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Mobility, Structure, and Domain Size in Polyimide−Poly(dimethylsiloxane) Networks Studied by Solid-State NMR Spectroscopy

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ABSTRACT: Dynamics, structure, and domain size in polyimide−poly(dimethylsiloxane) networks (PI−PSX) with various compositions were investigated by solid-state NMR spectroscopy. ^{29}Si and ^{13}C MAS NMR spectroscopy revealed the presence of PSX chains in two motional states, and their relative content was estimated. The overall mobility as well as local motions was studied by 1D and 2D ^{1}H wide-line spectroscopy. 2D WISE spectra proved large differences in molecular mobility of PSX and PI chains. High mobility of PSX is not imparted to rigid PI, and the interfacial region is located in the PSX phase. This region corresponds to the immobilized PSX chains at the surface of PSX domains, which link PI chains. The spherical morphology and domain sizes at the nanometer scale were determined from analysis of spin diffusion processes. Molecular mechanics and dynamics calculations were performed to design PSX domains at the atomic level. Correlation of the structure and morphology with mechanical and thermal properties is discussed.

Introduction

In our previous studies,[1,2] we focused our attention on the determination of the structure, size, and dynamics of domains in hybrid siloxane networks, technologically important materials used in several fields like catalysis, separation, microelectronics, etc. The interest in hybrid networks follows from the possibility to prepare new materials with well-designed properties, which cannot be achieved by using single polymers. As only a small number of polymer pairs form thermodynamically stable mixtures on the molecular level, cross-linking of polymer components is used to prepare more stable materials.

Increasing interest in scientific and practical fields is nowadays devoted to a combination of aromatic polyimides with polysiloxanes. Aromatic polyimides (PI), which possess very good mechanical and dielectric properties as well as thermal stability up to 200 °C, are often used in separation, microelectronics, aircraft industry, and space research.[3] Linear copolymers based on copolymerization of PI with poly(dimethysiloxane) (PSX) have become important and interesting materials.[4] Random or block copolymers are formed by incorporation of suitably terminated flexible oligo(dimethylsiloxanes) in PI chains. Their final properties depend on the type of copolymer as well as on the amount and molecular weight of both components. Polyimide−poly(dimethylsiloxane) (PI−PSX) copolymers usually have higher solubility, impact strength, and lower sorption of water compared to those of neat PI. The presence of PSX chains, on the other hand, decreases thermal and chemical stability and tensile strength.[4,5] To increase the overall stability of such materials, linear polymer chains have to be cross-linked into a three-dimensional network.[6] Preparation of PI cross-linked by short −Si−O− sequences starts from poly(amic acid) (PAA) terminated by 4-(aminophenyl)trimethoxysilane (APTMS)[7] (see Scheme 1). After water addition, hydrolysis of methoxy groups takes place, and during subsequent heating PAA transforms to PI. Cross-linking units −Si−O− are formed by condensation of silanol groups. In our previous work[8] we used this procedure to prepare hybrid material PI−SiO$_2$. In the present report we report materials prepared from PAA based on 4,4′-oxydiphthalic anhydride (ODPA) and 4,4′-oxydianiline (ODA) terminated by APTMS. Dimethoxy(dimethyl)silane (DMDMS) was used to form PSX cross-links between PI chains. A cross-linked material is formed during thermal exposure of a thin layer of the reaction mixture.[9] Four PI−PSX networks with various composition (0−30 wt % of PSX) and thermal behavior (with single and/or two glass transitions temperatures T_g) were investigated (see Table 1).

Table 1. Poly(dimethylsiloxane) Contents in Networks, *w*(PSX), Number-Average Molecular Weight, M_n, Polymerization Degree, X_n, Lower and Higher Glass Transition Temperatures T_g (K), and Tensile Strength σ (MPa)

network	w(PSX) (wt %)	T_g (K) lower	T_g (K) higher	X_n (PSX)[a]	M_n (PSX)	σ (MPa)
PI	0		563			127
PI−PSX 90−10	10		542	5.6	358	96
PI−PSX 80−20	22	156	541	14.5	928	80
PI−PSX 70−30	31	156	528	22.3	1427	67

[a] Number-average polymerization degree (X_n) of PSX chains was calculated from single-pulse ^{13}C MAS NMR (determining relative amount of PI and PSX chains) and ^{29}Si RAMP/CP/MAS spectra (determining functionality of terminal unit of PI chain $f = 2.7$).

To understand the properties of these polymer networks at molecular level, it is necessary to obtain detail knowledge about the microphase structure, molecular dynamics, and the degree of phase separation. It was suggested that two competing effects control the location

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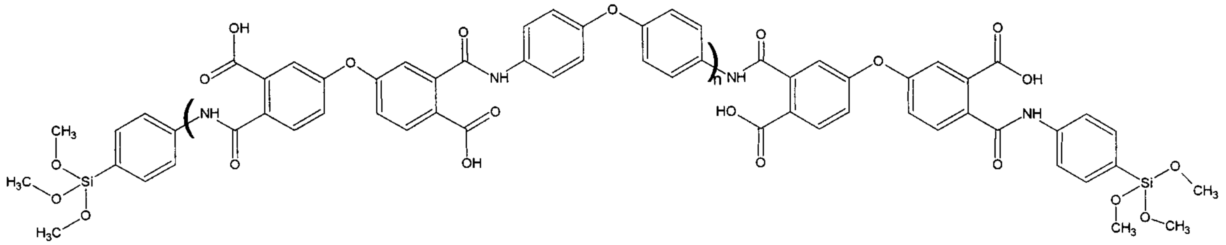
Scheme 1



of the PSX phase. While covalent links between PI and PSX blocks tend to keep both phases separated to assemble PSX chains into large domains, entropic effects favor a uniform distribution of relatively small PSX domains through the PI phase. Two glass transition temperatures (T_g) were found in networks containing high amounts of the PSX component, suggesting heterogeneity on the 10−100 nm scale.[9] On the other hand, single T_g determined for networks containing low amounts of PSX indicates that both components are miscible on the ∼10 nm scale. However, to examine miscibility of the systems on the scale below 10 nm, 1D and 2D solid-state NMR experiments have to be carried out. Another open question is the presence of motional heterogeneities in the sample. The presence of highly mobile PSX chains may increase the local mobility of PI chains. In particular, the interaction between different components in the interfacial region is interesting.

To study molecular dynamics and morphology and to determine the size of the domains in these heterogeneous systems, which is the main purpose of this work, several solid-state NMR techniques were used. In particular, 2D wide-line spectroscopy (WISE) experiment[10−14] provides the desired information about the local dynamics of both components and the interfacial region, and by the combination with the ^{1}H spin diffusion,[10,13,15] long-range ordered structures can be studied on the 0.5−200 nm scale. The obtained global structural data were used in the molecular mechanics and molecular dynamics simulations in an attempt to design a reliable molecular model of these networks.

