A solid-state n.m.r. study of microphase structure and segmental dynamics of poly(styrene-*b*-methylphenylsiloxane) diblock copolymers

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Solid-state n.m.r. techniques have been used to study the microphase structure of poly(styrene-*b*-methylphenylsiloxane) (PS-*b*-PMPS) diblock copolymers with different compositions and molecular weights. The proton n.m.r. spectra display motionally narrowed lines of the PMPS component at ambient temperatures. The mobility of the segments in the copolymers is different, however, from that in the homopolymer. This can be related to the shift of the glass transition temperature (T_g) for the siloxane-rich phase, not detected by d.s.c. By measuring the proton spin diffusion with ^{13}C detection—combining a dipolar filter with line-narrowing techniques—the microdomain dimensions have been evaluated quantitatively. The results are compared with determination of the phase separation by SAXS and TEM. It is shown that solid-state n.m.r. is able to detect heterogeneities on a scale as small as 2 nm in systems that exhibit only a single T_g in the d.s.c. measurement. In addition, an interphase in the phase-separated PS-*b*-PMPS systems is revealed by spin diffusion measurements and confirmed by two-dimensional heteronuclear wideline separation n.m.r. spectroscopy.

(Keywords: n.m.r. spectroscopy; diblock copolymers; poly(styrene-*b*-methylphenylsiloxane); phase separation; molecular dynamics)

INTRODUCTION

The microphase structure of block copolymers is a research subject of both scientific and practical importance. Various experimental techniques are available to study the heterogeneity in these materials[1,2], the simplest and most commonly used one being thermal analysis, e.g. d.s.c. In phase-separated, heterogeneous systems the glass transition temperatures (T_gs) of the individual phases are observed. They often differ, however, from those of the pure components. For homogeneous systems a single T_g is obtained. Electron microscopy has been widely used for directly observing the phase morphology and domain sizes. X-ray scattering is a powerful method for studying the phase separation process and determining microdomain sizes. Other techniques such as dielectric relaxation, dynamic mechanical analysis, etc., also provide information in particular about dynamic processes in the microphases.

Recent developments in high-resolution solid-state n.m.r. provide new possibilities in this area[3,4]. N.m.r. signals of solid samples are broadened by dipole–dipole interactions and anisotropic chemical shifts. These may be partially averaged by various kinds of molecular motions. The n.m.r. lineshape then contains useful information about the structure and dynamics of the molecules in the solid. Of particular interest in block copolymers is the interaction between the different components, especially in the interfacial region. The higher the mixing level, the stronger is the interaction between the components resulting in a greater modification of the n.m.r. spectrum relative to that of the pure components. Therefore the deviation of the spectrum of the copolymer from the superposition pattern of the constituent homopolymers allows a direct judgement of the phase structure.

The detailed determination of structural heterogeneity and domain dimension is mainly based on observing the time dependence of nuclear magnetization transfer from one distinct part of the spin system to another by spin diffusion[5]. This magnetization transport is achieved by the magnetic dipole–dipole interaction. On the one hand, the nuclear environment can be probed down to a scale of below 1 nm, on the other hand the magnetization can migrate over a significant distance, so that domain dimensions in a range of tens of nanometres can be detected. Indeed, various spin diffusion techniques have been used to probe chemical or physical heterogeneities in polymer systems[6–9].

The spin diffusion experiment consists of three sections. An initial pulse sequence selects the nuclear magnetization in one of the components, producing a magnetization gradient in the phase boundary. In the subsequent 'mixing' time, the magnetization can redistribute in space by 'spin diffusion'. The integral distribution of magnetization between the phases is detected afterwards in

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the n.m.r. spectrum. One of the crucial steps in this method is the selection of magnetization which can be achieved by exploiting motion or chemical shift differences between the components. The Goldman–Shen pulse sequence[10], for instance, selectively destroys the magnetization of the rigid phase and keeps that of the mobile species. It has been widely applied to characterize the domain structure in block copolymers, polymer blends and other heterogeneous polymer systems[11–15]. Spin diffusion is favourable for this purpose, provided the nuclear magnetization in one of the phases in the system can be selected and the n.m.r. lines for the different components are resolved. The rate of spin diffusion between the different components reflects their mixing level and gives information about the domain size. In order to exploit the chemical shift difference of the components, a multiple-pulse sequence of selective excitation has been applied to determine the phase structure of polymer blends[16,17]. Combined rotation and multiple pulse spectroscopy (CRAMPS) was employed in both the selection (preparation) and detection periods, in order to narrow the proton n.m.r. lines. Recently, another advanced method for studying the phase structure by proton spin diffusion has been introduced[18]. There, again a selection technique based on ^{1}H chemical shifts resolved by CRAMPS, the 'chemical shift filter', is used. High spectral resolution in the detection period, after spin diffusion has taken place, is achieved by taking a magic angle spinning (MAS) ^{13}C spectrum after transfer of the proton magnetization to carbons via cross-polarization (CP). The selection of ^{1}H magnetization in this experiment can also be based on motional differences, e.g. using the simple Goldman–Shen selection or the 'dipolar filter' pulse sequence[19]. Applications to semi-crystalline polymers and polymer blends[18–20] have already been reported.

In the present work, the dipolar filter with spin diffusion is used to characterize the microphase structure in poly(styrene-*b*-methylphenylsiloxane) (PS-*b*-PMPS) diblock copolymers with different compositions. For these copolymers, the molecular dispersity can be finely controlled during 'living' anionic polymerization. Variations of the microphase structure at ambient temperature are expected for different compositions because of the limited compatibility of styrene and methylphenylsiloxane monomers and the upper critical solution temperature phase behaviour of the block copolymers. The T_gs of homopolymer polystyrene (PS, $T_g = 373$ K) and PMPS ($T_g = 245$ K) measured by d.s.c. differ by ~130 K, which indicates the large difference of molecular mobility between the two kinds of polymer chains. This is of benefit in the solid-state n.m.r. study, and allows for the use of the dipolar-filter method. Moreover, the dependence of phase separation of the copolymers on their molecular mass and composition has been studied by SAXS and TEM[21]. Thus the results of the different techniques can be directly compared.

As for studying the microheterogeneity of the molecular dynamics, n.m.r. is a powerful tool. A recently developed two-dimensional (2D) heteronuclear wideline separation (WISE) n.m.r. technique[22] is particularly suitable for this purpose. By means of this experiment, the wide ^{1}H n.m.r. lines, overlapping completely in the conventional one-dimensional (1D) ^{1}H spectrum, can be spread out according to the chemical shifts of the corresponding carbon nuclei. The molecular dynamics can thus be correlated with the chemical structure. The heterogeneity of the mobility is exposed directly by the ^{1}H lineshapes of different chemical groups. It is of special significance in the case of low contrast of the mobilities, e.g. in the interfacial region of copolymers. In this work, the 2D method is used to unravel the heterogeneity of the mobility in the system, which can hardly be detected by conventional experimental techniques, and particularly the mobility in the mixed interphase region.

