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N.m.r. investigation of interphases in dimethylsiloxane–styrene block copolymers: influence of block molecular weight

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^{1}H n.m.r. relaxation data, determined via either wide-line ^{1}H n.m.r. or high-resolution solid-state ^{13}C n.m.r., were used to analyse the existence and extent of interphasic regions in dimethylsiloxane–styrene block copolymers. Results thus obtained have shown that copolymers having very short blocks possess relatively large interphases characterized by intermediate mobility. In addition, some styrene units are trapped in the dimethylsiloxane soft microphase. With increasing block molecular weights, the extent of the phase of intermediate mobility, as well as the percentage of styrene units trapped in the dimethylsiloxane soft microphase, decrease. In agreement with the conclusions previously deduced from d.s.c. experiments, and within the sensitivity of the n.m.r. technique, the samples with the longest blocks are sharply phase-separated.

(Keywords: n.m.r.; dimethylsiloxane; styrene)

INTRODUCTION

The properties of a series of phase-separated dimethylsiloxane (DMS)–styrene (S) block copolymers were investigated by Krause *et al.*[1] and Wang and Krause[2]. Variations of the glass transition temperature (T_g), of the width of the glass transition interval (ΔT_g) and of the change in specific heat at T_g (ΔC_p) were determined as a function of the block molecular weight by d.s.c. for both microphases. They were compared with the same quantities obtained on homopolystyrene (PS) and homopolydimethylsiloxane (PDMS) of comparable molecular weight[1]. In DMS-S samples with a S block molecular weight $> 39 \times 10^3$, the S microphases exhibit T_gs and ΔC_ps very close to those of the PS samples of similar molecular weight. The only noticeable difference between the high molecular weight S microphases and PS is the ΔT_g value of the S microphases which is about twice that of PS. The DMS glass transitions of the amorphous DMS microphases were broader than those of PDMS, just as the S glass transitions of the S microphases were broader than those of PS. At lower S block molecular weights, the S phase properties diverged from those of PS homopolymers of comparable molecular weight. The divergences were especially noticeable for S block molecular weights $< 8.2 \times 10^3$: in the low molecular weight S block copolymers, the T_gs of the S microphases were always lower than those of PS samples of comparable molecular weights and the ΔT_gs were larger. The lowering of T_g was attributed to the existence of soft DMS segments in the S microphase, either throughout the hard S microphase or only near the interface between microphases. This point was corroborated by the fact that many (but not all) of the low molecular weight S microphases exhibited ΔC_ps larger than those of PS. However, since some low molecular weight S microphases had lower ΔC_ps, admixing of DMS segments is not the only phenomenon that affects ΔC_p[1]. There could be an effect from the connectedness of the S with the DMS blocks across the interface between microphases due to either dynamic interaction[3] or to the large specific surface area between microphases[4]. Moreover, in most cases, no clear indication concerning the eventual admixture of DMS segments into the S microphases could be derived from the change in specific heat at the T_g of the DMS microphase. Therefore, although the above sets of data[1,2] indicate that some DMS units are not in the soft microphase, they do not lead to definite conclusions concerning the soft and hard phase compositions, the extent of the interphase and the fact that some S units may not belong to the hard microphase.

N.m.r. is a powerful technique for investigating microphase-separated block copolymers. ^{1}H free induction decays reflect the local environment and mobility of the monomer units. They can be used to probe the existence of different phases in a heterogeneous material. For example, in S–butadiene block copolymers investigated by Tanaka and Nishi[5], ^{1}H free induction decays led to the quantification of hard phase, soft phase and interphase regions. The interpretation of the spin-lattice relaxation times in the rotating frame, $T_{1\rho}(^1\mathrm{H})$, is based on the spin-diffusion phenomenon, which induces identical

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relaxation for chemically different species in solid samples provided they are spatially close enough to one another. Non-selective $T_{1\rho}(^1H)$ measurements obtained from wide-line ^1H n.m.r. permitted the demonstration of the existence of large interphases in S–butadiene block copolymers[5]. Until now, the selective $T_{1\rho}(^1H)$ determinations via high-resolution solid-state ^{13}C n.m.r.[6] have been mostly applied to the study of the phase behaviour of polymer blends. When, in a polymer blend, polymers are incompatible and form domains whose size is $> \sim 1\ \mu m$, then the selective measurements of $T_{1\rho}(^1H)$ for each of the components in the blend yield the $T_{1\rho}(^1H)$ value of the pure component. In contrast, if the polymers are miscible at the n.m.r. spatial scale of ~ 10 Å, the $T_{1\rho}(^1H)$s associated with the different species may become equal. Besides, in materials that consist mainly of an intimate blend of two polymers, some small regions where a given component is not uniformly mixed with the other polymer[6], or heterogeneities occurring during the preparation of the samples[7], were detected.