Experimental Section

Materials. Synthesis of PAA and a typical PI−PSX network as well as thermogravimetry analysis (TGA), measurement of tensile strength (σ), and dynamic mechanical analysis (DMA) are described in detail in our previous study.[9] ODPA was dissolved in *N*-methyl-2-pyrrolidone (NMP). Terminating agent APTMS was then added and allowed to react with ODPA. ODA was subsequently added to the reaction mixture, and the system was stored at room temperature for 24 h. After the formation of PAA, the cross-linking agent DMDMS and water were added to a 15 wt % solution of PAA in NMP under stirring. The originally heterogeneous mixture which homogenized about an hour was stirred for additional 24 h. The resulting solution was spread onto a substrate, and the resulting thin layer was kept at 60 °C/24 h, 90 °C/5 h, 150 °C/2 h, 200 °C/2 h, and finally 240 °C/2 h. The experimentally determined polymerization degree (X_n) of PSX chains, tensile strength, and T_g are listed in Table 1.

NMR Spectroscopy. NMR spectra were measured using a Bruker DSX 200 NMR spectrometer at frequencies of 39.75, 50.33, and 200.14 MHz (for ^{29}Si, ^{13}C, and ^{1}H, respectively). Samples were placed in a 4 mm ZrO_2 rotor. Magic angle spinning (MAS) frequencies were 4 and 10 kHz, and the intensity of B_1 field (^{1}H, ^{13}C, and ^{29}Si) was 62.5 kHz. ^{13}C RAMP/CP/MAS (ramped/cross-polarization/magic angle spinning) and single-pulse NMR experiments were used with repetition delays of 4 and 20 s, respectively. The CP contact pulse was 1 ms. Repetition delay for measurement of single-pulse ^{29}Si MAS NMR spectra was set to 5 s to detect only mobile components. 2D wide-line spectroscopy (WISE) employed 260 scans per increment. The evolution period (t_1) between the ^{1}H 90° pulse and contact pulse consists of 128 increments of 10 μs. The ^{29}Si and ^{13}C scales were calibrated by external standard M_8Q_8 (−109.80 ppm; the highest field signal) and glycine (carbonyl signal at 176.03 ppm), respectively. Temperature of bearing inlet air was set to 30 °C. The actual sample temperature due to the frictional heating of rotor was higher by 2−14 °C at 4−10 kHz of MAS frequency.[16]

Molecular Modeling and Calculation. Geometry optimization and molecular dynamics calculations were performed with the Hyperchem 5.02 program package using the MM+ force field. Geometries of all molecular systems were completely optimized by using the Fletcher−Reeves and block-diagonal Newton−Rhapson algorithms. To obtain a reliable model of the optimized structures, the entropy of systems was first increased by the molecular dynamics calculations at 900 K and obtained geometries of the systems were again completely optimized. To compare molecular mobility of some selected PSX species, molecular dynamics calculations at 300, 600, and 900 K were performed. Computational time was 100 ps with steps of 0.001 ps.

Results and Discussion

^{29}Si MAS NMR. Information about the structure and dynamics of the PSX component of the prepared polymer networks were obtained by a combination of ^{29}Si RAMP/CP/MAS and single-pulse MAS NMR spectra (cf. Figure 1). Narrow signals of highly mobile dimethylsiloxane monomer units were predominantly detected in single-pulse ^{29}Si MAS NMR spectra measured with short repetition delay (smaller spectra in the upper part of Figure 1). Signals of rigid units are suppressed by their long T_1(^{29}Si) relaxation times. In the single-pulse ^{29}Si MAS NMR spectra of all prepared materials we observed a weak signal at −19.50 ppm, corresponding to dimethysiloxane units in the cyclic tetramer.[1,17] The presence of this signal indicates cyclization reactions during polycondensation of DMDMS, the extent of which is, however, small (estimated from the relative signal intensity). As only very weak signals with ^{29}Si NMR chemical shifts ranging from −10 to −14 ppm were found in single-pulse NMR spectra, there is only a very small amount of free terminal units of highly mobile PSX chains in the prepared products. Both ends of mobile PSX chains are thus chemically bound to the PI phase.

Narrow and partially overlapped signals at ca. −22.5 ppm predominate in ^{29}Si MAS NMR spectra of materials containing large amount of the PSX component (PI−PSX 70−30 and 80−20). These signals reflect inner highly mobile dimethylsiloxane monomer units in longer polymer chains (number of dimethylsiloxane monomer units is larger than 10)[18]. In the ^{29}Si MAS NMR spectrum of product PI−PSX 90−10 only a weak signal at −21.8 ppm was found. It indicates formation of short

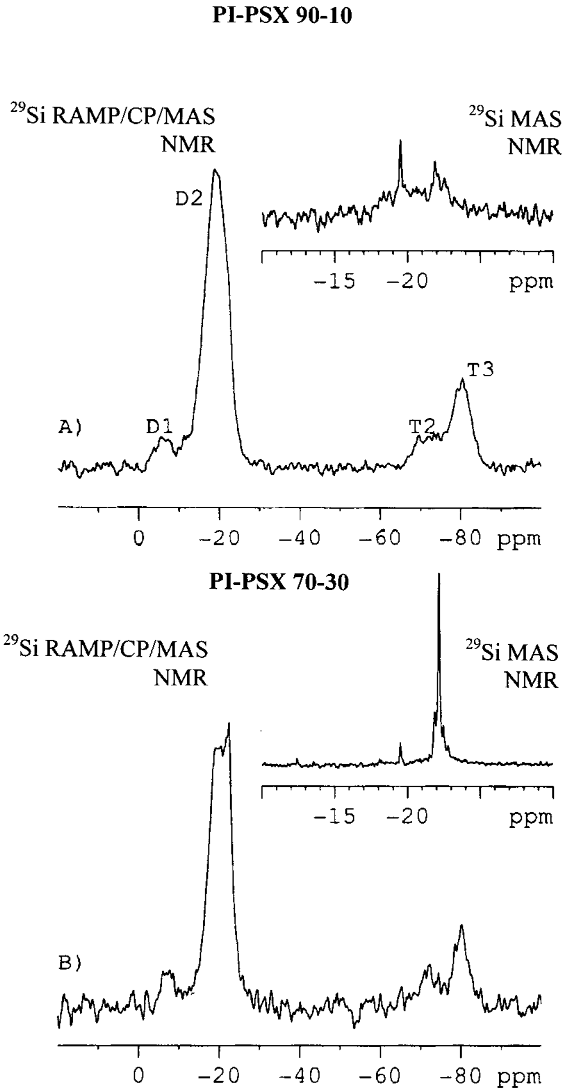


Figure 1. ^{29}Si RAMP/CP/MAS and single-pulse MAS NMR spectra of polymer networks PI−PSX 90−10 (A) and PI−PSX 70−30 (B). The upper traces are single-pulse ^{29}Si MAS NMR spectra.

