# Determination of polysoprenen-block-poly (methyl methacrylate) domain sizes using 1H spin diffusion

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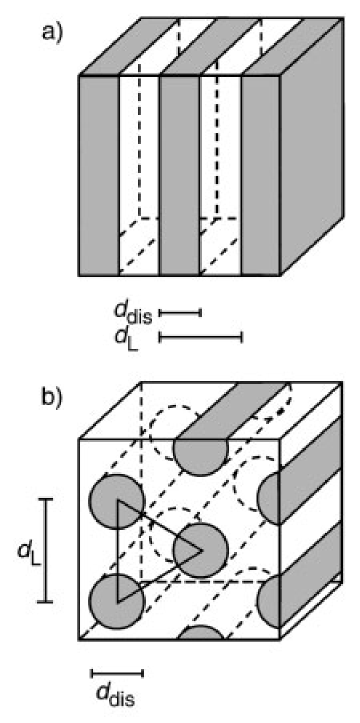
**Full Paper:** The microphase structure of polyisoprene-*block*-poly(methyl methacrylate) diblock copolymers was studied using solid-state NMR techniques. Wideline separation spectroscopy reveals a narrow interphase between the two polymers. The domain sizes of a lamellar sample and a sample with hexagonally ordered cylinders were determined using $^1$H spin diffusion. The lamellar sample shows a domain size of 16 ± 2 nm for the minor polyisoprene phase and a long period of 33 ± 4 nm. The cylindrical structure has a long period of 38 ± 7 nm, the diameter of the PMMA cylinders is 21 ± 4 nm. These results are about 20% below the estimates obtained from theoretical calculations according to Helfand and Wasserman.



Morphologies of an a) lamellar, and b) hexagonally ordered cylindrical sample (schematic). The triangle in (b) indicates the symmetry that can be used to calculate the $d_L$.

# Determination of Polyisoprene-*block*-poly(methyl methacrylate) Domain Sizes Using $^1$H Spin Diffusion

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## Introduction

Diblock copolymers are materials of considerable interest to the polymer industry. The intrinsic connectivity of the blocks in a block copolymer melt prevents block copolymers from macrophase separation. If the two blocks of a diblock copolymer are immiscible, microphase separation occurs and domains are formed with characteristic microscopic morphologies. Immiscible polymers generally show a different $T_g$ when observed with DSC, they have a positive enthalpy of mixing, different solubility parameters $\delta$, a positive Flory-Huggins interaction parameter $\chi$, while the IR, UV and NMR spectra remain the same upon blending. The diblock copolymer system can adopt three main morphologies that are classified in terms of their dimensionalities $\varepsilon$: a lamellar structure with $\varepsilon = 1$, a structure of hexagonally arranged cylinders in a matrix with $\varepsilon = 2$, or body-centered cubic ordered spheres in a matrix (bcc) with $\varepsilon = 3$. The morphology of the block copolymers can be tailored by using particular block copolymers with specific lengths. Which morphology is formed depends on the volume fractions $\phi_A$ and $\phi_B$ of the different blocks.[1,2] Lamellar structures occur for volume fractions $0.35 < \phi_A < 0.5$ of the minor component, hexagonally ordered cylinders[3–5] for $0.15 < \phi_A < 0.4$, and spheres for

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fractions $\phi_A < 0.2$.[6,7] The domain size and morphology crucially affect the properties of the material. The combination of a rubber and a thermoplastic is especially interesting, because it combines the flexibility of the rubber with the strength and rigidity of the thermoplastic. In the present model investigation polyisoprene (PI) and poly(methyl methacrylate) (PMMA) were chosen because both polymers are used in many applications. PMMA is a rigid thermoplastic with a $T_g$ of 120 °C. PI, a rubber, is a mobile polymer with a $T_g$ of −57 °C. They are incompatible polymers. They show separate $T_g$'s in block copolymers, they have a low maximum mutual solubility in benzene,[8,9] different solubility parameters,[10] and $\chi > 0$.[11,12] PI-*b*-PMMA diblock copolymers will therefore form microphase separated domains.

