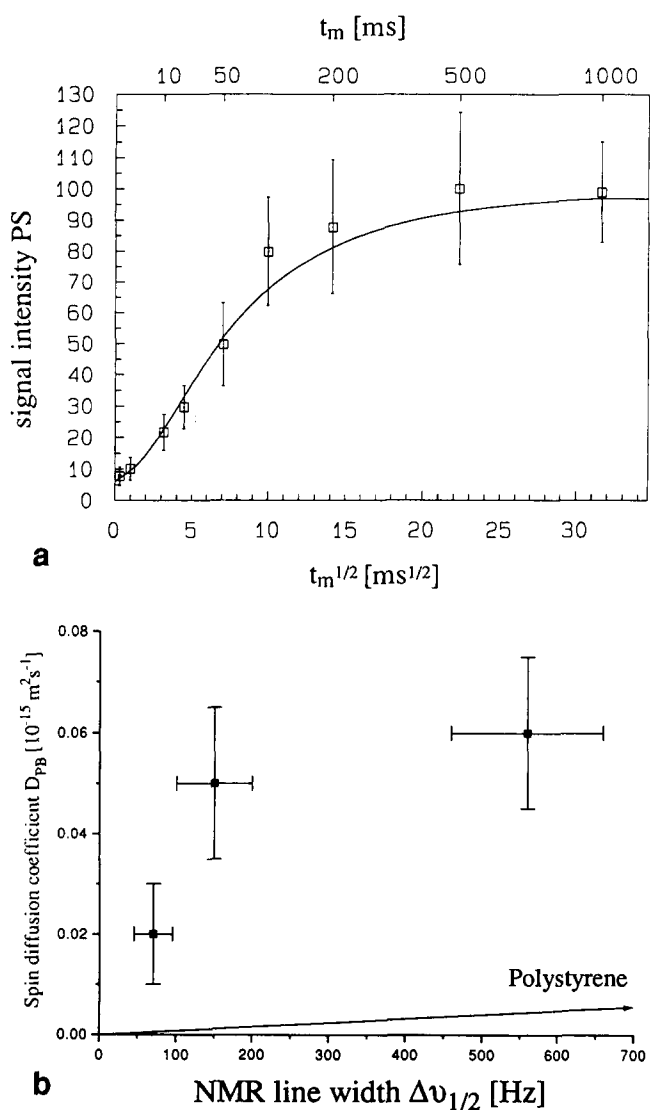
### Results and discussion

Typical  $^{13}\text{C}$  n.m.r. spectra obtained in a spin diffusion experiment are plotted in Figure 1, together with a CP/MAS spectrum and one in which the spinning sidebands are eliminated by the total suppression of sidebands (TOSS) sequence<sup>14</sup>. The most intense polystyrene signal in the  $^{13}\text{C}$  n.m.r. spectrum at 127 ppm overlaps with a signal of the 1,4-polybutadiene. Therefore

an accurate determination of the polystyrene intensity is hardly possible by following the intensity of the central band. However, strong spinning sidebands (SSB) are observed for the aromatic polystyrene signals, whereas they vanish for the highly mobile polybutadiene<sup>15</sup> (see Figure 1). The polystyrene peak at 147 ppm would allow the direct measurement of a polystyrene signal but its intensity is rather low. Thus the more intense first-order sidebands (at 167 and 87 ppm) were used to monitor the build-up of the polystyrene magnetization. The spectra for the different mixing times  $t_m$  are corrected for the loss of absolute intensity caused by longitudinal ( $T_1$ ) relaxation. The correction factor  $\exp(t_m/T_1)$  was obtained from spectra taken with the same pulse sequence but without selection, i.e. without applying the dipolar filter; for a detailed discussion see ref. 6. The bottom spectrum, recorded with a very short spin diffusion time,  $t_m = 1$  ms, demonstrates the effect of the dipolar filter resulting in a total suppression of the polystyrene signals, clearly visible, for example, from the vanishing intensity of the spinning sidebands. Although spin diffusion as described before involves only an exchange of  $^1\text{H}$  magnetization, one can observe an initial increase of the total intensity of the  $^{13}\text{C}$  n.m.r. spectra with increasing spin diffusion time  $t_m$ . This is due to the fact that the efficiency of the polarization transfer from  $^1\text{H}$  to  $^{13}\text{C}$  by CP depends on the strength of the heteronuclear dipolar coupling<sup>16</sup>. This is significantly smaller for the mobile polybutadiene than



**Figure 1**  $^1\text{H}$  spin diffusion experiment at 297 K after selecting the mobile polybutadiene component, with the indicated spin diffusion times  $t_m$ . The increasing intensity of polystyrene signals is detected in the  $^{13}\text{C}$  CP/MAS n.m.r. spectrum after polarization transfer. Top two rows:  $^{13}\text{C}$  CP/MAS n.m.r. spectrum with total suppression of spinning sidebands using the TOSS pulse sequence<sup>14</sup> and  $^{13}\text{C}$  CP/MAS n.m.r. spectrum exhibiting spinning sidebands (SSB) at  $\pm 40$  ppm due to the macroscopic rotation of the sample under MAS conditions with a spinning frequency of 3000 Hz



**Figure 2** (a) Mixing time dependence of experimental intensities of polystyrene spinning sidebands after  $^1\text{H}$  spin diffusion at 297 K. Solid line: simulation for a two-dimensional model with a polystyrene cylinder 11 nm in diameter, based on electron microscopy. (b) Dependence of the  $^1\text{H}$  spin diffusion coefficient of polybutadiene on the  $^1\text{H}$  n.m.r. linewidth; increasing mobility leads to decreasing linewidth and decreasing diffusion coefficient. The solid line represents an extrapolation based on equation (2) with constant  $\langle a^2 \rangle$

for the rigid polystyrene. With increasing spin diffusion time, increasing portions of  $^1\text{H}$  magnetization are found in the polystyrene component. Therefore, the overall efficiency of polarization transfer increases, resulting in the observed increase of integral intensity in the  $^{13}\text{C}$  n.m.r. spectra.