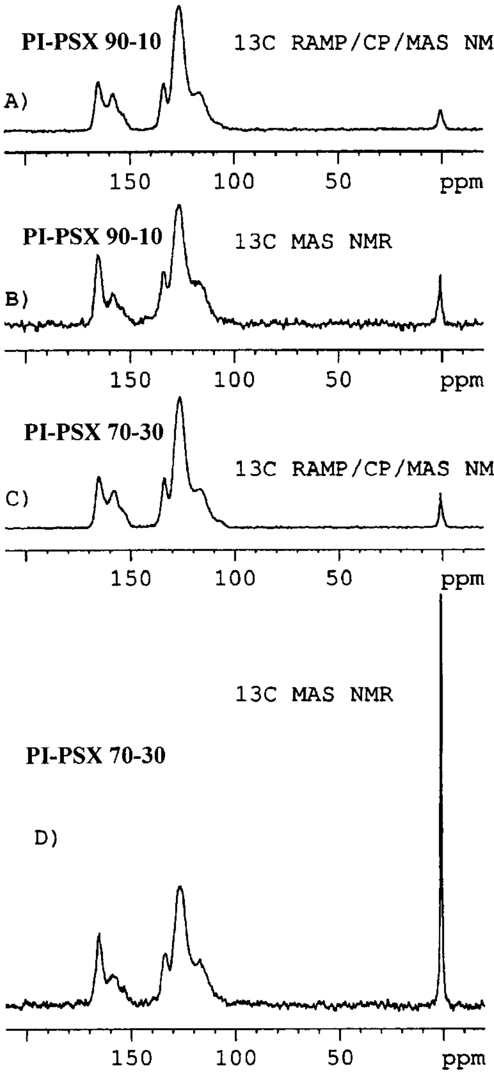


Figure 2. ^{13}C RAMP/CP/MAS NMR and single-pulse MAS NMR spectra of polymer networks PI−PSX 90−10 (A, B) and PI−PSX 70−30 (C, D), respectively.

PSX chains with ca. 5 monomer units.[18] Because of hindered molecular motion and various local magnetic environments, their signals are inhomogeneously broadened and thus almost undetectable.

The structure of partially immobilized PSX component is reflected by ^{29}Si RAMP/CP/MAS NMR spectra. As a relatively slow spinning speed (4 kHz) and an amplitude-modulated shaped pulse for cross-polarization[19,20] were used, dimethylsiloxane units possessing anisotropic motion with various degrees of immobilization were observed. Signals ranging from −70 to −90 ppm correspond to terminal structure units of PI chains (residue of the termination agent, APTMS). The terminal structure units (T^n) of PI, which should be essentially trifunctional due to the condensation reactions, are reflected by two signals. A more intensive signal at ca. −80 ppm indicates T^3 structure unitswith all three hydroxy groups condensed. (They form siloxane bonds with dimethylsiloxane units.) The other signal at ca. −70 ppm corresponds to the T^2 terminal structure units containing one residual hydroxy group. The presence of these T^2 signals points to a partially irregular polymer network and smaller average functionality of terminal groups of PI chains ($f = 2.7$).

The strong peak ranging from −10 to −30 ppm consists of several overlapping signals corresponding to immobilized dimethylsiloxane units D^n which are close to terminal groups of PI chains. According to their ^{29}Si chemical shifts, these signals reflect both dimethylsiloxane monomer units directly bonded to the terminal groups of PI and inner monomer units in immobilized dimethylsiloxane chains.[1,2] The latter give rise to upfield signals at ca. −22 ppm. This is apparent in the ^{29}Si RAMP/CP/MAS NMR spectrum of the sample PI−PSX 70−30 (Figure 1B). The signal at ca. −8 ppm indicates a small portion of the immobilized free terminal D^1 structure units in oligo(dimethylsiloxane) chains [−O−Si(CH$_3$)$_2$−OH]. For steric reasons very short PSX chains tend to be attached by one end only. From the signal intensity we can estimate that such a short PSX chain is linked approximately to every sixth or seventh terminal structure unit of PI.

^{13}C MAS NMR. Single-pulse ^{13}C MAS NMR spectra enable to determine the relative content of both polymer phases in the prepared materials (PI and PSX). In addition, their comparison with ^{13}C RAMP/CP/MAS spectra offers information about the dynamics of both polymer phases (cf. Figure 2) so that the fraction of highly mobile and partially immobilized PSX chains can be estimated.

It is known that the efficiency of cross-polarization process, which is substantial for the detection of CP/MAS NMR spectra, strongly depends on the strength of homonuclear ^{1}H$-$^{1}H and heteronuclear ^{1}H$-$^{13}C dipolar interactions. Increasing local mobility gradually reduces the strength of these interactions and, consequently, also the efficiency of cross-polarization process. Fast isotropic motion leads to complete averaging of these interactions to zero so that no cross-polarization NMR spectra can be detected. As was expected, comparison of ^{13}C single pulse MAS and RAMP/CP/MAS NMR spectra revealed that most of the PSX chains possess much higher molecular mobility than PI chains. Detection of the ^{13}C NMR signal of such highly mobile PSX methyl groups by cross-polarization would require a very long contact time. Therefore, the signal detected in ^{13}C RAMP/CP/MAS NMR spectra at ca. 0 ppm measured at a relatively short contact time (1 ms) corresponds only to those PSX chains, which are immobilized by the intimate interaction with rigid PI chains. The content of this intimately mixed PSX phase, relative to the PI component, is nearly the same in all samples. The amount of this immobilized PSX fraction defined as the ratio of signal intensities of PSX and PI units (in ^{13}C RAMP/CP/MAS NMR spectra; see Figure 2) ranges from 0.032 to 0.034, which corresponds to 9.5$-$10 immobilized monomer units per one PI chain. From the differences in the intensities of the PSX signal in ^{13}C RAMP/CP/MAS NMR and ^{13}C MAS NMR spectra, we calculated the fraction of mobile PSX units, which are at large distance from PI and cannot be detected in ^{13}C RAMP/CP/MAS NMR spectra. For quantitative evaluation of ^{13}C RAMP/CP/MAS NMR spectra, variable contact-time experiments[21] were done, correlating integrated intensities with spin dynamics. The calculated fraction of more mobile poly(dimethylsiloxane) chains decreases with their decreasing length from 83 to 27 mol % of the PSX phase. These values are in accord with $T_{1\rho}(^{13}\mathrm{C})$ relaxation measurements revealing double-exponential decay. Relative intensities of both components well correspond with fractions of the PSX phases determined from ^{13}C NMR spectra. Our results indicate that the size of the PSX domains increases with increasing content of poly(dimethylsiloxane) in the networks.