Two polymer systems were studied: a system IM-1 with volume fractions in the range of lamellar systems, $\phi_{PI} = 0.47$, and one IM-2 with volume fractions in the range where hexagonally ordered cylinders are formed, $\phi_{PMMA} = 0.28$. The PI-*b*-PMMA diblock copolymers were prepared, and were studied using solid-state NMR techniques. Solid-state NMR is a relatively novel method to determine structural and dynamic properties of polymeric materials.[13] This non-invasive method can be applied without sample modification, and is therefore widely applicable. From $^1$H spin diffusion measurements the domain sizes were determined. These domain sizes were compared with theoretical predictions according to Helfand and Wasserman.[14,15] The general trends in domain sizes observed with spin diffusion experiments for samples with different molecular weights are very reliable,[7] although the absolute error for any specific sample can be relatively large. The purpose of this study is to investigate the accuracy of NMR spin diffusion measurements for the PI/PMMA system, from a comparison between NMR data and theoretical predictions.

## Experimental Part

### *Preparation of Materials*

PI-*b*-PMMA diblock copolymers were prepared by sequential living anionic polymerization of isoprene and methyl methacrylate. Experimental details are described in ref.[16] For the block copolymer IM-1 we found $\overline{M}_n$ (PI) = 31 000; $\overline{M}_n$ (PMMA) = 45 000; MWD = 1.14. Block copolymer IM-2 was prepared accordingly with $\overline{M}_n$ (PI) = 40 500; $\overline{M}_n$ (PMMA) = 21 000; MWD = 1.06.

DSC: $T_g = -54$ °C, 104 °C.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta = 0.85$ ($CH_3$, syndio PMMA), 1.01 ($CH_3$, hetero PMMA), 1.24 ($CH_3$, iso PMMA), 1.59 ($CH_3$, 1,4-*trans* PI + $CH_3$, 3,4 PI), 1.67 ($CH_3$, 1,4-*cis* PI), 1.81 ($CH_2$, PMMA), 2.03 ($CH_2$, PI), 3.60 ($OCH_3$, PMMA), 4.65 (=$CH_2$, 3,4 PI), 4.75 (=$CH_2$, 3,4 PI), 5.12 (–CH=C, 1,4-*cis* PI + 1,4-*trans* PI).

$^{13}$C NMR (50.1 MHz, $CDCl_3$): $\delta = 15.9$ ($CH_3$, 1,4-*trans* PI), 16.8 ($CH_3$, syndio PMMA), 19.6 ($CH_3$, hetero PMMA), 23.4 ($CH_3$, 1,4-*cis* PI), 26.4 ($C^4$, PI), 32.2 ($C^1$, 1,4-*cis* PI), 40.0 ($C^1$, 1,4-*trans* PI), 44.5 ($C_q$, syndio PMMA), 44.8 ($C_q$, hetero PMMA), 51.7 ($OCH_3$, PMMA), 54.6 ($CH_2$, PMMA), 124.1 ($C^3$, 1,4-*trans* PI), 124.9 ($C^3$, 1,4-*cis* PI), 135.1 ($C^2$, PI), 176.8 (C=O, hetero PMMA), 177.7 (C=O, syndio PMMA).

Microstructure: PI: 72% 1,4-*cis*, 21% 1,4-*trans*, and 7% 3,4; PMMA: 80% syndio triads, 20% hetero triads.

### *General Remarks*

Size exclusion chromatography was carried out at 30 °C in THF using a Hewlett Packard 1090 liquid chromatograph equipped with four columns ($10^5$, $10^3$, 500 and 100 Å) and a HP1037 A refractive index detector. Calibration was performed with polystyrene and PMMA standards.