EXPERIMENTAL

Samples

A series of PS-*b*-PMPS diblock copolymers, as well as the homopolymer PMPS were synthesized by anionic ring-opening polymerization of 1,3,5-trimethyl-1,3,5-triphenyl-cyclotrisiloxane. Details of the polymerization procedure and sample characterization are published elsewhere[23]. For convenience, the compositions and characterization of the samples are given in *Table 1*. The molecular weights were determined by g.p.c. to be in the range from $M_w = 11\,800$ to $70\,000\,\mathrm{g\,mol^{-1}}$ for the copolymers, and from $M_w = 6200$ to $33\,600\,\mathrm{g\,mol^{-1}}$ for the PMPS blocks. G.p.c. measurements were made with a silica gel column with tetrahydrofuran as eluent and a calibration curve based on PS standards. The T_gs were determined by d.s.c. (Perkin-Elmer DSC 7) at a heating rate of $20\,\mathrm{K\,min^{-1}}$. The samples span a considerable range of block lengths and display different morphologies as discussed in references 21 and 23 and in the following text.

N.m.r. measurements

^{1}H and ^{13}C n.m.r. spectra were recorded on a Bruker MSL-300 n.m.r. spectrometer equipped with a standard Bruker CP/MAS probehead. All the samples were spun

Table 1 Sample characterization

<table>
<tr><th>Polymer</th><th>M_w(copolymer) ($\mathrm{kg\,mol^{-1}}$)</th><th>M_w/M_n</th><th>Φ_{PMPS}[a] (mol%)</th><th>M_w(PMPS) ($\mathrm{kg\,mol^{-1}}$)</th><th>T_{gl}[b] (K)</th><th>T_{gh}[b] (K)</th></tr>
<tr><td>C-1</td><td>70</td><td>1.06</td><td>41</td><td>33.6</td><td>245</td><td>364</td></tr>
<tr><td>C-2</td><td>61</td><td>1.06</td><td>37</td><td>26.2</td><td>245</td><td>370</td></tr>
<tr><td>C-3</td><td>60</td><td>1.03</td><td>21</td><td>15.6</td><td>247</td><td>353</td></tr>
<tr><td>C-4</td><td>48</td><td>1.06</td><td>16</td><td>9.6</td><td colspan="2">348</td></tr>
<tr><td>C-5</td><td>28</td><td>1.12</td><td>26</td><td>9.0</td><td colspan="2">335</td></tr>
<tr><td>C-6</td><td>11.8</td><td>1.12</td><td>45</td><td>6.2</td><td colspan="2">258–348</td></tr>
<tr><td>PMPS</td><td>48</td><td>1.04</td><td></td><td>48</td><td>245</td><td></td></tr>
<tr><td>PS</td><td>50</td><td>1.06</td><td></td><td></td><td></td><td>373</td></tr>
</table>

[a] ϕ_{PMPS}, mole fraction of PMPS in the samples

[b] T_{gl} and T_{gh}, T_g measured by d.s.c. in the lower (l) and higher (h) temperature regions, respectively

at frequencies of ~4 kHz. The 90° pulse lengths were in the range of 3.4–3.8 μs. During the detection of the ^{13}C magnetization, dipolar decoupling (DD) and the total suppression of sidebands (TOSS) were used to eliminate the large ^{13}C–H dipolar coupling and the spinning sidebands, respectively. The dipolar filter is discussed below and described in reference 19 and the WISE heteronuclear pulse sequence is discussed in detail in reference 22. All chemical shifts (^1H and ^{13}C) are given relative to tetramethylsilane.

RESULTS AND DISCUSSION

Lineshapes of proton n.m.r. spectra

The molecular dynamics of the segments in the copolymer blocks PS and PMPS are vastly different at room temperature. This is reflected in very different ^1H wideline spectra. In order to obtain an overview of the degree of phase separation, proton n.m.r. spectra at ambient temperature for different PS–PMPS block copolymers were recorded and are displayed together with those of the pure homopolymers in *Figure 1*. The spectrum of the homopolymer PMPS (*Figure 1a*) consists of separated narrow lines corresponding to the methyl and phenyl groups, reflecting the high molecular mobility. In contrast, the PS spectrum is a featureless broad line with a width of ~40 kHz. With the single pulse excitation used to record the spectra displayed in *Figure 1*, this spectrum is not faithfully detected and gives a baseline signal only (*Figure 1h*). The sharp contrast between the spectra of the two components makes it possible to judge the degree of phase separation from the ^1H lineshape.

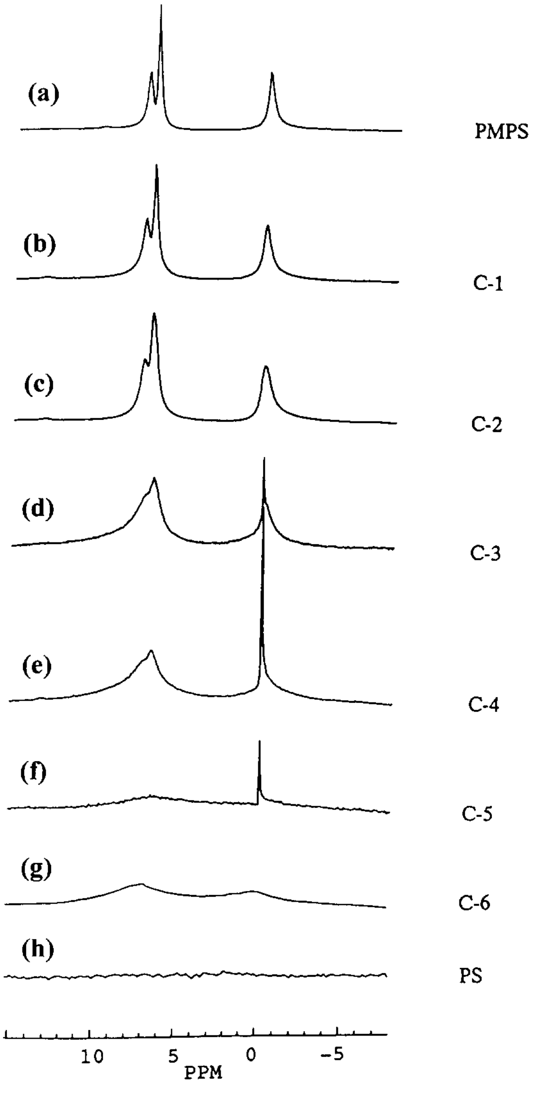

Figure 1 Room temperature ^1H spectra of PS–PMPS copolymers together with homopolymer PMPS (a) and PS (b), recorded after single-pulse excitation. Within the spectral width of 7 kHz plotted here, only the motionally narrowed PMPS signals show up as peaks