^{1}H MAS and Static NMR. While the techniques discussed above provide information about the distribution of local sites in the networks, ^{1}H wide-line spectra and in particular two-dimensional wide-line separation spectroscopy (WISE) can give insight into relative molecular mobility of both polymer components. The size of their domains can be determined by two-dimensional experiments combined with ^{1}H spin diffusion.

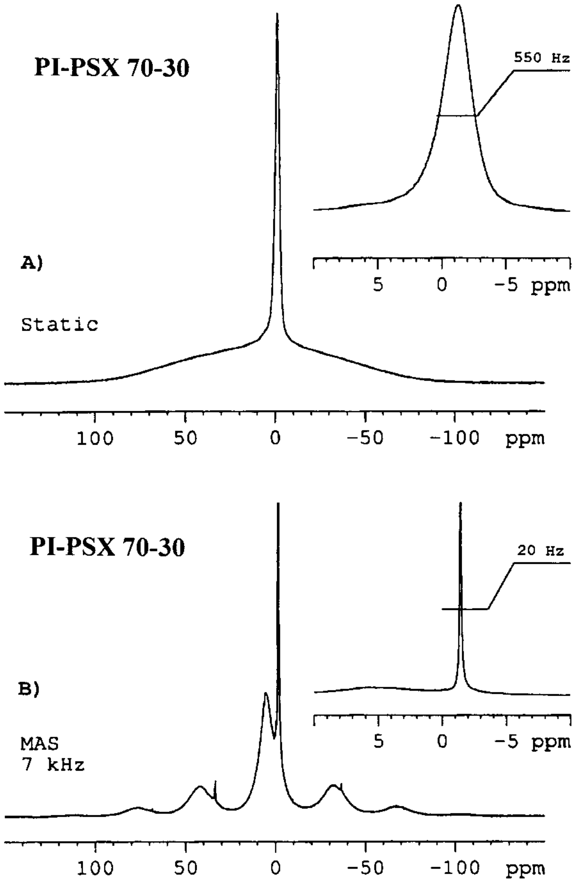


Figure 3. ^{1}H static and MAS NMR spectra, (A and B, respectively) of network PI$-$PSX 70$-$30. Upper traces are details of the narrow signal corresponding to the PSX component.

A typical ^{1}H wide-line NMR spectrum (cf. Figure 3A) reflects immobile segments of PI as a broad line. This line is only slightly affected by sample rotation at the rate of 4 kHz, whereas broad spinning sidebands are formed at 7 kHz. This indicates slow molecular motions with rates of tenths to hundredths of a kilohertz. On the other hand, a narrow signal (half-width of about 0.6 kHz) corresponding to PSX chains is narrowed by MAS to a line width of ca. 20 Hz (see Figure 3B). This significant line narrowing and the presence of weak spinning sidebands reflect anisotropic motions with correlation frequencies exceeding 1 MHz. Nevertheless, a proton line width of ca. 0.6 kHz in static ^{1}H NMR spectra indicates restricted molecular motion of poly(dimethylsiloxane) chains. Poly(dimethylsiloxane) chains in the PSX domains are neither liquidlike nor soft rubbery materials. This follows from comparison with the static ^{1}H NMR spectra of model PSX networks (cf. Figure 4), prepared by sol$-$gel copolymerization of diethoxy(dimethyl)silane (DEDMS) with tetraethoxysilane (TEOS) at the mole ratio 4:1 and 9:1. The ^{1}H line width of the former product, a very soft rubbery-like material, is about 80 Hz. The latter material, which is viscous liquid, has a proton signal with line width of only 40 Hz. Taking this into account, we can conclude that the domains of poly(dimethylsiloxane) chains in PI$-$PSX materials are relatively small and rather uniformly distributed within the whole copolymer network. In addition, the broadening of the poly(dimethylsiloxane) lines (from 550 to 640 Hz) with decreasing content of PSX in the networks indicates reduction of molecular mobility.

2D WISE and Spin Diffusion. 2D WISE spectroscopy[11$-$13] provides detailed information about molecular dynamics and the presence of mobility heterogeneities. Molecular motion is probed by ^{1}H wide-line shapes, which are separated in the second dimension by the ^{13}C chemical shift. Highly mobile segments are reflected by narrow ^{1}H lines, and vice versa. 2D WISE spectra as well as ^{1}H dipolar slices for protons of the PI and PSX components are shown in Figure 5. All signals corresponding to PI are significantly broader than the signal of PSX segments. From this difference one can see that the high mobility of PSX is not imparted to the PI phase.

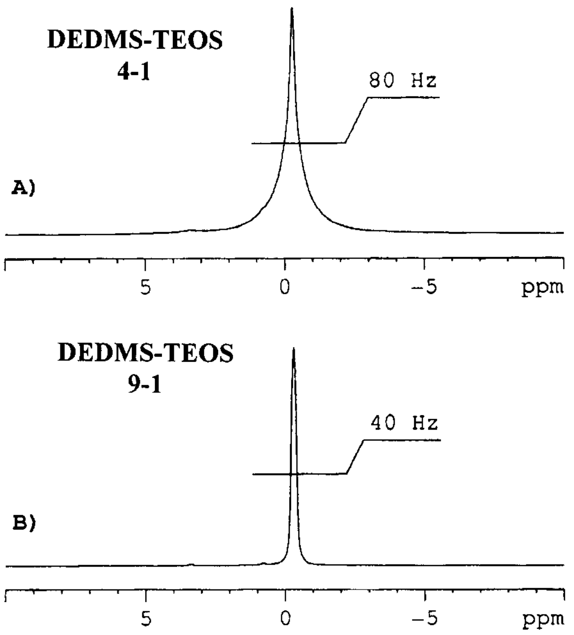


Figure 4. ^{1}H static NMR spectra of model poly(dimethylsiloxane) networks prepared by copolymerization of DEDMS and TEOS with molar ratio 4:1 and 9:1 (A and B, respectively).

On the other hand, in proton dipolar spectra of poly(dimethylsiloxane) units of the PI−PSX 80−20 network, one can resolve a broad component indicating the presence of interfacial region with segmental motion restricted due to intimate interactions with the PI chains. ^{1}H dipolar spectra of aromatic signals of PI contain additional information about local motions. According to the literature,[12] presence of intensive spinning sidebands in ^{1}H dipolar spectra measured at relatively slow MAS (3−4 kHz) corresponds to intensive phenyl flips along the $C2$ axis. As no spinning sidebands are observed in proton dipolar spectra of any of the studied PI−PSX networks, we cannot expect high-amplitude flips of aromatics rings in the PI chains. Similarity in the shapes of the ^{1}H of aromatic signals in neat PI and in PI−PSX networks proves that the presence of highly mobile PSX does not change the motional properties of polyimide chains. From this follows that the increased impact strength of PI−PSX networks is induced only by the flexibility of PSX chains. 2D WISE NMR spectrum with the same features (large differences in the line shapes of dipolar slices) was obtained also for the PI−PSX 90−10 network containing the lowest amount of PSX. Although a single T_g indicating homogeneous system was found by DMA for this PI−PSX 90−10 network,[9] the 2D WISE NMR experiment clearly detects substantial motional heterogeneities.