Solution $^1$H NMR and $^{13}$C NMR spectra were recorded on a Jeol FX-200, a Bruker DPX-300, a Bruker AM-400, or a DMX-600 spectrometer using tetramethylsilane (0 ppm; $^1$H) and $CDCl_3$ (77 ppm; $^{13}$C) as internal standards. Solid-state NMR spectra were recorded with a Bruker MSL-400 spectrometer equipped with a Bruker double resonance magic angle spinning (MAS) probe. The sample was rotated at frequencies either between 2 and 3 kHz or at a frequency of 10 kHz to avoid spectral overlap of centerbands and spinning sidebands. The 90° $^1$H pulse length was 5.4 µs. CP/MAS $^{13}$C experiments were performed using cross-polarization with a contact time $\tau_{CP}$ of 2 ms, and with dipolar decoupling during acquisition. $T_1$ measurements were performed using an inversion recovery experiment. Wideline separation measurements were performed according to ref.[17] using a spinning frequency of 10 kHz. A $T_2$-filter was used in the spin diffusion experiment for the selection of the mobile phase. Spin diffusion measurements using $^1$H and $^{13}$C detection were used, see Figure 1. A series of spin diffusion times was used from 0 ms up to 2 s with an emphasis on the first 500 ms. The spin diffusion mixing times $t_m$ were corrected for the spin diffusion occurring with half the dipolar coupling strength during CP, by adding ½ $\tau_{CP}$.[18–20] The spin diffusion curve is corrected for $T_1$ relaxation.[7,12–24] This correction is achieved by multiplying all intensities by exp. ($t_m/T_1$), where $T_1$ is the relaxation time for the detected domain. For PMMA the value of $D$ has been determined at $0.8 \pm 0.2\ \text{nm}^2 \cdot \text{ms}^{-1}$.[3] For PI the value of $D$ is determined using Equation (1).[25]

$$D = (8.2 \times 10^{-6}\ T_2^{-1.5} + 0.007)\ \text{nm}^2/\text{ms} \quad \text{for} \quad 0 < 1/T_2 < 1\,000\ \text{Hz} \qquad (1)$$

This relation yields a value for $D_{PI}$ of $0.05\ \text{nm}^2 \cdot \text{ms}^{-1}$ using $T_2 = 3.2$ ms.[23,25] The dimensionality of the systems is determined using the volume fractions. For IM-1 the volume fraction for PI $\phi_{PI} = 0.47$. This is in the range for lamellar systems. For IM-2 PMMA is the minor phase, with $\phi_{PMMA} = 0.28$. This value is well within the range for a hexagonal cylindrical structure with $\varepsilon = 2$. The parameters that were used in the calculations are: $\rho_{PI} = 0.91\ \text{g} \cdot \text{cm}^{-3}$, $\rho_{PMMA} = 1.19\ \text{g} \cdot \text{cm}^{-3}$, $\rho_{H,PI} = 0.107\ \text{g} \cdot \text{cm}^{-3}$, $\rho_{H,PMMA} = 0.095\ \text{g} \cdot \text{cm}^{-3}$, and the monomer molecular weight of both polymers: $68\ \text{g} \cdot \text{mol}^{-1}$ for PI and $100\ \text{g} \cdot \text{mol}^{-1}$ for PMMA. For the theoretical calculations the following parameters were used: the mixing

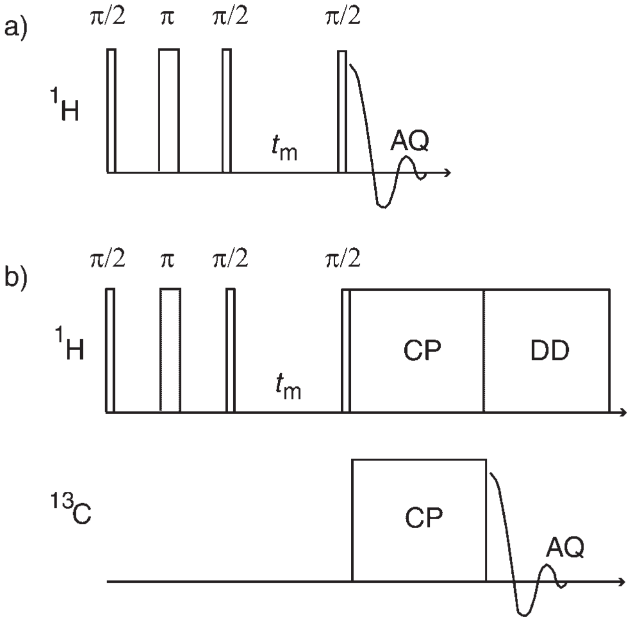

Figure 1. Pulse programs used for spin diffusion measurements using a) $^1$H detection, and b) $^{13}$C detection. Using a Hahn echo pulse sequence the mobile fraction is selected. During $t_m$ spin diffusion occurs.