The spectra in *Figures 1b* and *c* are similar to that of the homopolymer PMPS superimposed on a broad base of the PS line. This indicates that samples C-1 and C-2 are phase-separated systems with extended microdomains in which the chain mobilities are close to those in the respective homopolymers. This is consistent with the results obtained by d.s.c., TEM and SAXS[21]. The spectra in *Figures 1d–g* display obvious deviations from a simple superposition. The broadened lines of the siloxane result from the enhanced proton dipole–dipole coupling due to a slowing down of the molecular motions of the siloxane in the presence of PS. With increasing PS fraction and/or decreasing molecular weight of the copolymer, the broadening of the lineshape becomes more pronounced, indicating a reduction of polymer segregation. The PMPS line feature disappears almost entirely in the spectrum shown in *Figure 1f* except for a narrow line of low integral intensity. In fact, system C-5 appeared to be homogeneous in other experiments[24], as will be discussed later. The extra narrow line remains sharp down to temperatures as low as 233 K, and its chemical shift corresponds to that of the methyl protons in dimethylsiloxane. Therefore, this signal is attributed to the -Si(CH$_3$)$_3$ end groups of the PMPS chain, introduced via the terminal agent ClSi(CH$_3$)$_3$, used to control the PMPS chain length. For the low molecular weight copolymer C-6, the ^1H line is also broad, but some of the PMPS line features are still found in *Figure 1g*.

The reduction of the siloxane mobilities in the different samples can be related to respective shifts of the dynamic glass transition temperature (T_{gd}) of the PMPS-rich phase. In order to quantify these shifts, ^1H spectra of the homopolymer PMPS were recorded as a function of temperature (*Figure 2a*). As expected from the Williams–Landel–Ferry equation[25], well resolved lines, requiring motions with rates exceeding 100 kHz, are observed only at temperatures $T > T_g + 50$ K, where T_g is the glass transition temperature as determined by d.s.c. In order to better estimate the shift of T_{gd} for the PMPS-rich phase in the block copolymers, temperature-dependent ^1H spectra were recorded (*Figure 2b*). Since the ^1H lines in the less phase-separated samples C-3 to C-6 are rather broad even at elevated temperatures, it could be argued that they are not solely due to PMPS, but also due to PS in a mobile mixed PMPS/PS phase. However, the 2D WISE n.m.r. spectra indicate insufficient mobility of the PS.

By comparing the temperature dependencies of ^1H spectra in the block copolymers with that of PMPS itself (see *Figure 1*) the shifts of T_g are estimated to be: +10 K for C-1 and C-2, +35 K for C-3, +50 K for C-4 and C-6, and >60 K for C-5. The values of T_g determined in this way are plotted for C-1 to C-5 in *Figure 3*, together with those determined from d.s.c., as a function of molecular weight of the PMPS component. It is evident that d.s.c. detects the glass transition of the PS-rich phase, which represents the larger fraction of the materials, whereas

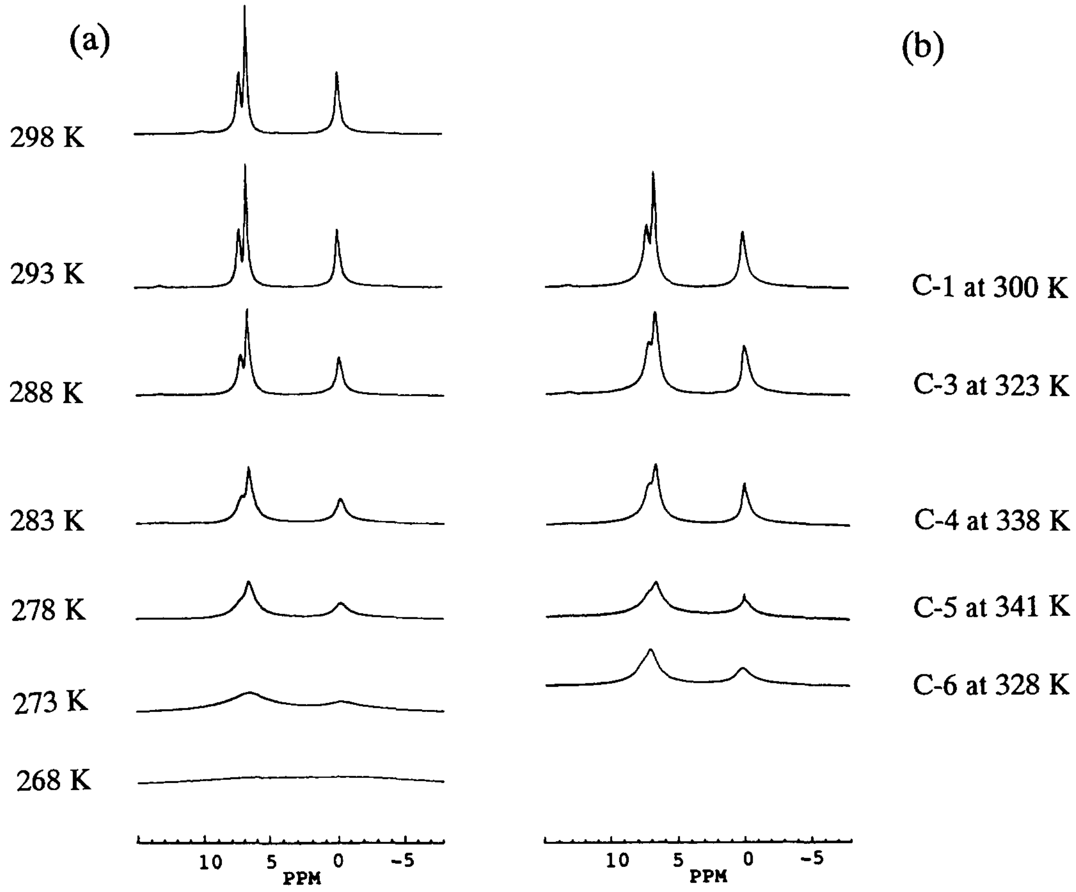

Figure 2 ^1H spectra at different temperatures: (a) PMPS homopolymer; (b) PMPS–PS copolymers