The present paper is devoted to the n.m.r. investigation of the phase behaviour of some representative low and high block molecular weight DMS-S copolymers studied elsewhere[1,2]. In the following, we will report results obtained from the determination of ^1H n.m.r. free induction decays and $T_{1\rho}(^1H)$ values via both wide-line ^1H n.m.r. and high-resolution solid-state ^{13}C n.m.r.[6].

EXPERIMENTAL

Materials. The DMS-S block copolymers have been described previously[1,2]. *Table 1* lists the origins and characteristics of the homopolymers and DMS-S block copolymers under study.

As indicated elsewhere[1,2], samples were annealed at 150°C for 30 min and then cooled to room temperature at $10\ K\ min^{-1}$.

N.m.r. ^1H relaxation was observed using either wide-line ^1H n.m.r. or high-resolution solid-state ^{13}C n.m.r.

^1H free induction decays were obtained at 100 MHz with a Bruker CXP 100 spectrometer using the solid-echo pulse sequence[8,9]. The 90° pulse length was taken as 2 or 4 μs, depending on the ^1H n.m.r. linewidth. The $T_{1\rho}(^1H)$ values were determined in a 6 G rotating field using the spin-locking pulse sequence. ^1H spin-lattice relaxation times, $T_1(^1H)$, were measured by the inversion–recovery technique: $180°–t_{ir}–90°$.

The high-resolution solid-state ^{13}C n.m.r. experiments were conducted at 75.47 MHz with a Bruker CXP 300 spectrometer, with quadrature detection and a single radiofrequency coil which was double tuned for both ^{13}C and ^1H. Experiments were carried out using the well-known techniques of proton dipolar decoupling (DD), cross-polarization (CP) and magic angle spinning (MAS). ^1H free induction decays were observed via high-resolution solid-state ^{13}C n.m.r. using the pulse sequence described by Tékély *et al.*[10]. The pulse sequence used for $T_{1\rho}(^1H)$ determination was the delayed-contact CP pulse sequence described by Stejskal *et al.*[6]. In all these CP-based pulse sequences, the contact duration was 1 ms and the matched spin-lock CP transfers were carried out with ^{13}C and ^1H magnetic field strengths of 62 kHz. During the delay time of the delayed-contact CP pulse sequence, the ^1H magnetic field strength was 25 kHz, corresponding to a 6 G rotating field applied to the proton spins. The samples were contained in Al_2O_3 rotors. The spinning speed was around 4000 Hz. Spin-temperature inversion techniques allowed the minimization of baseline noise and roll[11]. Flip-back was used to shorten the delay time between two successive pulse sequences[12].

RESULTS AND DISCUSSION

Polystyrene

The ^1H spin-lattice relaxation of PS is an exponential function of the time interval, t_{ir}, of the inversion–recovery pulse sequence $180°–t_{ir}–90°$. It is characterized by a $T_1(H)$ equal to 1.3 s at room temperature, close to the 1 s value determined at the same temperature by Wardell *et al.*[13] for a PS with a molecular weight of 10^4.

As shown in *Figure 1*, the PS ^1H spin-lattice relaxation in the rotating frame is also an exponential function of time, characterized by a $T_{1\rho}(^1H)$ of 6 ms in the 6 G rotating field. This value is comparable to the 6.3 ms $T_{1\rho}(^1H)$ determined by Connor[14] in a 10 G rotating field for a PS sample of molecular weight 1.08×10^6. In a 10.5 G rotating field, Schaefer *et al.*[15] have measured a $T_{1\rho}(^1H)$ of 5.3–5.6 ms for a high molecular weight atactic PS using high-resolution solid-state ^{13}C n.m.r.

The PS ^1H free induction decay obtained at room temperature is shown in *Figure 2*. It exhibits a rapidly decaying quasi-Gaussian behaviour characteristic of a solid-like behaviour. The T_2 value, calculated assuming a Gaussian decay, is equal to 18 μs.

Table 1 Origin and characteristics of the homopolymers and DMS-S block copolymers under study

		M_n		Number of units		^1H (%)		Wt%	
Sample code[a]	Origin	S	DMS	S	DMS	S	DMS	S	Destination in refs 1 and 2
PDMS			5000		68				
PS	Polysciences	34 100		328					
DMS-S 0.8/3	Krause	3070	870	30	12	77	23	78	I-25
DMS-S 3/5	Krause	5430	3770	52	51	58	42	59	I-15, DI-3
DMS-S 3/16	General Electric	16 100	3100	155	42	83	17	84	D-2, DI-9
DMS-S 41/115	General Electric	115 000	41 000	1106	554	73	27	74	R-5