parameter $\alpha = \rho_0 \times \chi = 1.1 \times 10^3$ mol · m$^{-3}$, the Kuhn segment lengths $b_{k,PI} = 0.63$ nm, $b_{k,PMMA} = 0.64$ nm, and the segment densities $\rho_{0k,PI} = 13.6 \times 10^{-3}$ mol · m$^{-3}$, $\rho_{0k,PMMA} = 11.6 \times 10^{-3}$ mol · m$^{-3}$.[15,26]

## Results and Discussion

The specific aim of this study is to characterize the polymer heterogeneity in terms of the dimensionality of the morphology and the characteristic domain sizes. Polymer heterogeneity can be determined with various solid-state NMR techniques. Proton spin diffusion measurements can yield information about domain sizes as well as the thickness of the interphase between the domains.[7] Domain sizes from a few nm and up to 100–200 nm can be determined, depending on the spin-lattice relaxation time $T_1$ and the spin diffusion constant $D$.[27–31] From $^1$H spin diffusion measurements, the domain sizes of microphase separated structures can be determined, using the initial rate approximation.[3,31] For systems with a relatively small interphase, i.e. strongly incompatible polymers, it has been shown that for short mixing times $t_m$ the signal is proportional to $\sqrt{t_m}$, independent of the dimensionality $\varepsilon$ of the system. A relation is derived for spin diffusion from a semi-infinite source to a semi-infinite sink, valid for the initial stages of the spin diffusion process.[3] Two conditions have to be satisfied, namely the polarization transfer between domains should not be hindered by the $T_1$ relaxation, and the interphase between the two polymers has to be narrow, in order for the initial rate approximation to be valid.

### *The Polarization Transfer in the PI/PMMA Diblock System Occurs on the Time Scale of $T_1$ Relaxation*

The $T_1$ relaxation behavior of a polymer system is sensitive to the degree of mixing of the phases. The occurrence of separate $T_1$ values is an indicator for the immiscibility of the polymers. In contrast, for a homogeneous polymer mixture, a single $T_1$ is observed. For a heterogeneous system, separate $T_1$ values are observed, although they can differ from their pure homopolymer counterparts due to spin diffusion. It is generally thought that spin diffusion leads to an averaging effect on the spin-lattice relaxation times of the different domains.[22] Alternatively, differences in mobility can be induced by small changes in the free volume of the block copolymer, when compared to the corresponding bulk polymers.[32,33] The $T_1$ values for PMMA and PI homopolymers are $T_1 = 1\,400$ ms for PMMA, for PI $T_1 = 290$ ms.[7,22] For the block copolymers values of 550 ms and 430 ms were determined for the PMMA and PI blocks respectively. The convergence of the $T_1$ values in the diblock system indicates that spin diffusion has occurred during the relaxation measurement and that spin diffusion and spin-lattice relaxation occur on the same time scale.[22] Increased dynamics due to free volume changes is not obvious here, since this is expected to lead to pronounced line narrowing in the spectra, which is not observed (see below).

### *The WISE Experiment Shows that the Interphase between the Domains is Narrow*

Wideline separation (WISE) measurements can reveal the mobility of the various phases in a polymer system. The presence of an interphase between the two phases can be demonstrated using a WISE experiment.[17] The experiment shows the proton wideline spectrum for the various $^{13}$C responses. With this technique the molecular dynamics of the different phases in a phase-separated structure can be probed on time scales of ms to µs, since such motions affect the dipolar coupling strength, and lead to line narrowing in the $^1$H dimension. From this an estimate of the relative thickness of the interphase can be made.[17] A more sensitive method for the determination of the interphase thickness would be double-quantum MAS NMR spectroscopy.