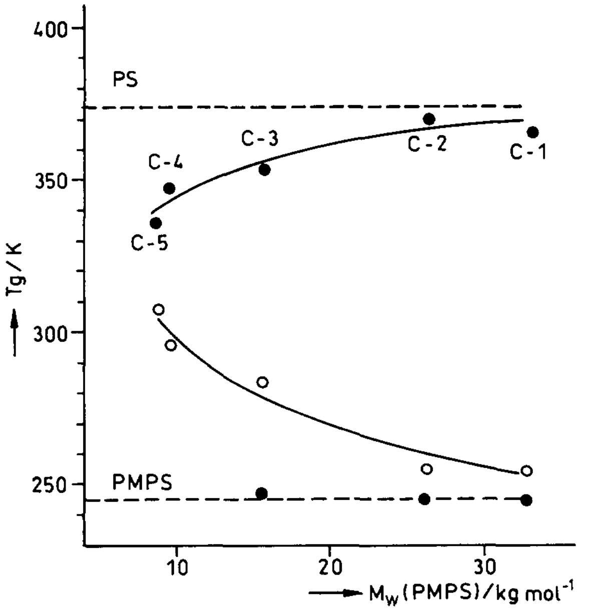

Figure 3 Glass transition temperatures of PS-*b*-PMPS block copolymers as determined by ^1H n.m.r. (○) plotted as a function of molecular weight of the PMPS component. The molecular weight of the PS component is $>20\,kg\,mol^{-1}$ in all cases. D.s.c. data (●) are shown for comparison

the glass transition of the PMPS-rich phase is not faithfully monitored. Note that the molecular weight of the PS component is above $20\,kg\,mol^{-1}$ in all these samples. The dependence of the T_g values on the PMPS molecular weight found by both d.s.c. and n.m.r. indicate that the compositions of the PS and PMPS-rich phases also change within the series.

Although the mobility of the PMPS segments in the copolymers is reflected in the 1D ^1H spectra, better insight is provided through heteronuclear 2D WISE n.m.r. spectroscopy[22]. Protons in very mobile segments display motionally narrowed lines in the ^1H dimension, those in a rigid phase exhibit broad lines. *Figure 4* shows 2D WISE spectra for sample C-6 at three temperatures. Along the ^{13}C dimension the PS signal of the aliphatic polymer backbone around 42 ppm is clearly separated from that of the methyl group of PMPS near 1 ppm. The signals near 128 ppm on the other hand, are due to the phenyl groups of both PS and PMPS. The line at 146 ppm is due to the quaternary carbon of PS alone. At 298 K both PS and PMPS segments exhibit low mobility, but they are not completely uniform, as can be inferred from their different ^1H lineshapes. A small fraction of PMPS segments ($\sim 10\%$) still possess high mobility (the narrow portion of the methyl peak). When the temperature is raised to 328 K, a highly mobile PMPS fraction becomes evident including $\sim 40\%$ of the PMPS segments. At an intermediate temperature of 308 K the mobility lies in between. The aliphatic carbon peak of the PS segments can be divided into a very rigid and a less rigid component, but clearly the mobility increase of the PS segments is lower than in PMPS, as the PS signals at 42 ppm are substantially broader in the ^1H dimension than the PMPS methyl lines at 1 ppm. In order to relate the ^1H dimension in the 2D WISE n.m.r. spectra with the single-pulse ^1H n.m.r. spectra discussed above, such spectra are included as insets in *Figure 4*. They emphasize

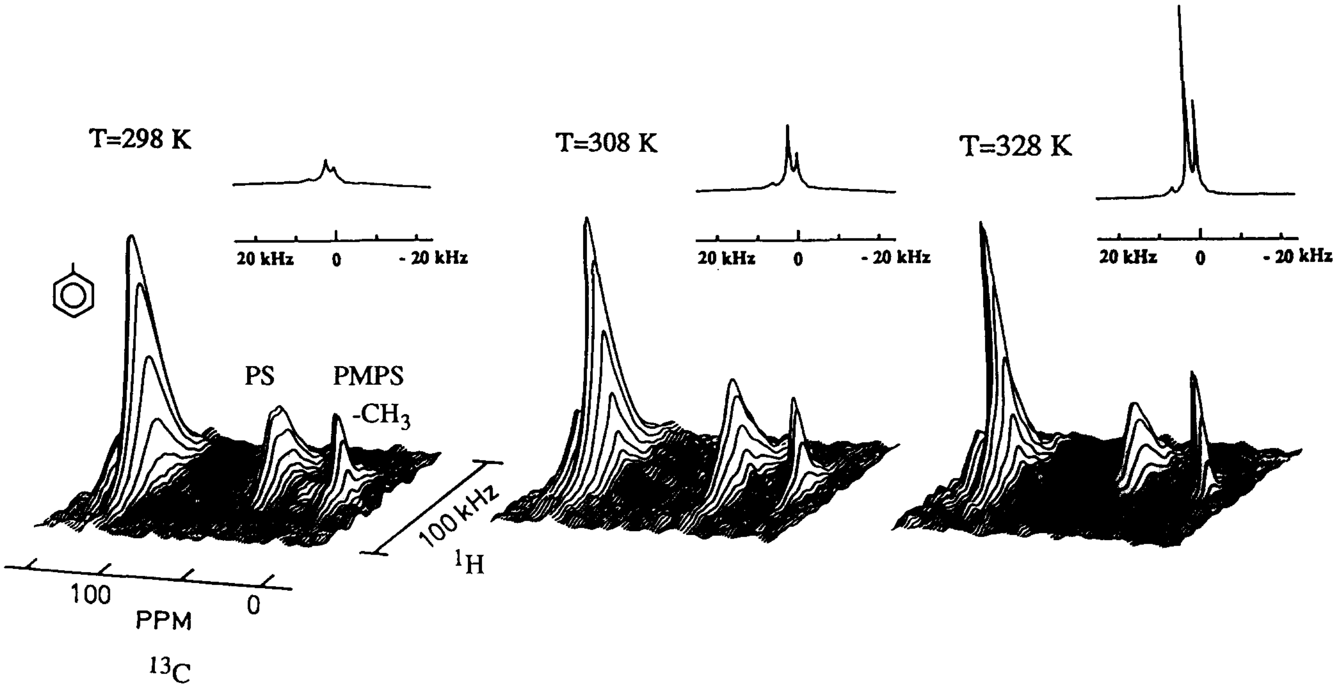

Figure 4 2D WISE spectra of copolymer C-6 at different temperatures. The insets show the corresponding ^{1}H 1D spectra