[a] Molecular weight of each block in units of 1000

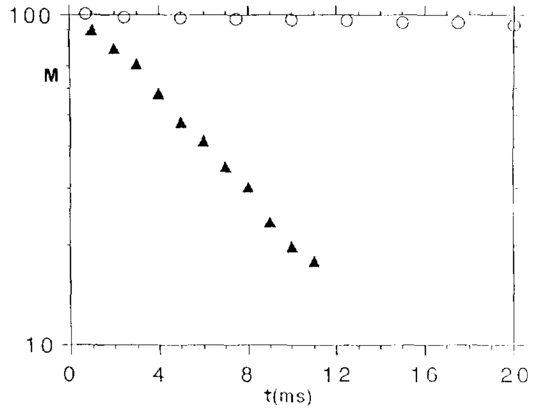

Figure 1 Room temperature PS and PDMS $T_{1\rho}(^1H)$ magnetization decays: (▲) PS; (○) PDMS

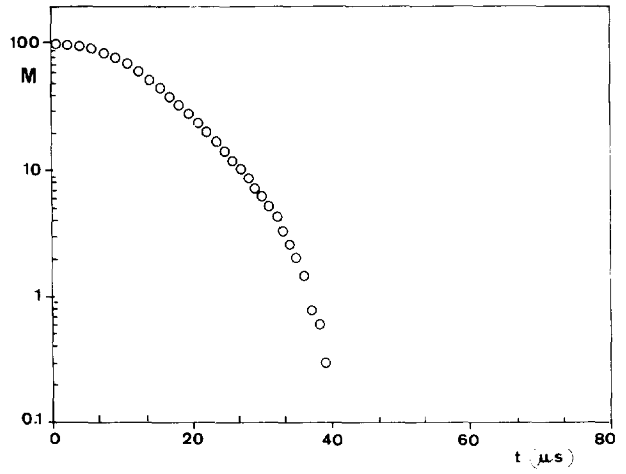

Figure 2 Room temperature PS ^{1}H free induction decay

Polydimethylsiloxane

In *Figure 1* is shown the $T_{1\rho}(^1H)$ magnetization decrease determined for the PDMS protons at room temperature. It is an exponential function of the spin-locking time and has a very long decay under the experimental conditions used.

The ^{1}H free induction decay measured for PDMS at room temperature is given in *Figure 3*. It displays a non-exponential time dependence, which was already observed by Folland *et al.*[16] and Cohen-Addad *et al.*[17-20]. In a rubbery compound, such a behaviour is specific to the presence of topological constraints that restrict the amplitude of the molecular motions and induce a residual dipolar interaction. At room temperature, the ^{1}H magnetization decay of PDMS as a function of time, t, can be expressed as:

$$M(t) = M_0 e^{-(t/T_2)^p} \qquad (1)$$

with $p = 1.6$ and $T_2 = 16\,\text{ms}$.

DMS-S block copolymers

N.m.r. experiments on block copolymers were performed at room temperature. At this temperature, the hard S blocks are in the glassy state, whereas the soft DMS blocks are well above their glass transition and melting temperatures. Therefore, the two phases exhibit very different chain mobilities, which should result in very different nuclear magnetic relaxation properties.

As shown in *Figure 4*, the variation of the $[M(0) - M(t_{ir})]/2M(0)$ ratio is an exponential function of the time interval, t_{ir}, of the inversion-recovery pulse sequence, in all the block copolymer samples, but DMS-S 41/115. Therefore, during durations of the order of T_1(H), the spin-diffusion is efficient over the different domains of DMS-S 0.8/3, 3/5 and 3/16 whose block sizes are relatively small. In the DMS-S 41/115 sample, whose blocks are longer, the spin diffusion is not rapid enough to ensure an identical spin-lattice relaxation for all the protons. The T_1(H) values of the different samples are listed in *Table 2*.