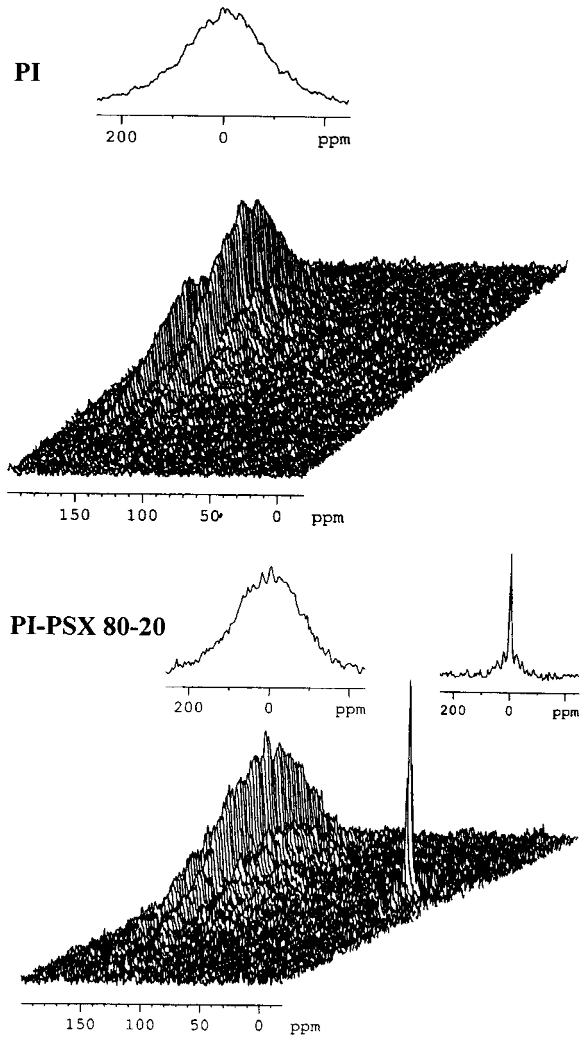


Figure 5. 2D WISE NMR spectra and ^{1}H dipolar slices of neat PI sample and PI−PSX 80−20 network.

The presence of dynamic heterogeneities in the networks makes possible to perform the 2D spin diffusion experiment proposed by Schmidt-Rohr et al.[12] to determine the size of domains of both components and morphology of the system. The motional narrowing of PSX proton lines is transferred to the broad signals of PI carbons at a rate proportional to $1/r_{ij}^3$ during a mixing time allowing spin diffusion. At short mixing times, polarization is transferred to spins near the magnetization source. At longer times, relayed transfer to further spins can occur. Gradual increasing of the intensity of the narrow component in the originally broad line reflects spin diffusion process (see Figures 5 and 6). Two samples with one and two values of glass transition temperatures T_g (PI−PSX 90−10 and PI−PSX 80−20, respectively) were selected for this experiment. The experimentally determined and simulated spin diffusion dependences are shown in Figure 7. The strategy of evaluation of spin diffusion curves is described in detail in contributions by Schmidt-Rohr et al.[10,13] Analysis of the spin diffusion process starts from a two-phase system with an interface and with variable dimensionality $\epsilon = 1-3$. The effective diffusivity is defined by the following equation:

$$\sqrt{D_{\mathrm{eff}}} = \frac{2r_{\mathrm{d}}\sqrt{D_{\mathrm{PSX}}D_{\mathrm{PI}}}}{\sqrt{D_{\mathrm{PSX}}} + r\sqrt{D_{\mathrm{PI}}}} \qquad (1)$$

where r_{d} is proton spin density ratio ($r_{\mathrm{d}} = \rho_{\mathrm{PI}}/\rho_{\mathrm{PSX}}$). The diffusivity expressed in terms of local dipolar fields proposed by Cheung[23,24] was used to determine coefficients D_{PI} and D_{PSX}. Considering alternative approach relating diffusivity to T_2 relaxation,[15,25,28] we compared our calculated coefficients with those previously determined for rigid and highly mobile organic solids. Diffusivities for mobile PSX protons and rigid aromatic PI protons were calculated using the following equations, which are valid for Lorentzian and Gaussian line shape, respectively:[29]

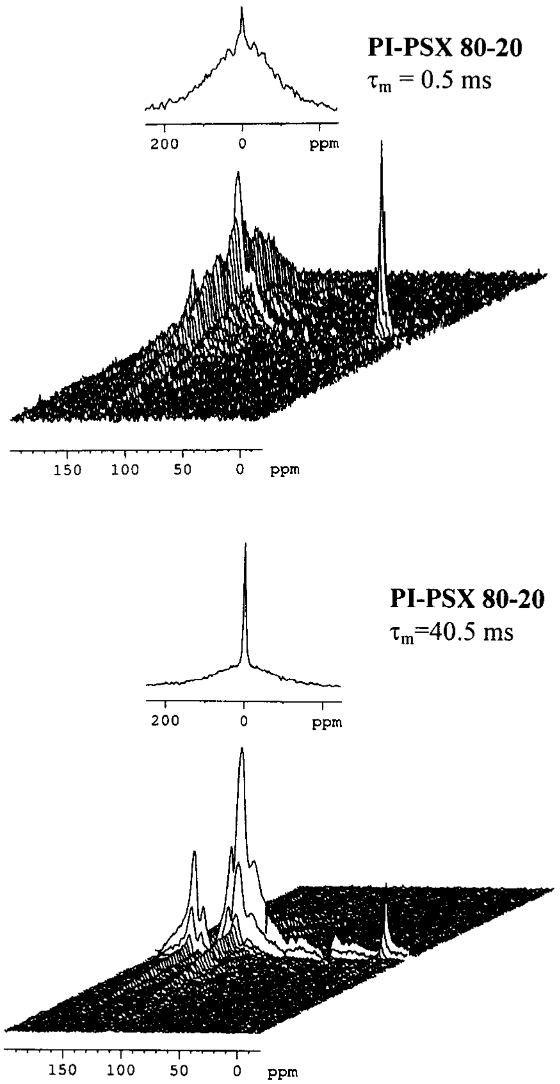


Figure 6. 2D WISE NMR spectra and ^{1}H dipolar slices PI–PSX 80–20 network with spin diffusion mixing time 0.5 and 40.5 ms.

$$D_{\mathrm{PSX}} = \frac{1}{6}\langle r^2\rangle[\alpha\Delta\nu_{1/2}]^{1/2} \qquad (2)$$

$$D_{\mathrm{PI}} = \frac{1}{12}\sqrt{\frac{\pi}{2\ln 2}}\langle r^2\rangle\Delta\nu_{1/2} \qquad (3)$$

$\langle r^2\rangle$ is the mean-square distance between the nearest spins (typically 0.2–0.25 nm[13,14]); α is cutoff parameter, and $\Delta\nu_{1/2}$ is full width at half-intensity of signals.