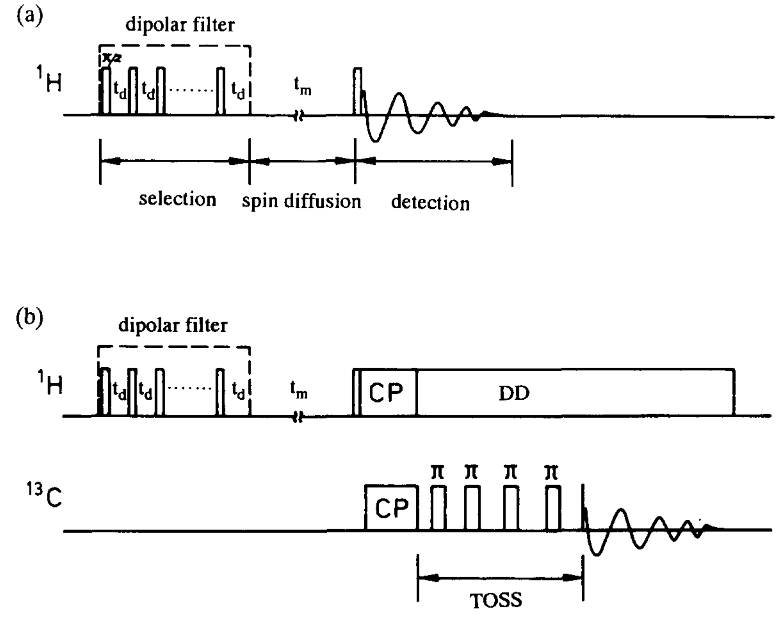

Figure 5 Pulse sequences for the dipolar filter experiment with t_m for spin diffusion: (a) proton detection; (b) CP from protons to carbons for ^{13}C detection with DD and TOSS

the mobility differences, however the PS signal is essentially lost.

Dipolar filter and spin diffusion

The significant difference in mobilities between PMPS and PS allows application of the dipolar filter technique to discriminate between these two components. As indicated in *Figure 5*, the 'filter' pulse cycle consists of twelve 90° proton pulses separated by a delay time t_d, with vanishing average Hamiltonian after the twelve pulses. By using a sufficiently large t_d value and repeating the filter cycle several times, the proton magnetization of the immobile component with its strong dipolar couplings can be selectively destroyed because, decaying too much during the t_d delays, it is not refocused by the pulse sequence. This gives rise to a magnetization gradient at the interface between mobile and immobile phases. Subsequently, the proton magnetization in the immobile phase recovers by spin diffusion from the mobile phase during a variable mixing time t_m. In *Figure 6*, the effect of the dipolar filter as applied to copolymer C-1 can be seen: the broad component of the proton signal has been eliminated. By comparison with the ^{1}H spectra of the homopolymers in *Figure 1*, the selected lines can be ascribed to PMPS. Note that the 'filtered' spectrum has narrower ^{1}H lines than PMPS itself. The dipolar filter selects the most mobile components of the PMPS-rich phase.

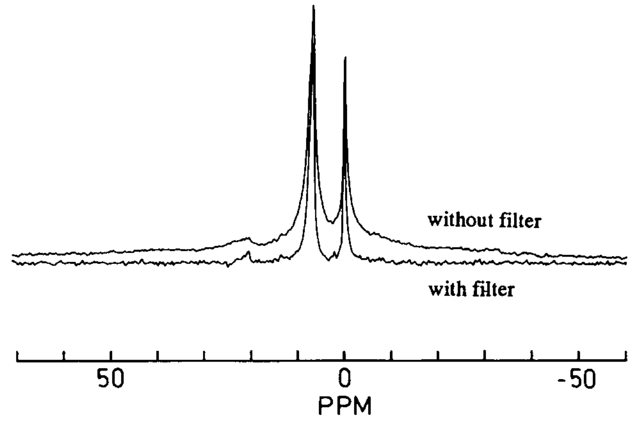

Figure 6 ^{1}H spectra of sample C-1 at 300 K. Lower trace: after a dipolar filter of 6×12 90° pulses and $T_d = 14\,\mu$s. Upper trace: reference spectrum without dipolar filter

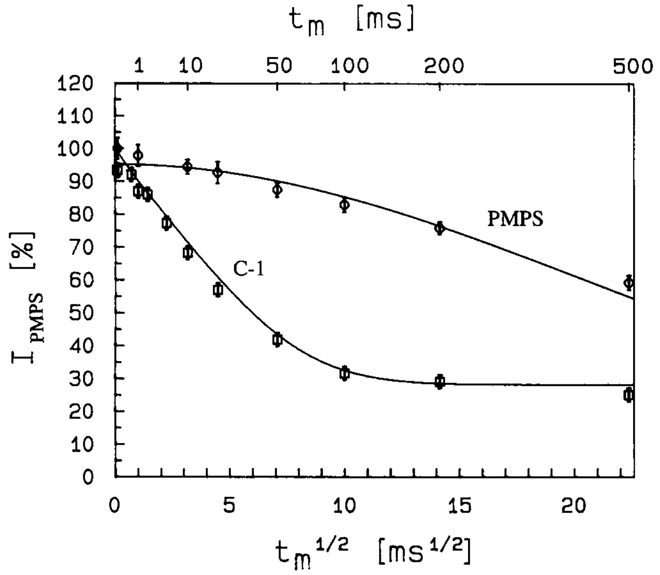

Figure 7 Decays of the proton magnetization of the phenyl ring in PMPS segments for copolymer C-1 and homopolymer PMPS at 300 K, as a function of t_m. The data for the homopolymer are fit by an exponential decay with a $T_1 = 900$ ms. The data for the copolymer have been corrected for this relaxation effect, thus reflecting purely the decrease of PMPS signal intensity due to spin diffusion to the PS

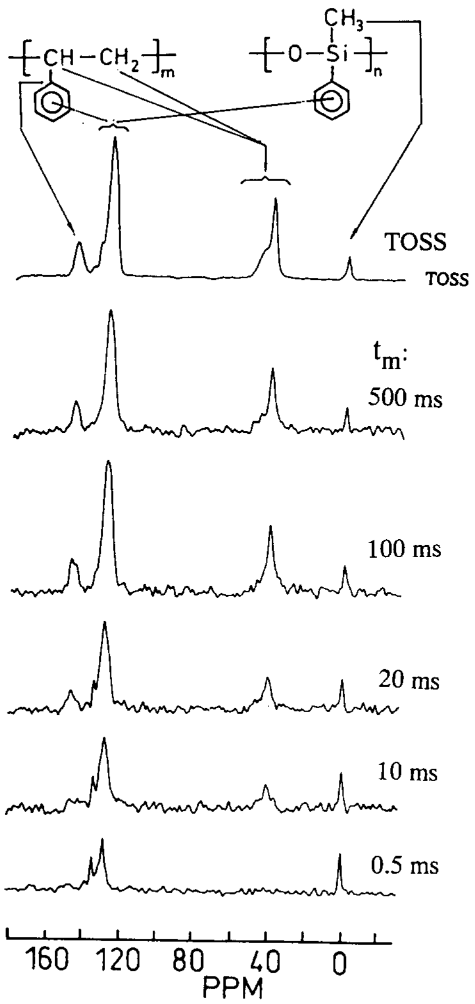

Figure 8 ^{13}C CP/MAS TOSS spectra of copolymer C-1 in a dipolar-filter experiment (cf. *Figure 5b*) for the pulse sequence, with different t_m values as indicated. The initially suppressed proton magnetization of the PS recovers by spin diffusion during t_m and is then detected in CP TOSS spectra. Top trace: ^{13}C TOSS spectrum (no proton selection) with chemical shift assignment