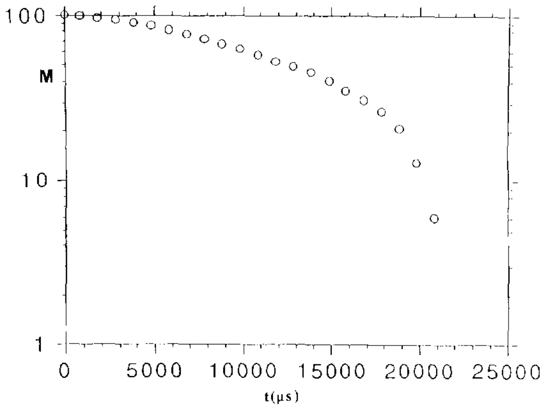

Figure 3 Room temperature PDMS ^{1}H free induction decay

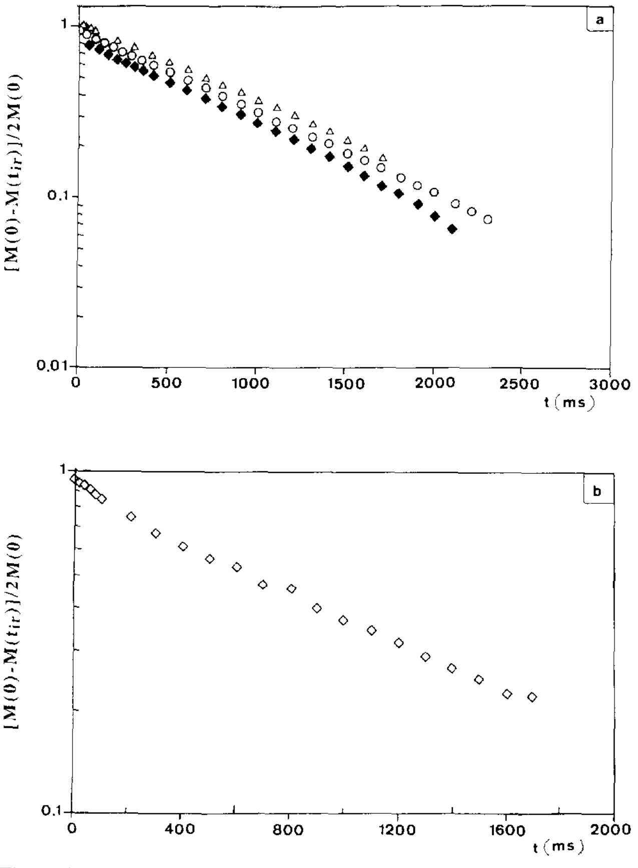

Figure 4 Variation of the $M(t_{ir}) - M(0)$ differences as a function of the time interval, t_{ir}, of the inversion–recovery pulse sequence. (a) (○) DMS-S 0.8/3; (◆) DMS-S 3/5; (△) DMS-S 3/16. (b) (◇) DMS-S 41/115

As an example, the high-resolution solid-state ^{13}C n.m.r. spectrum of the DMS-S 0.8/3 copolymer is given in *Figure 5*. The line assignment is also given in this figure. It must be noticed that the CP pulse sequence accentuates the contribution of the more rigid carbons compared to that of the more mobile ones. The sensitivity of the CP technique for carbons belonging to the DMS soft microphase is therefore poor.

The intensity decreases of the different lines as a function of the delay time in the delayed-contact CP pulse sequence were determined for all the DMS-S copolymers (*Figure 6*). The styrene carbon lines exhibit an exponential decay characterized by a $T_{1\rho}(^1H)$ equal, within experimental error, to the $T_{1\rho}(^1H)$ of the PS homopolymer. In contrast, the DMS carbon line of the DMS-S 0.8/3, 3/5 and 41/115 samples has a non-exponential decay, which indicates that the selective $T_{1\rho}(^1H)$ experiment probes different environments for the DMS units. In all the samples, for values of the delay time <5 ms, the intensity decrease is quite close to the decay observed for the PS homopolymer. Such a behaviour can be attributed to DMS units in the close neighbourhood of the S blocks of the hard phase. As for d.s.c. experiments, these DMS units that do not belong to the soft microphase may be situated either in a thin interface or in the hard S phase. However, since the behaviour at short delay times is identical for the four copolymers under study, one may speculate that it rather reflects the interphasic regions resulting from the connectedness of the S and DMS blocks. The component which is responsible for the decay at longer delay times can be assigned to DMS units remote from the hard phase.

Table 2 Spin-lattice relaxation times, $T_1(H)$, of the DMS-S block copolymers

Sample code	$T_1(H)$ (s)
DMS-S 0.8/3	0.9
DMS-S 3/5	0.84
DMS-S 3/16	1
DMS-S 41/115	0.64; 1.2

^1H free induction decays obtained at room temperature for the DMS-S copolymers are shown in *Figure 7*. They exhibit a fast and a slow relaxing component which correspond to rigid and mobile protons, respectively. As for the PDMS ^1H free induction decay, the time dependence of the free induction decay of the slow relaxing component is well-described by equation (1). The relative amount of mobile protons is determined by extrapolating the slow relaxing component to zero time. The values of T_2, exponent p and the percentage of mobile protons are listed in *Table 3* for the different block copolymers.

Comparison of the PS ^1H free induction decay with the copolymer fast relaxing component, obtained after subtracting the slow relaxing component from the free induction decay, is shown in *Figure 8* for the four block copolymers. The difference between the two signals can be attributed to protons belonging to a phase of intermediate mobility. The extent of this phase is of the order of 14% in the DMS-S 0.8/3 sample and 2% in the DMS-S 3/5 sample. There is no detectable effect in the DMS-3/16 and 41/115 copolymers.