From the 2D WISE experiment the respective half-widths are of ca. 1.0 kHz (PSX: CH_3– signal at 0.0 ppm) and of ca. 35 kHz (PI: aromatic –CH= signal at 126.1 ppm). The calculated diffusivity of 0.09 nm^2 ms^{-1} for PSX is in good agreement with literature data[13,22,29–33] for analogous polymer systems. For mobile amorphous poly(ethylene oxide) with the ^{1}H NMR line width of 0.6 and 1.7 kHz and amorphous polyethylene with the line width of ca. 1.8 kHz, diffusivities were reported[13,30,33] in the range 0.09–0.15 nm^2 ms^{-1}. Spiegel et al.[25] determined a diffusivity of 0.05 nm^2 ms^{-1} for polyisoprene. For soft polyurea segments[31] and highly mobile aliphatic side chains,[34] spin diffusion coefficients were determined to be 0.04 and 0.05 nm^2 ms^{-1}, respectively. For a rubbery poly(epichlorohydrin)/poly(vinyl acetate) blend,[32] even the value of 0.01 nm^2 ms^{-1} was reported.

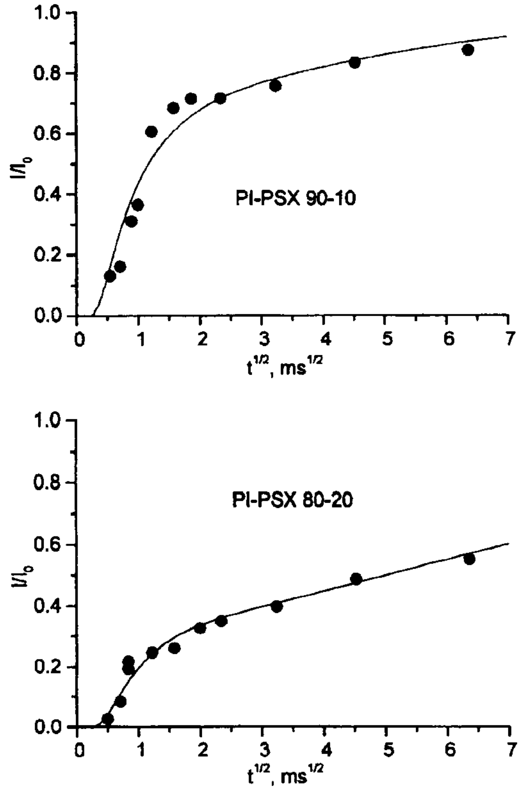


Figure 7. Experimental data (dots) and simulated spin diffusion curves of PI–PSX 90–10 and 80–20 networks.

Table 2. Calculated Spin Diffusion Coefficients, D_{PI} and D_{PSX}, Proton Fraction, Φ, Density, ρ_{PI} and ρ_{PSX}, and Spin Density, $\rho(s)_{\mathrm{PI}}$ and $\rho(s)_{\mathrm{PSX}}$

polymer	D, nm^2 ms^{-1}	Φ	ρ, g cm^{-3}	$\rho(s)$, g cm^{-3}
PI (rigid)	0.31	0.03	1.28	0.04
PSX (mobile)	0.09	0.08	0.97	0.08

Also, recent measurements of the spin diffusion coefficients based on T_2 relaxation of mobile phases reported by Mellinger et al.[26] (of ca. 0.03–0.08 nm^2 ms^{-1}) are very close to our calculated values. The calculated diffusivity of the PI component has a value of 0.31 nm^2 ms^{-1}, which is also in a good agreement with the literature data. A diffusivity of 0.4 nm^2 ms^{-1} was determined[34] for aromatic main-chain protons of hard segments of poly(1,4-phenyleneterephthalimide) and poly(1,4-phenylenepyromellitimide) as well as for aromatic poly(ester–urethane) elastomer.[23,35] Spin diffusion coefficients are assumed to be 0.29–0.32 nm^2 ms^{-1} for rigid hard domains of crystalline poly(ethylene oxide).[30] Much higher diffusivities were reported for highly rigid crystalline and dense packed polymers; e.g., the diffusivity of polyethylene with ^{1}H NMR line width around 70–80 kHz[30,33] is about 0.7–0.8 nm^2 ms^{-1}, and the diffusivity of crystalline alanine[36] is about 0.6–0.8 nm^2 ms^{-1}.

Parameters that are necessary for analysis of the spin diffusion process are summarized in Table 2. In the first approximation, a two-component phase-separated system consisting of particles of mobile PSX domain on one hand and rigid PI particles on the other were taken into account. Experimental and calculated data for two PI–PSX networks (PI–PSX 90–10 and 80–20) presented in Figure 7 show the increase in the intensity of narrow component in originally broad proton dipolar spectra of the selected aromatic carbon. The increase in the intensity is a function of mixing time. However, the model of a simple two-phase system with interface is

Table 3. Calculated Domain Sizes of Poly(dimethylsiloxane), Polyimide, and Interface Regions and Long Periods (d_{PSX}, d_I, and d_{PI}, Respectively) in nm in PI−PSX Networks Obtained by Simulation of Spin Diffusion Experiments

	fast process I			slow process II		
polymer	d_{PSX}	d_I	d_{PI}	d_{PSX}	d_I	d_{PI}
PI−PSX 90−10	0.1	0.5	3.1	3.5	3.7	6.5
PI−PSX 80−20	0.1	0.6	2.7	10.0	3.4	5.2

valid neither for the PI−PSX 90−10 nor for the PI−PSX 80−20 network. We observe deviation of magnetization behavior in the intermediate and late-time regions of the spin diffusion process. To analyze the spin diffusion curves for both networks, we modified numerical simulation of the spin diffusion so that single-spin diffusion process was extended to a double-spin diffusion process. The slow and fast spin diffusion processes are superimposed and take place simultaneously. We propose that the studied systems consist of two PSX components (mobile and partially immobilized chains), interface (boundary between PSX and PI), and a rigid PI phase.