These signals of the initially selected magnetization then decrease with increasing t_m due to the spin diffusion to the rigid PS segments. *Figure 7* gives the magnetization intensity decay as a function of t_m for sample C-1. For comparison, the data for the PMPS homopolymer in the same experiment are also shown. The magnetization decay in the homopolymer is caused by proton spin-lattice relaxation, which manifests itself in a moderate reduction rather than a strong build-up of magnetization here. This is achieved by a phase cycle aligning the magnetization along the $+z$ and $-z$ direction during the t_m in alternating scans. The additional decay in copolymer C-1 is due to the spin transfer from PMPS segments to PS. To identify the chemical species and determine the spin diffusion quantitatively, high-resolution ^{13}C spectra are acquired via CP/MAS TOSS after the t_m (ref. 18). One series of the ^{13}C spectra with different t_m values are given in *Figure 8*. The normal TOSS spectrum is shown in the top trace with chemical shift assignment. For the shortest t_m (0.5 ms), only signals from PMPS segments are detected. However, when t_m is increased up to 500 ms, almost the full signal of the PS portion is observed: the methylene and methine carbons in the main chain (44 and 41 ppm, respectively), the quaternary carbons (146 ppm) and the other carbons in the phenyl ring (overlapping with those of PMPS).

The intensities of magnetization recovery of the aliphatic carbons in PS as a function of t_m for copolymer samples C-2, C-3 and C-4 are plotted in *Figure 9*. In order to facilitate the data analysis (see below) the data have been recorded at different temperatures, namely 260 K for C-2, 299 K for C-3 and 311 K for C-4, respectively. This corresponds to temperatures between 15 K and 19 K above the T_gs of the corresponding PMPS-rich phases, such that the mobility of the PMPS in the PMPS-rich regions is comparable for the different samples, as indicated by the similar ^{1}H linewidths. The build-up of PS magnetization by spin diffusion is clearly much faster in sample C-4 than in sample C-2, with sample C-3 falling in between. Within the t_m values relevant here, ^{1}H T_1 relaxation results only in small changes of signal intensities, easily corrected for by relaxation factors determined in experiments without a selective pulse sequence, and with negligible temperature dependencies. The data of *Figure 9* indicate different

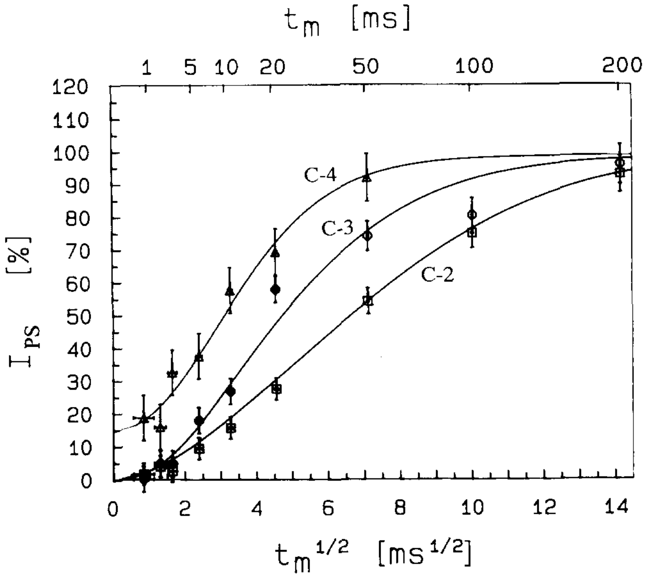

Figure 9 Spin diffusion behaviour of copolymers C-2, C-3 and C-4. Integrated intensity of the carbon signal from the PS backbone *versus* t_m. Data for sample C-2 were taken at 260 K, for C-3 at 299 K and for C-4 at 311 K, such that the dipolar couplings (^1H linewidths) were similar. For the selection, a dipolar filter of 6 × 12 90° pulses and $t_d = 14\,\mu s$ was employed. The solid lines are the theoretical fits, computed using a one-dimensional (for copolymer C-2) or three-dimensional (for C-3 and C-4) diffusion model, with $D_{PS} = 0.6\,nm^2\,ms^{-1}$ and $D_{PMPS} = 0.05\,nm^2\,ms^{-1}$ (for details see text and *Table 2*)

domain dimensions of the different samples. All the magnetization recovery curves are not exactly linear at small $t_m^{1/2}$ values, but exhibit rather a slightly sigmoidal shape. This is the characteristic of spin diffusion for a system containing a considerable interphase region[19] and will be discussed in detail later.

In order to quantify the results, the diffusion equation is used to describe the magnetization transfer:

$$\dot{m}(r,t) = \nabla[D(r)\nabla m(r,t)] \qquad (1)$$

where m is the local magnetization density at site r and time t and $D(r)$ is the diffusion coefficient, which may be spatially dependent.

The spin diffusion coefficient D is related to the strength of the dipolar couplings as reflected in the ^1H linewidths. The interactions are reduced by molecular mobility of large rate and amplitude. Since the two components (PMPS and PS) in the copolymers exhibit very different ^1H linewidths and molecular mobilities, the differences of the D values for the individual phases must be taken into account. Thus, the spin diffusion problem in a system consisting of multiple phases (including the interphase region) with different D values has to be solved. The boundary conditions, which have a considerable influence on the actual diffusion behaviour, are determined by the morphology of the sample. The geometry of packing can be characterized in terms of the dimensions relevant in the diffusion process: one dimension for lamellar (layer) structures, two dimensions for long rods, and three dimensions for spheres (particles) in a matrix[12].

The magnetization transfer rate is consequently determined by $D(r)$, the morphology of the sample (diffusion model) and, most importantly, the domain sizes of the phases.