As shown in *Table 3*, in the DMS-S 0.8/3 sample, the amount of protons situated in the soft microphase is equal, within experimental error, to the number of protons of the DMS units. However, in this sample, the interphasic regions are quite large and also contain a number of DMS units. Therefore, one is led to the conclusion that all the protons of the soft microphase cannot belong to DMS units. Some S units must be

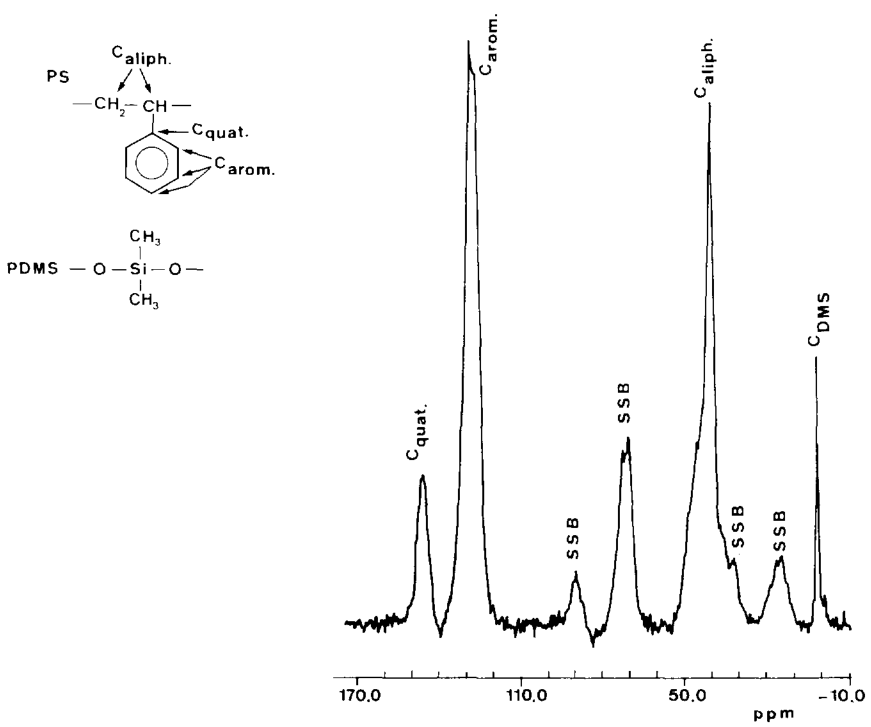

Figure 5 High-resolution solid-state ^{13}C n.m.r. spectrum of the DMS-S 0.8/3 copolymer. Spinning side-bands are denoted by SSB

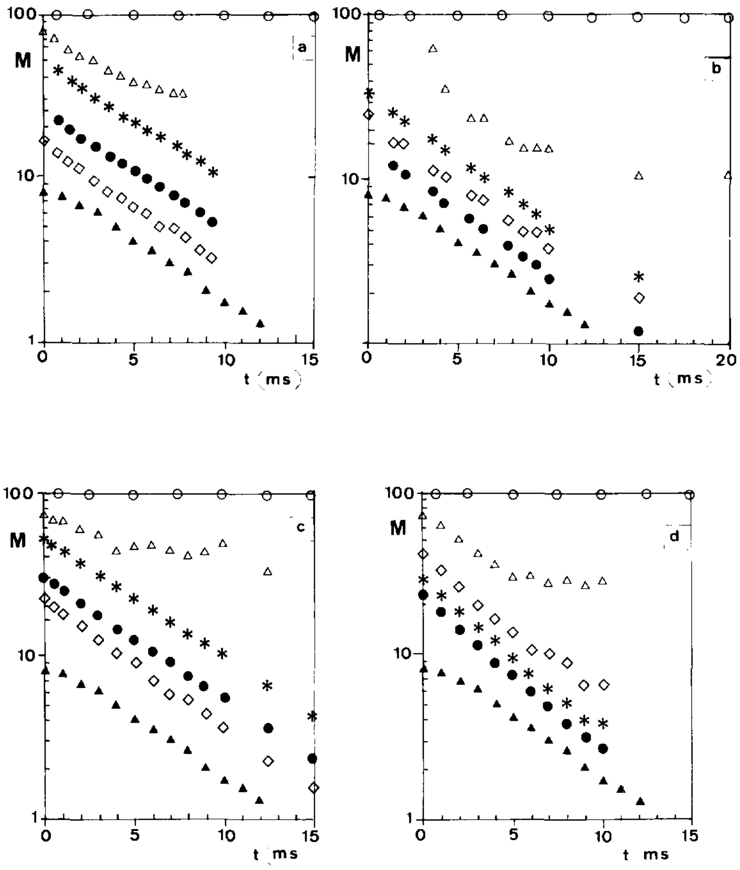

Figure 6 Intensity decreases of the S and DMS carbon magnetizations as a function of the delay time, t, in the delayed-contact CP pulse sequence. (a) DMS-S 0.8/3; (b) DMS-S 3/5; (c) DMS-S 3/16; (d) DMS-S 41/115. Symbols: (∗) PS aliphatic CH carbon; (◇) PS CH_2 carbon; (●) PS aromatic carbon; (△) DMS carbon. For comparison, results obtained for PS (▲) and PDMS (○) homopolymers using wide-line ^1H n.m.r. are also shown