Figure 2 shows the WISE spectrum of IM-1. Narrow lines with linewidths of 550 Hz are visible for the following PI resonances: 16 ppm: $CH_3$ 1,4-*trans*, 23 ppm: $CH_3$ 1,4-*cis*, 27 ppm: C4, 32 ppm: C1 1,4-*cis*, 40 ppm: C1 1,4-*trans*, and 125 ppm: C3. The quaternary signal for PI at 135 ppm is not detected because of a low cross polarization efficiency. Broad signals with linewidths of centerbands of 3 kHz show the PMMA carbons at 14–20 ppm: $CH_3$, 44 ppm: quaternary C, 52 ppm: $OCH_3$, 55 ppm: $CH_2$, and 178 ppm: C=O. These $^{13}$C all resonate with the same chemical shifts

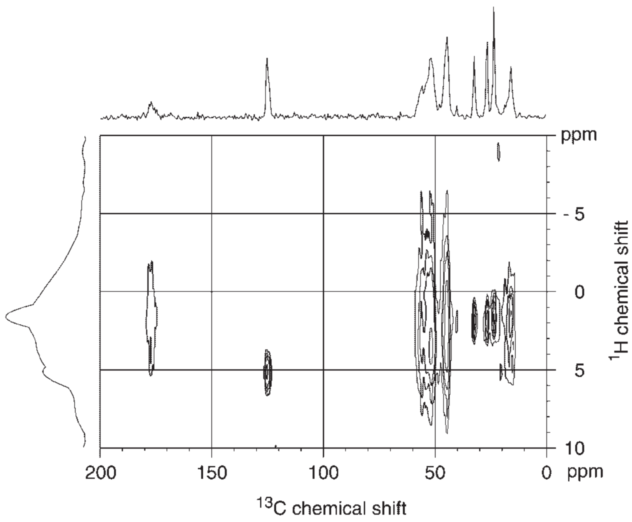

Figure 2. IM-1 WISE spectrum collected with a spinning frequency of 10 kHz. The traces along the axes are the projections in both directions. $^{13}$C spectra were measured with a spectral width of 50 000 Hz, 256 increments were used for the $^1$H direction.

as the $^{13}$C of the respective homopolymers. Since the WISE experiment shows no broadening of the $^1$H wideline spectra for PI, and no narrow component at PMMA resonances, mixing of the two phases is not detected. Hence the interphase between the two phases must be narrow.

### *Determination of the Domain Sizes with Spin Diffusion Measurements*

In order to measure the domain sizes with NMR, the magnetization of one of the polymer fractions has to be suppressed, while the other is selected to be conserved. In the measurements the PI phase is selected using a $T_2$-filter. During the mixing time $t_m$ spin diffusion takes place and magnetization is transferred to the PMMA phase. In the experiment with IM-1 $^{13}$C detection takes place after cross-polarization. The PI intensities in the $^{13}$C spectrum are very low or absent because the cross-polarization is much less efficient for the PI than for the PMMA. For the shortest mixing time no PMMA is detected. With increasing $t_m$ the PMMA signal increases, until equilibrium is reached. For IM-2 $^1$H detection is used. Here the decrease of the PI signal is measured. The spin diffusion curves obtained from these data are shown in Figure 3. From these curves the size of the minor domains $d_{dis}$ can be determined according to ref.[3]

$$d_{dis} = \left(\frac{\rho_{H,A}\phi_A + \rho_{H,B}\phi_B}{\phi_A\phi_B}\right) \times \frac{4\varepsilon\phi_{dis}}{\sqrt{\pi}} \frac{\sqrt{D_A D_B}}{\rho_{H,A}\sqrt{D_A} + \rho_{H,B}\sqrt{D_B}} \sqrt{t_m^*} \qquad (2)$$

Here $\rho_{H,A}$ and $\rho_{H,B}$ are the proton densities of each phase, and $\phi_{dis}$ is the volume fraction of the dispersed (minor) phase. $t_m^*$ is defined as the time at which intersection of the extrapolation of the linear part of the spin diffusion curve and the equilibrium magnetization level occurs,[3] see Figure 3.