Phase structure and domain size

For block copolymers in which both blocks are non-crystalline, three basic morphologies are well established[1,2]. The minority component can form spheres or cylinders. For systems of equal (50:50) fractions, the two components pack as alternating lamellae. More recently, a bicontinuous morphology has also been reported[26–28]. Which domain structure is formed depends mainly on the weight fraction of the components. The overall molecular weight of the copolymer has much less of an impact[29,30]. In our PS-*b*-PMPS diblock copolymers a so-called ordered bicontinuous double diamond (OBDD) structure[28] for sample C-1, lamellar morphology for sample C-2 and spherical domains of PMPS with body centred cubic packing in the PS matrix for C-3 were observed by TEM[21]. Thus, two-, one- and three-dimensional diffusion models can be adopted for samples C-1, C-2 and C-3, respectively.

To model the phase structure, we consider three regions, namely a PS-rich phase, a PMPS-rich phase and an interphase. For simplicity, the composition of the latter is treated as varying linearly.

The spin diffusion coefficient is determined by the dipole–dipole interactions and can be expressed as[5]:

$$D = kr^2 m_2^{1/2} \qquad (2)$$

where r is the distance between neighbouring spins, k is a numerical factor, m_2 denotes the second moment of the ^1H n.m.r. lineshape and $m_2^{1/2}$ is approximately proportional to the linewidth. If the spin diffusion data for different copolymers are recorded at appropriate temperatures where their ^1H n.m.r. spectra have similar lineshapes, the same value of D can be used for all the fits. Obviously, this increases the accuracy with which the changes in domain sizes within the series can be determined.

Values of 5×10^{-12}–$8 \times 10^{-12}\,cm^2\,s^{-1}$ (0.5–$0.8\,nm^2\,ms^{-1}$) for D in rigid polymers like PS at temperatures $< T_g$ are well accepted and have recently been experimentally confirmed[31]. The D value for highly mobile but not yet fluid materials, such as rubber-like polymers, is known to be significantly smaller, but no reliable data have been published so far. Recent work in our laboratory[32], relating spin diffusion data on clearly phase-separated block copolymers with domain sizes determined by TEM, has shown that simple scaling with the linewidth yields D values which are smaller than the experimentally acceptable values, indicating the influences of the r^2 prefactor or other processes, e.g. diffusion of mobile segments in space. For instance, D values of $\sim 0.05\,nm^2\,ms^{-1}$ for polybutadiene in a well-characterized poly(butadiene-*b*-styrene) diblock copolymer have been determined above T_g, with similar ^1H linewidths as in our systems. Thus, in our analysis we use $D = 0.05\,nm^2\,ms^{-1}$ for the PMPS-rich domain and $D = 0.6\,mm^2\,ms^{-1}$ for the PS-rich domain. In the interphase region, the diffusivity is assumed to change in a linear fashion. The estimated accuracy of absolute domain sizes is ±20%, that for relative changes being considerably better. The simulation programs rely on discretized versions of the diffusion equation to be described in detail elsewhere.

The fits are shown in *Figure 9* as solid lines. For sample C-1, the consistency of the domain sizes of both the ^{13}C PS and ^1H PMPS data was also confirmed. The domain sizes determined in this way are summarized in *Table 2*, and compared to the SAXS results. It is evident that the n.m.r. results are comparable to those of SAXS for samples C-1, C-2 and C-3. As expected, the domain sizes of the mobile component in the copolymers decrease with

Table 2 Microphase domain sizes of PS-*b*-PMPS diblock copolymers

		Domain size (nm)				
		From n.m.r.				From SAXS
Sample	Morphology[a]	d_{PMPS}[b]	$d_{interphase}$[b]	d_{PS}[b]	$L_{n.m.r.}$[c]	L_{SAXS}
C-1	OBDD	8	4	3	14–24	24–27
C-2	Lamellar	5	4	9.5	19–27	19–25
C-3	Spherical	6	4	3	13–21	18–20
C-4	(Spherical)	3.5	4	2.5	9–18	
C-5	(Spherical)	1.5	1.5	0.5	2–8	
C-6	(Lamellar)	2	2.5	2.5	6–12	

[a] Parentheses used for morphology suggested by composition and n.m.r. data

[b] d_{PMPS}, $d_{interphase}$ and d_{PS}, smallest diameter of PMPS-rich, interphase and PS-rich domains, respectively

[c] L, long period; $L_{n.m.r.} = d_{PMPS} + 2d_{interphase} + d_{PS}$

reduction in length of the PMPS segments. This confirms that meaningful values for domain sizes can be determined via ^1H spin diffusion even in cases where the mobilities of the two components are vastly different.

Microheterogeneity of molecular dynamics

Let us now consider the samples C-4 to C-6. From *Table 1* it is clear that in these copolymers the length of the PMPS component is approximately the same and considerably shorter than in samples C-1, C-2 or C-3. Likewise, from the overall molecular weight of these copolymers (*Table 1*) it follows that M_w(PS) is reduced from ~36 to 19 to 5.6 kg mol^{-1} for C-4, C-5 and C-6, respectively. Remembering the increase in compatibility with decreasing molecular weight[1,2], it is not surprising that with conventional methods no phase separation is found in these systems[21]. By d.s.c., a single T_g is found for C-4 and C-5 and an extremely broad glass transition region spanning a temperature range of 90 K is observed for C-6. Very broad distributions of correlation times in the primary glass–rubber relaxation are detected by photon correlation, dielectric and dynamic mechanical relaxation techniques in these systems[24].

However, as noted above, even a simple n.m.r. technique like single-pulse ^1H n.m.r. detects substantial motional heterogeneities (see *Figures 1* and *2*). This is confirmed by applying more advanced methods like the 2D WISE n.m.r. experiment. The spin diffusion data plotted in *Figure 9* for C-4 clearly demonstrate that small spatially separated regions with different mobilities and compositions exist, i.e. nanoheterogeneities. Due to the proximity of the PMPS and PS segments and the smallness of the PMPS-rich domains, it is difficult to completely select the PMPS n.m.r. signal. This manifests itself in the 15% offset for the shortest t_m values ($t_m \rightarrow 0$) in the spin diffusion curve (*Figure 9*). Nonetheless, the data can be analysed quantitatively to yield domain sizes in the region of 2–4 nm (see *Table 2*). In order to estimate the sizes of the PMPS-rich regions in copolymers C-5 and C-6, simple proton magnetization decay curves after a dipolar filter, as in *Figure 7*, were measured, requiring considerably less measuring time than the ^{13}C experiments. In samples C-5 and C-6, the diameters of the PMPS-rich regions were found to be <2 and 2 nm, respectively. Recently, composition fluctuations in copolymer C-6 have also been detected by photon correlation and dielectric spectroscopy[24].