According to the analysis of spin diffusion curves, the PSX domains are formed by spherical particles. The above-mentioned ^{29}Si and ^{13}C MAS NMR experiments revealed that the PSX phase consists of poly(dimethylsiloxane) chains that are at least in two motional states. The surface of the particles is composed by immobilized short oligo(dimethylsiloxanes), while the inner part is formed by longer chains possessing higher molecular mobility. As the relative amount of the immobilized PSX phase is constant for all studied networks, we suggest that these short dimethylsiloxane oligomers are located only near the ends of PI chains, and most of them form links between neighboring polyimide chains. Consequently, the first process apparent at the beginning of spin diffusion is fast magnetization transfer from the immobilized dimethylsiloxane monomer units to adjacent PI chains. As the relative amount of the immobilized PSX phase in the PI−PSX 90−10 network is high, the fast spin diffusion process is dominant. The slow spin diffusion process corresponds to the magnetization transfer from the more distant and more mobile inner part of the PSX domains. The amplitude of this process is low in the PI−PSX 90−10 network due to the low fraction of mobile PSX segments. In contrast, slow magnetization transfer predominates during the whole spin diffusion process in the PI−PSX 80−20 network where the relative amount of the mobile PSX segment is higher (see Figure 7). Using this model, experimental and calculated curves are in a good agreement.

The calculated distances are listed in Table 3. The results are divided into two columns according to the spin diffusion process (fast, I; slow, II). The fast process (I) is considered only between immobilized dimethylsiloxane oligomers at the surface of PSX domains and neighboring PI chains. The dimensionality of $\epsilon = 1$ for this process is the best choice, because there is only one possible direction of magnetization transfer. From this first spin diffusion process the size of the poly(dimethylsiloxane) surface layer was estimated. The calculated size of the PSX surface layer (see Table 3) of about 0.1 nm is too small to be reasonable. However, taking into account also the dimension of the interface located only in the PSX phase (as indicated by 2D WISE), we obtain the thickness of the surface layer about 0.6 nm. This is in a good agreement with the estimated cross section of the poly(dimethylsiloxane) chain taking into account the van der Waals radii as well as with reported thickness of the interface in block copolymer polystyrene-*block*-poly(dimethylsiloxane)[12] (1 nm). As the determined thickness of the surface layer is comparable with the estimated experimental error, it has to be considered as an approximate value. The fact that the same value of the thickness was determined for both systems under study indicates that the thickness of the surface layer is independent of the PSX content in the copolymer network. The dimension of the PI phase calculated from the fast spin diffusion process has no physical sense in this case, and it is considered as a part of the interfacial region for the second spin diffusion process. From this second spin diffusion process, the dimensionality of which is $\epsilon = 3$ (magnetization is transferred from spherical particles in three directions), we calculated the size of the inner more mobile part of the PSX domain. The inner part of the PSX domain is significantly smaller in the PI−PSX 90−10 system (3.2 nm) compared with the PI−PSX 80−20 system (10.0 nm). The overall size of the PSX domains is then 4.4 and 11.2 nm for PI−PSX 90−10 and 80−20, respectively. The smallest distance between the surfaces of neighboring PSX domains is 9.6 and 7.9 nm (PI−PSX 90−10 and 80−20, respectively). Schematic models for both systems are shown in Figure 8. The determined values should be taken as the smallest diameters rather than the average size of domains, because the spin diffusion experiments are more sensitive to the smallest distances. The above-mentioned spin diffusion data agree with the results obtained from the DMA measurements.[9] Two glass transition temperatures corresponding to the individual PI and PSX phases were obtained for the PI−PSX 80−20 system, indicating heterogeneity on the 10−100 nm scale, whereas single T_g determined for PI−PSX 90−10 indicates a homogeneous system on the 10 nm scale.

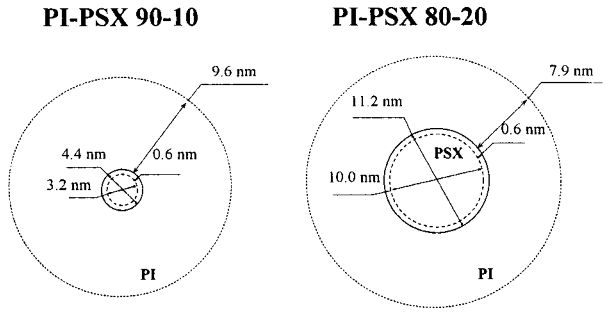


Figure 8. Schematic representation of PSX and PI domains of networks PI−PSX 90−10 and 80−20.

Experimentally determined dimensions of the PSX particles in these PI−PSX networks (4.4 and 11.2 nm) are smaller than the previously reported data (ca. 20 nm) for block copolyimides (polysiloxane-*b*-polyimide) with a roughly similar molecular weight of the PSX phase.[37,38] This reflects the compact structure and tough ordering of PSX particles formed by the sol−gel process and corresponds well to the previously determined[9] elongation at break (5−20%) of these materials, which is significantly smaller than value reported in the literature[39] (ca. 90%) for linear block copolymers with similar composition. Although the tensile strength of PI−PSX decreases with increasing PSX content (Table 1) due to the plasticizing effect of flexible PSX particles, cross-linking increases the overall stability of these materials. These networks prepared by sol−gel process

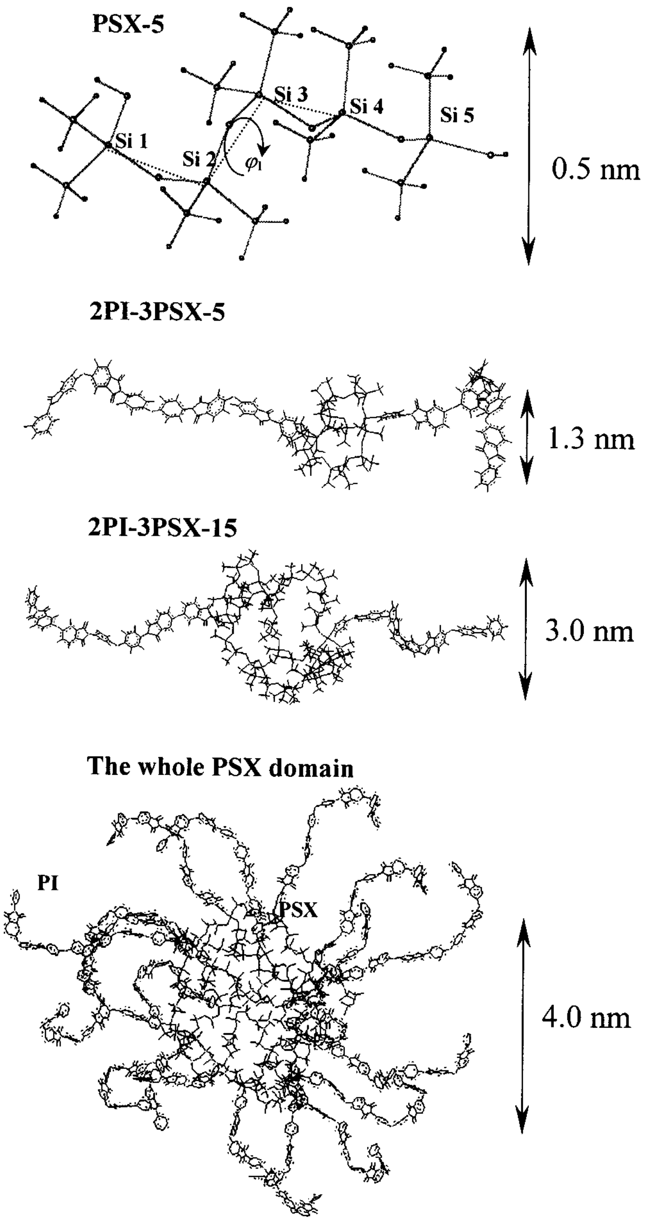


Figure 9. Examples of geometry-optimized model systems used for molecular dynamics calculations: dimethylsiloxane pentamer (PSX-5), system consisting of two PI monomer units coupled together by three PSX-5 and PSX-15 chains, (2PI-3PSX-5 and 2PI-3PSX-15), respectively, and the whole PSX domain.