The polystyrene intensities for spin diffusion times  $t_m$  between 1 and 1000 ms at 297 K are plotted as a function of the square root of  $t_m$  in Figure 2a. A plateau indicating the equilibrium of magnetization is reached after a spin diffusion time of about 1000 ms. The time dependence of the magnetization is simulated by a two-dimensional model with the known parameters for cylinder diameter and macroscopic composition. Only the diffusion coefficient of the mobile polybutadiene component is used as an adjustable parameter for fitting the experimental data. Since both blocks are incompatible, the spin diffusion coefficient  $D_{\text{PB}}$  is assumed to be independent of the position  $\vec{r}$  within the polybutadiene phase. The resulting

simulation with a spin diffusion coefficient of  $D_{\text{PB}} = 0.05 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$  is shown as the solid line in Figure 2a. Similar experiments were carried out at 283 and 343 K and analysed in an analogous way. The results are collected in Table 1. In addition to the values of the spin diffusion coefficients  $D_{\text{PB}}$ , the  $^1\text{H}$  linewidths  $\Delta\nu_{1/2}$  as measured from  $^1\text{H}$  one-pulse n.m.r. spectra are given. Under these conditions the broad  $^1\text{H}$  n.m.r. line of polystyrene with a width of about 50 kHz gives only a negligible contribution to the baseline in the region of the sharp polybutadiene lines. The  $^1\text{H}$  linewidths of the polybutadiene at various temperatures were determined by fitting the spectra using isotropic chemical shifts of polybutadiene in solution<sup>17</sup>. The relation between  $D_{\text{PB}}$  and  $\Delta\nu_{1/2}$  is displayed in Figure 2b. As expected from equation (2), the diffusion coefficient decreases with decreasing linewidth because of the shrinking strength of the dipolar interaction. However, there is no simple linear dependence and the values are about one order of magnitude larger than one would obtain from a direct extrapolation of a rigid polymer according to equation (2), shown by the solid line. This was calculated by considering polystyrene with a  $^1\text{H}$  n.m.r. linewidth of about 50 kHz and a  $^1\text{H}$  spin diffusion coefficient<sup>8</sup> of  $0.8 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ . The spin diffusion coefficient of polybutadiene at 297 K with a  $^1\text{H}$  n.m.r. linewidth of about 150 Hz would then be expected to be  $0.002 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$  rather than  $0.05 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ .

### Conclusions

This study demonstrates appreciable  $^1\text{H}$  spin diffusion even for a highly mobile polymer with weakened dipolar interaction. The decrease of the  $^1\text{H}$  spin diffusion coefficient with decreasing dipolar interaction, and thereby decreasing  $^1\text{H}$  n.m.r. linewidth, is confirmed. However, in this regime of partially narrowed  $^1\text{H}$  n.m.r. lines there is no linear dependence between diffusion coefficient and linewidth. Calibration measurements, such as those presented here, are necessary for the quantitative application of  $^1\text{H}$  spin diffusion experiments, in particular as the resulting spin diffusion coefficients of highly mobile polymers are about one order of magnitude larger than an extrapolation from values of rigid polymers would yield. However, for linewidths below 100 Hz, such as in polybutadiene at 343 K, the simple approach used here may not be justified. Such narrow lines should therefore be avoided in quantitative measurements. Apparently the spin diffusion coefficient is relatively insensitive to the  $^1\text{H}$  n.m.r. linewidth in the range of 300–600 Hz. Thus domain sizes can be determined by spin diffusion experiments not only for rigid polymers<sup>8</sup> but also in cases where one of the components is rather mobile. In fact, this has been exploited already in one study of poly(styrene-*b*-methylphenylsiloxane) diblock copolymers<sup>10</sup>, resulting in domain sizes consistent with X-ray scattering and electron microscopy. Therefore, spin

**Table 1**  $^1\text{H}$  spin diffusion coefficients  $D_{\text{PB}}$  and  $^1\text{H}$  n.m.r. linewidths  $\Delta\nu_{1/2}$  of polybutadiene at different temperatures

$T$ (K)	$D_{\text{PB}}$ ( $10^{-15} \text{ m}^2 \text{ s}^{-1}$ )	$\Delta\nu_{1/2}$ (Hz)
283	$0.06 \pm 0.015$	$560 \pm 100$
297	$0.05 \pm 0.015$	$150 \pm 50$
343	$0.02 \pm 0.010$	$70 \pm 25$

diffusion techniques can be applied to yield quantitative results in a wide range of heterogeneous polymers such as block copolymers, polymer blends and semicrystalline polymers.

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