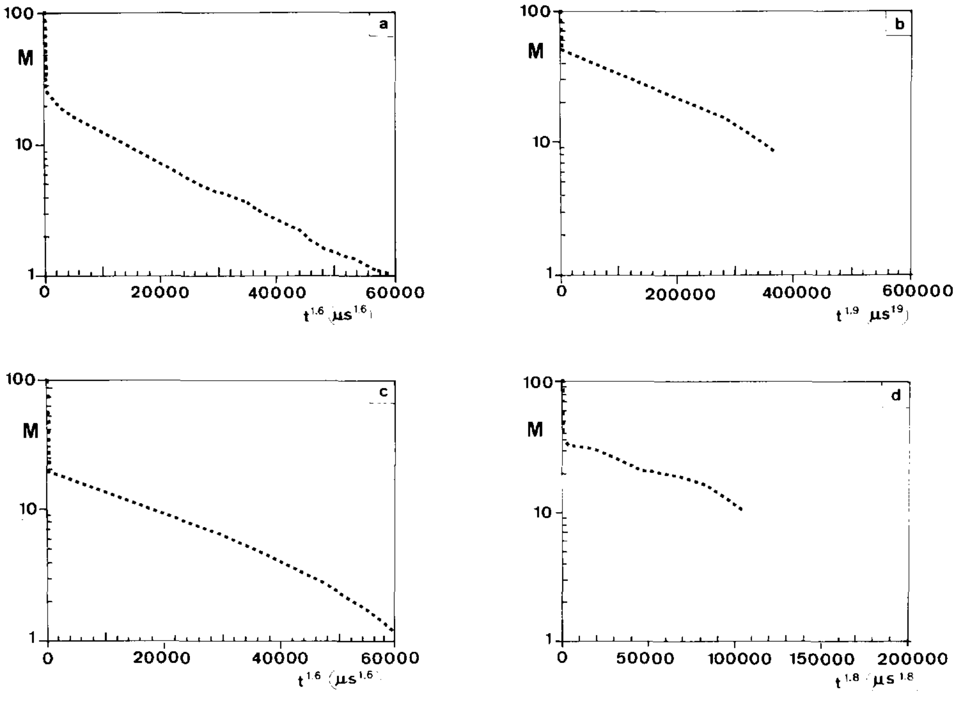

Figure 7 Room temperature ^1H free induction decays: (a) DMS-S 0.8/3; (b) DMS-S 3/5; (c) DMS-S 3/16; (d) DMS-S 41/115

trapped in the mobile phase of the DMS-S 0.8/3 sample. In the DMS-S 3/5 copolymer, the percentage of protons in the soft phase is slightly higher than the percentage of protons belonging to the DMS units, which indicates that there may also exist a very small number of S units trapped in the soft phase of this material. In the DMS-S 3/16 and 41/115 copolymers, which do not exhibit a phase of intermediate mobility, the amount of protons in the mobile and rigid phases is very close to the amount of protons belonging to the DMS and S units, respectively. Within experimental error, the soft phase is made of DMS units only and the hard phase of S units only. Therefore, these two samples appear to be sharply phase-separated.