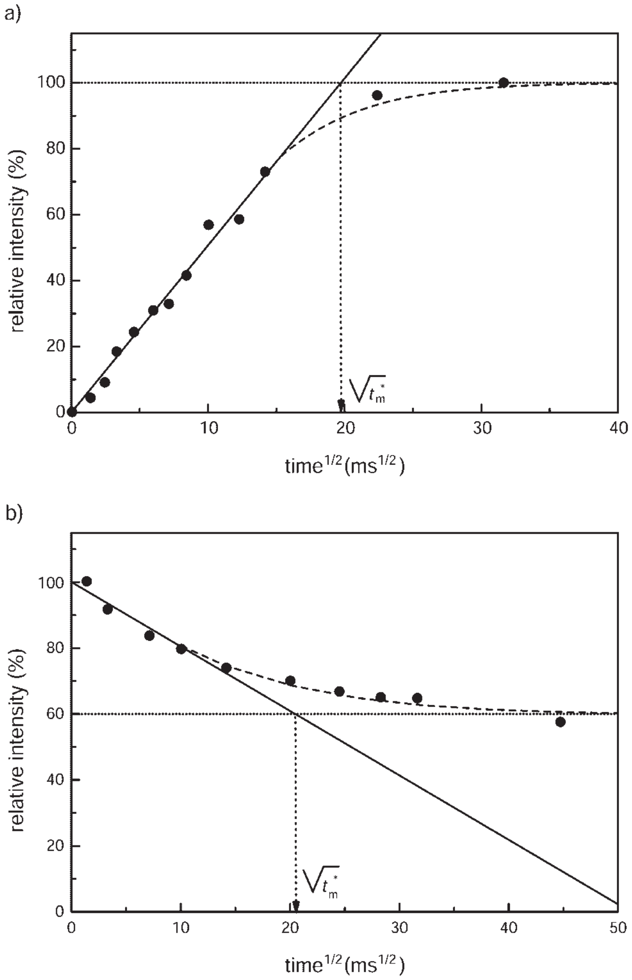

Figure 3. Spin diffusion curves obtained for a) IM-1 using $^{13}$C detection, and b) IM-2 using $^1$H detection. The dashed curved lines are guides to the eye.

For both systems $t_m^*$ was determined using the initial rate approximation. For IM-1 $t_m^* = 390 \pm 80$ ms. The domain size of the PI phase is calculated using Equation (2), yielding $d_{dis} = 16 \pm 2$ nm. The long period $d_L$ is then easily calculated from the volume fractions, and is $33 \pm 4$ nm. For IM-2 $t_m^* = 420 \pm 150$ ms, and a domain size of $21 \pm 4$ nm was determined for the PMMA phase. For IM-2 $d_L$ is calculated to be $38 \pm 7$ nm. This calculation is based on geometrical considerations for hexagonally ordered cylinders.[15] In Figure 4 the total area of the triangle $\times\ \phi_{dis}$ is equal to $\frac{1}{2}\pi \times (\frac{1}{2}d_{dis})^2$. This leads to the expression

$$d_L = \frac{\frac{1}{2}\sqrt{2\pi}\cdot d_{dis}}{\sqrt{\phi_{dis}}\sqrt[4]{3}} \approx 0.95\frac{d_{dis}}{\sqrt{\phi_{dis}}} \qquad (3)$$

for the calculation of the long period.