with DMDMS can be considered as an intermediate state between linear block copolymers and nanocomposite polyimide–silica hybrids prepared by sol–gel process with trifunctional phenyltriethoxysilane. For the latter materials with silica particles having a diameter of less than 50 nm the plasticizing effect is not observed at all. Formation of a silica network restricts the chain motion, which results in the reinforcement of the hybrid materials.[40]

Molecular Modeling. On the basis of NMR spectra and spin diffusion data, we created a model of poly(dimethylsiloxane) particles in the PI–PSX 90–10 system at atomic level by using molecular mechanics calculations. From several trials to design the PSX domain, we propose following composition of the particles, which is in a good agreement with experimental data: (i) approximately 20 PI chains are linked to the surface of one PSX domain; (ii) from 60 reactive silanol groups of the terminal units of PI chains five remain free as –SiOH, while the rest take part in the formation of siloxane bonds; (iii) the surface of spherical PSX particles consists of three short dimethylsiloxane oligomers ($X_n \sim 2$) with terminal unit D^1 (not included in the network formation) and from 23 oligomers ($X_n \sim 5$) providing links between neighboring PI chains; (iv) the inner part of the PSX domain is formed by three long poly(dimethylsiloxane) chains with average polymerization degree of $X_n \sim 15$ connecting more distant PI chains; (v) the diameter of the resulting PSX domain is around 4 nm (see Figure 9).

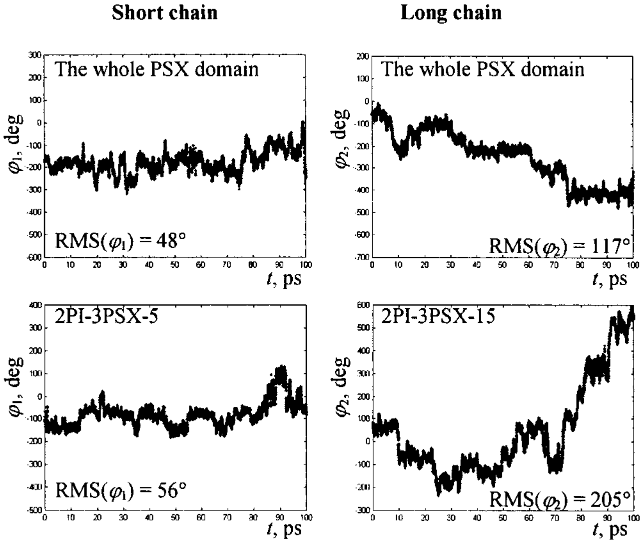


Figure 10. Plots of the φ_1 and φ_2 dihedral angles vs. time for selected short and long PSX chains computed for 600 K. Values greater than 180° or less than –180° were used in this figure to preserve continuity of the plots.

To support our experimental conclusions about different mobility of short and long PSX chains in the domain, molecular dynamics calculations of selected models were performed at three temperatures (300, 600, and 900 K). The higher temperatures are high enough to permit conformation transitions in reasonable computational time without rupturing a bond. In the calculations we recorded changes in a torsion angle of PSX chains, defined as following: for a short PSX chain (pentamer; PSX-5) the angle (φ_1) between the vectors connecting two nearest Si atoms (–Si(2)–Si(3)–Si(4)–Si(5)–, see dashed line in Figure 9); for a long PSX chain (pentadecamer; PSX-15) the angle (φ_2) between the vectors connecting two nearest Si atoms (–Si(7)–Si(8)–Si(9)–Si(10)–).

It was found that in calculations at 300 K the conformational changes are too slow to be observed in reasonable computational time. On the other hand, frequency and amplitude of the changes of the torsion angle calculated at 900 K are too high to be suitable for the comparison of molecular motions. Because of this fact, further calculations were performed at 600 K. The results obtained for models and the whole PSX domain (see Figure 9) are summarized in Figure 10. From the plots of the φ_1 and φ_2 dihedral angles vs time it is quite clear that the segmental motion of short PSX chains (PSX-5) is significantly slower compared with that of longer PSX-15 chains. These differences in segmental mobility are quantitatively expressed as root-mean-squared (rms) fluctuations of the torsion angles (cf. Figure 10). The obtained results provide another support for the acceptability of our model of poly(dimethylsiloxane) domains in the PI−PSX 90−10 network.

Conclusion

Three samples of PI−PSX networks with various compositions (PI−PSX 90−10, 80−20, and 70−30) were investigated by solid-state NMR spectroscopy. It was found that poly(dimethylsiloxane) chains in PSX domains are much more mobile than PI chains even for the system containing the lowest amounts of the PSX phase for which single T_g was determined by DMA. Despite the high molecular mobility of poly(dimethylsiloxane) chains, their overall molecular motion is hindered compared with the mobility of neat PSX networks due to the interaction with PI chains. In the PSX domains poly(dimethylsiloxane) chains occur in two motional states. The fraction of more mobile poly(dimethylsiloxane) chains located in the inner part of PSX domains increases with increasing amount of PSX phase in the networks, while the fraction of short poly(dimethylsiloxane) chains with restricted motion located at the surface of these particles is constant for all systems. As follows from the spin diffusion experiments, the surface of the domains is formed by a monolayer of short PSX chains with segmental mobility restricted by the interaction with PI chains. On the other hand, mobility of PI chains is not affected by the presence of mobile PSX component. Smaller PSX domains (4.4 nm) were determined from the spin diffusion experiments for the system characterized by single T_g, while larger domains (11.2 nm) were detected in the network for which two values of T_g were found. The determined compact structure and tough ordering of PSX domains are reflected by elongation at break (5−20%), which is significantly smaller than values previously reported (ca. 90%) for linear block copolymers with similar composition. A model of the smallest PSX particles at atomic level was created by using molecular mechanics calculations. Molecular dynamics calculations performed for several model systems confirmed differences in segmental mobility of poly(dimethylsiloxane) chains at the surface and in the inner part of the PSX domain.

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