^{1}H free induction decays were also measured at room temperature via high-resolution solid-state ^{13}C n.m.r. using the pulse sequence described by Tékély *et al.*[10]. The results obtained for the DMS units of the DMS-S 41/115 sample were not considered since the accuracy of the data was too poor. On the one hand, as shown in *Figure 9*, the S carbons exhibit the same quasi-Gaussian time dependence in the four block copolymers. The T_2 values thus determined range from 15 to 17 μs. They are very close to the T_2 of the PS homopolymer. Therefore, within the accuracy of the ^{13}C n.m.r. experiment, which accentuates the contribution of the rigid species, the spin-spin relaxation of the S protons is not modified by the presence of the DMS blocks in the copolymers. On the other hand, as shown in *Figure 10*, the spin-spin relaxation of the DMS nuclei is systematically faster in the block copolymers than in the PDMS homopolymer. Furthermore, the spin-spin relaxation is a multicomponent function of time in the DMS-S 0.8/3, 3/5 and 3/16 samples, indicating that the DMS protons can be found in several environments. For the DMS-S 0.8/3 copolymer, there first occurs a fast decay, only slightly slower than the PS ^{1}H free induction decay, followed by a slower decrease. In agreement with results obtained by analysing the wide-line ^{1}H n.m.r. free induction decay, the rapidly decaying component may be associated with DMS units mixed with the S microphase, whereas the slower component corresponds to DMS units in the interphase. In the other samples, the very fast decay of the DMS-S 0.8/3 copolymer is not detected, corroborating the fact that the amount of DMS units trapped in the S phase is either very low or equal to zero. In the DMS-S 3/5 sample, the behaviour at short time, which is quite similar to the slower component of the DMS-S 0.8/3 copolymer, is likely to be related to the interphasic regions. In the DMS-S 3/16 sample, the overall slow free induction decay is an indication that, within the sensitivity of the experiment, all the DMS protons belong to the soft DMS microphase. As indicated by the relative proportions of the fast and slow decays, the amount of DMS units that is not in the soft phase decreases from the DMS-S 0.8/3 sample to the DMS-S 3/5 copolymer and to the 3/16 sample.

Table 3 T_2 values, exponent p and the percentage of protons in the soft phase of the DMS-S block copolymers, and percentage of protons of intermediate mobility

Sample code	p	^{1}H (%) in the soft phase	DMS ^{1}H (%)	^{1}H in interphasic regions (%)	T_2 (μs)^a
PDMS	1.6				16000
PS	2.0				
DMS-S 0.8/3	1.6	21	23	14	480
DMS-S 3/5	1.9	49	42	2	690
DMS-S 3/16	1.6	19	17	0	590
DMS-S 41/115	1.8	32	27	0	620

^{a}Obtained from the long time behaviour

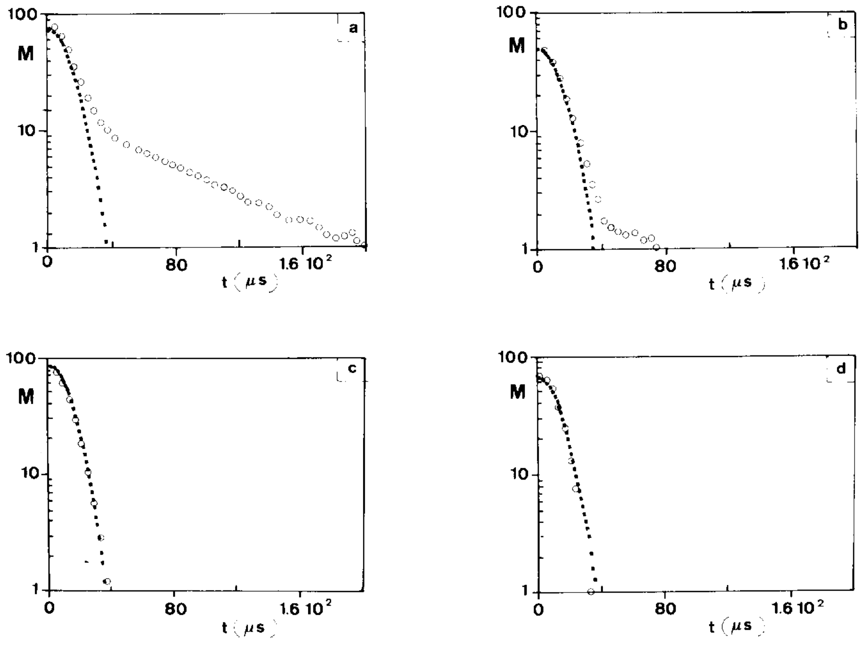

Figure 8 Comparison of the PS ^{1}H free induction decay (---) with the copolymer fast-relaxing component (○) obtained after subtracting the slow relaxing component from the free induction decay: (a) DMS-S 0.8/3; (b) DMS-S 3/5; (c) DMS-S 3/16; (d) DMS-S 41/115