Finally, for both systems, a comparison was made with theoretical values according to the statistical theory

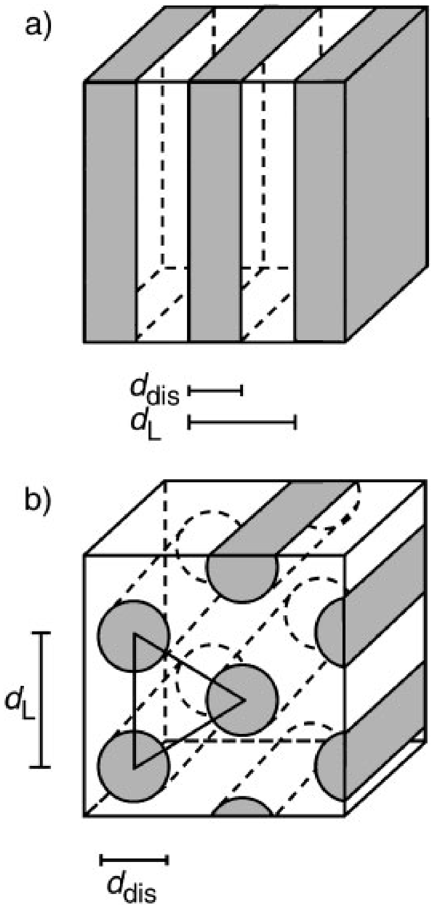

Figure 4. Morphologies of an a) lamellar, and b) hexagonally ordered cylindrical sample (schematic). The triangle in (b) indicates the symmetry that can be used to calculate the $d_L$.

developed by Helfand and Wasserman,[14,15,26] as shown in Table 1.

For IM-1 we calculated the domain sizes according to this theory.[14] For IM-2 we compared our results with theoretical calculations obtained in the literature for a comparable polymer with $\overline{M}_n = 46\,000{-}21\,000$.[15,34] Our polymer has the same length for the PMMA part, which forms the cylinders in the structure. The PI length is somewhat different, so the values for the long period can only be compared roughly. Table 1 compares the results from our NMR measurements with the theory. The experimental values for $d_{dis}$ are both ~20% lower than the theoretical estimates. In this way a systematic error between the theory and the experiment transpires. Usually the agreement between this theory and other experimental methods like small-angle X-ray scattering for polymers with $\overline{M}_n$ up to 100 000 is 10–14%.[14,15,26] Our results are in line with other recent examples from the literature where it has been found that the NMR methods somewhat underestimate domain sizes.[7,35–37] It is not clear at present what mechanisms may be responsible for the discrepancies, but it cannot be excluded that the microphase separation leads to increased dynamics at the interface that interfere with the spin diffusion processes.[32,33]

Table 1. Domain sizes determined using $^1$H spin diffusion, and comparison with literature and theoretical values.

| Polymer | | $d_{dis}$ | $d_L$ |
|---|---|---|---|
| | | nm | nm |
| IM-1 | NMR | $16 \pm 2$ | $33 \pm 4$ |
| | Theory | 19.8[a)] | 43.0[a)] |
| IM-2 | NMR | $21 \pm 4$ | $38 \pm 7$ |
| | Theory | 27.9[b)] | 44.1[b)] |

[a)] Calculated with Equation (V.3) from ref.[14]
[b)] Theoretical results for PI-*b*-PMMA with $\overline{M}_n$ 46 000–21 000[34] calculated in ref.[15]

## Conclusion

Solid-state NMR techniques were used to study microphase separated PI-*b*-PMMA diblock copolymers. $T_1$ measurements show two separate values, thus confirming microphase separation. Deviations from homopolymer values for $T_1$ indicate a substantial contribution from spin diffusion. In a WISE spectrum no mobility changes compared to the respective homopolymers were detected in the separate phases. This shows that the interphase between the polymers is narrow, as expected for highly incompatible polymers.

$^1$H spin diffusion measurements were performed to determine the domain sizes of the PI-PMMA diblock copolymers. For the lamellar sample IM-1 a characteristic domain size for the PI phase of $16 \pm 2$ nm is detected. For IM-2, with a hexagonally ordered cylindrical morphology, the dispersed PMMA phase measures $21 \pm 4$ nm. These results are ~20% smaller than theoretical values calculated according to Helfand and Wasserman, which indicates that the NMR underestimates domain sizes for the PI/PMMA diblock copolymer system.

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