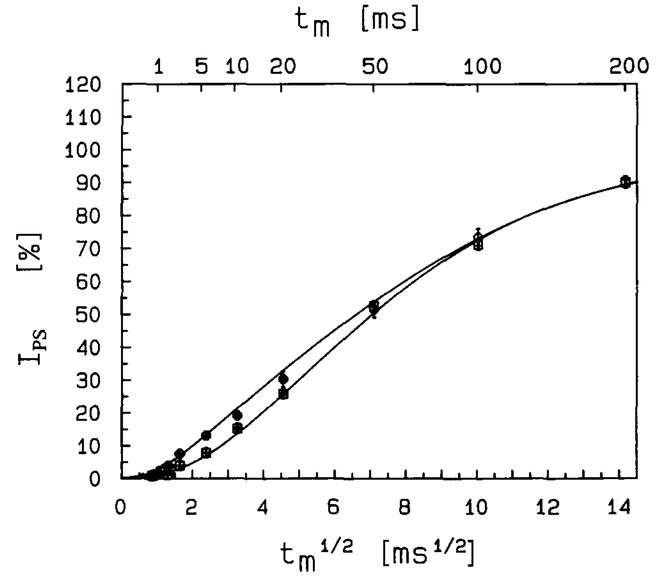

Figure 10 Magnetization recovery as a function of t_m for copolymer C-2 at 300 K, using the dipolar filter with 6 × 12 90° pulses, but different delays: $t_d = 12\,\mu s$ (weaker filter, upper trace) and $t_d = 14\,\mu s$ (stronger filter, lower trace). The different shapes of the initial sections of the spin-diffusion curves indicate the existence of a component-mixed interphase

Dipolar filter and interphase

The dipolar filter is based on differences of molecular mobilities in the sample. In general, there is a region of gradual change in structure and molecular mobility between different phases, an interfacial or interphase region. Because of its somewhat reduced mobility, a major portion of the proton magnetization of the mobile component in this region can be suppressed by the dipolar filter together with that of the rigid phase, if the filter is chosen to be sufficiently strong. For this reason, the variation of parameters for the dipolar filter can be useful in studying systems with interphase regions. As an example, *Figure 10* shows two sets of spin diffusion data of copolymer C-2 which were acquired using the dipolar filter (see *Figure 5*) with $t_d = 12\,\mu s$ for the upper curve and $t_d = 14\,\mu s$ for the lower curve. For short t_m values, a significant difference in the spin diffusion behaviour is found. Clearly, after stronger suppression of magnetization of less mobile PMPS segments (in the interphase), it takes the magnetization longer to reach the PS, leading to a more sigmoidal initial behaviour. As expected, in the theoretical fits, similar overall domain sizes are

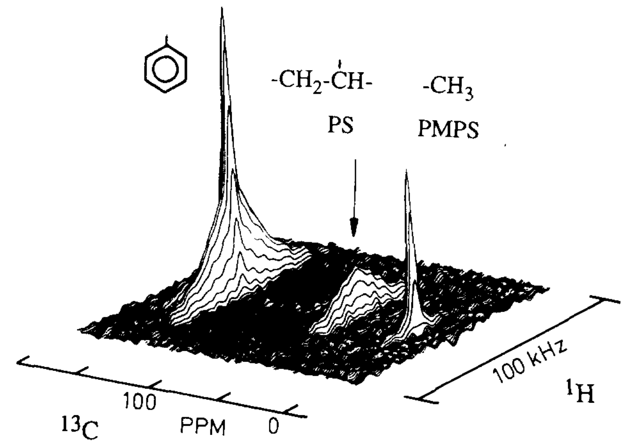

Figure 11 Heteronuclear 2D WISE n.m.r. spectrum of copolymer C-2 recorded at 300 K

obtained for both sets of data, but a region broader by 1 nm between the selected PMPS region and the PS-rich domain is found for the data obtained with the stronger filter.

Because the interphase in multicomponent systems is of special interest and still far from being well characterized, more effort is needed in this field. Heteronuclear 2D WISE n.m.r. is particularly suited for this purpose. *Figure 11* shows a 2D spectrum of copolymer C-2 recorded at room temperature. The methyl signal of the PMPS block displays a broadened component underneath the narrow line. This broad line is attributed to the interaction with the rigid PS block in the interphase region. It should be noted that a corresponding broad component is not observed in the PS–poly(dimethylsiloxane) (PDMS) system[22], where the components are strongly incompatible and the interphase region is <1 nm thick[22].

In fact, the broad interphase regions detected here for the PS–PMPS block copolymers by n.m.r. are consistent with the SAXS and TEM results[21]. The scattering intensity curve shows hardly any higher order reflections, in spite of the fact that the concentration profile is known from TEM micrographs to be periodic[21]. This indicates that the electron density profile is dominated by a single Fourier coefficient, i.e. on average it varies approximately like a sine function. The concentration profile used for the fits of the spin diffusion data actually represents a simple approximation of this property. It varies linearly between the two more or less ‘pure’ phases over length scales comparable with their domain sizes, such that no abrupt changes with considerable higher-order Fourier coefficients are present.

It is interesting to note that the n.m.r. data for all the block copolymers studied here could be fitted with a single length scale for the interphase region for copolymers C-1 to C-4 (*Table 2*). Since the diameter of the PMPS-rich regions is substantially reduced in samples C-4 to C-6, most of the PMPS component is in fact contained in the component-mixed interphase regions. Therefore, it is not surprising that these systems appear to be homogeneous in conventional experiments as mentioned above.

CONCLUSIONS

From a solid-state n.m.r. study on the PS-*b*-PMPS diblock copolymers with different block lengths and/or different total molecular weights, information about the microphase structure and the domain dimensions in the phase-separated copolymer systems are obtained. The proton n.m.r. spectra detected higher mobility of the PMPS component even in systems which in d.s.c. display a single glass transition only, and provide good estimates of T_g for the PMPS-rich phases. The spin-diffusion method, combining a dipolar filter with ^{13}C detection techniques, provides a powerful means for studying microdomain sizes of phase-separated block copolymers. From the time dependence of the spin transfer from the phase rich in the flexible PMPS to the rigid PS, the domain dimensions were calculated. The resulting microdomain sizes are comparable to those measured by SAXS for the microphase-separated systems. However, the n.m.r. method is more sensitive to the fine heterogeneity of the molecular mobility. Therefore, in copolymers in which no phase separation is detected by d.s.c., TEM and SAXS, regions rich in the more mobile PMPS are detected and their sizes determined to be in the range of 2–4 nm. Furthermore, an interphase region, ~ 4 nm in overall thickness, is deduced from n.m.r. spin diffusion data and is consistent with the 2D WISE n.m.r. Its presence explains the fact that despite the well-developed periodicity in the phase structure, the SAXS curves display only a single reflection. Thus, advanced n.m.r. techniques give information consistent with, and supplementing, established methods for studying two-component polymers.

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