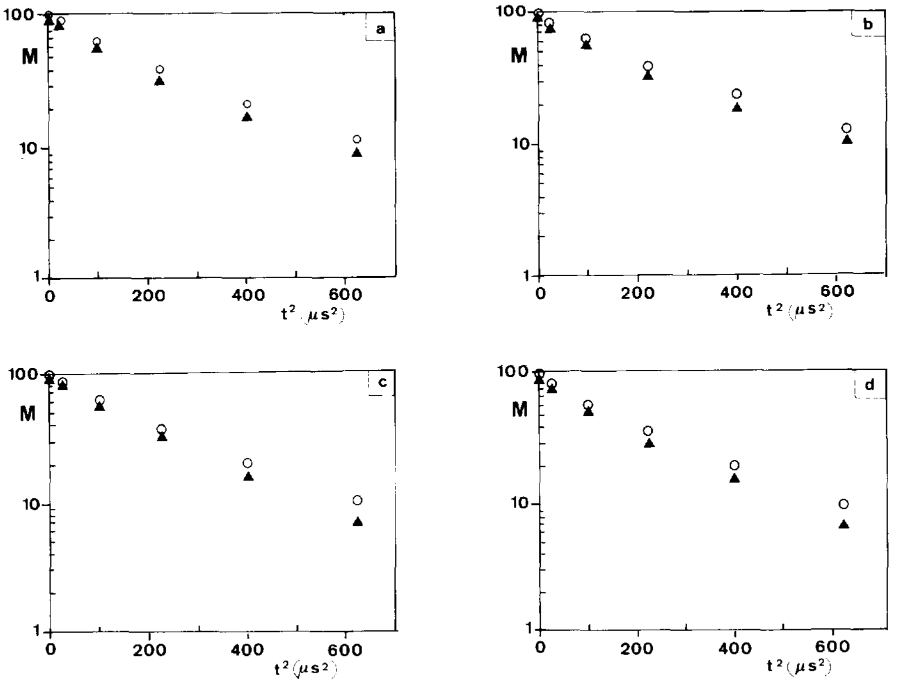

Figure 9 Spin-spin relaxation of the styrene protons observed at room temperature from high-resolution solid-state ^{13}C n.m.r. of PS aromatic (○) and aliphatic (▲) carbons: (a) DMS-S 0.8/3; (b) DMS-S 3/5; (c) DMS-S 3/16; (d) DMS-S 41/115

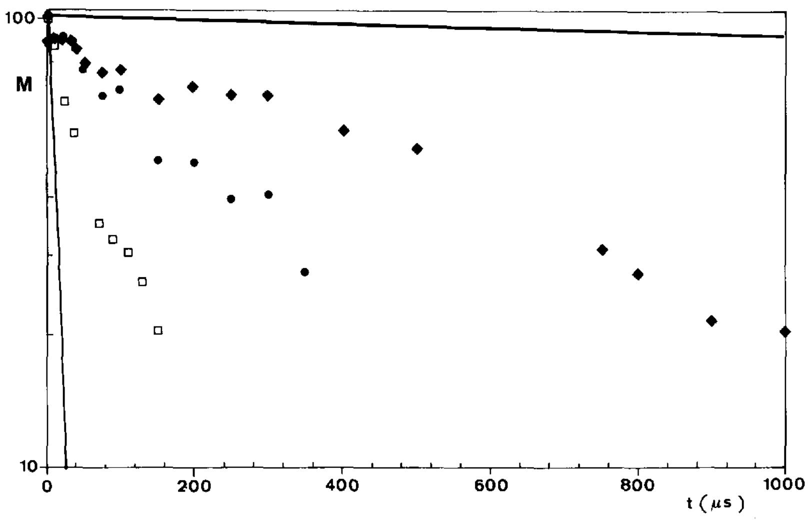

Figure 10 Spin-spin relaxation of the S and DMS protons observed at room temperature via high-resolution solid-state ^{13}C n.m.r.: (—) S; (□) DMS-S 0.8/3; (●) DMS-S 3/5; (◆) DMS-S 3/16. For comparison, the behaviour of the PDMS homopolymer (▬) is also indicated

CONCLUSIONS

In contrast with information derived from d.s.c. and $T_{1\rho}(^1H)$ measurements, the analysis of the ^1H free induction decays tends to indicate that one can separate the effect of a phase of intermediate mobility, which can be ascribed to an interphase, from the admixture of S units to the DMS microphase. The eventual mixing of DMS units to the S microphase seems to be more difficult to detect. The n.m.r. experiments reported here show that the DMS-S 0.8/3 sample possesses a relatively large phase of intermediate mobility, in agreement with the fact that, among the four samples considered, the DMS-S 0.8/3 copolymer has the shortest and, therefore, the most miscible, S and DMS blocks, as well as the largest inevitable surface phase. In addition, some S units are trapped in the DMS soft microphase. In the DMS-S 3/5 sample, whose blocks are somewhat longer than those of DMS-S 0.8/3, the phase of intermediate mobility is less developed. The amount of soft phase, derived from the analysis of the ^1H free induction decays, indicates the presence of some S units in the soft phase. For these two low molecular weight copolymers, the d.s.c. experiments demonstrated some microphase mixing[1]. For the DMS-S 3/16 and 41/115 samples that have long blocks, no interphase or S units trapped in the DMS soft microphase, were detected in any of the n.m.r. experiments. Within the sensitivity of the n.m.r. technique, it may be concluded that these two materials are sharply phase-separated, in agreement with the conclusions drawn from the d.s.c. technique.

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