Motional heterogeneity and the nature of the interphase in block copolymers: a ^{2}H nuclear magnetic resonance study†

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Poly(styrene-*b*-isoprene) block copolymers with 50 wt% styrene and $M_n = 10000$ and $20000 \, g \, mol^{-1}$ labelled by deuterated styrene (isoprene) segments at the block boundary have been studied by ^{2}H nuclear magnetic resonance spectroscopy and C_p measurements. In both the styrene- and isoprene-deuterated block copolymer spectra, two kinds of thermal transitions are observed, the main glass transition and an interphase transition. By simulation of the spectra and by T_1 measurements, the upper and lower limits for the correlation times of the motion of styrene and isoprene segments on both sides of the interface have been determined. The equivalent dynamical interphase width of isoprene units with restricted mobility in the interphase having mean correlation times of the order of 10^{-6} s at 300 K was evaluated to be 7 Å and 5 Å for $M_n = 10000$ and $M_n = 20000$ of the block copolymers, respectively. The analysis of the motional heterogeneity presents evidence of an asymmetric segmental density and motional profile characterized by a styrene-rich interphase, mixing of some isoprene segments into the glassy phase and negligible mixing of styrene segments into the elastomer phase.

(Keywords: Poly(styrene-*b*-isoprene); ^{2}H nuclear magnetic resonance; motional heterogeneity; interphase width; segmental density profile)

INTRODUCTION

Unlike macroscopically phase-separated homopolymer blends, the thermal transition behaviour of block copolymers generally has specific features associated with their microphase morphology. In systems where a soft component of large thermal expansion coefficient forms a disperse phase in a continuous hard matrix, a shift of the soft-phase T_g towards lower T_g compared with the homopolymer is often observed because of the negative hydrostatic pressure developed in the microdomains due to differences in thermal expansion coefficients[1]. Different explanations have been put forward to explain the low-temperature shift of the glass transition in cases where the hard phase forms microdomains in a continuous soft phase. The shift can be caused either by mixing of soft segments into the hard domains[2] or by the thermal forces of motion of the mobile soft segments acting on the surface of the microdomains[3]. Whether one or the other effect is responsible for the T_g depression in these systems is closely related to the distribution of segments of the constituent components in the interfacial region. Whereas the latter explanation is consistent with a perfectly sharp interface, the first requires a continuous transition of segmental densities. In fact, the thermal behaviour of low-molecular-weight poly(styrene-*b*-isoprene) block copolymers with styrene as the minor component as observed by d.s.c. has been explained by surface effects and a completely sharp interface[3]. This explanation is at variance with small-angle X-ray scattering (SAXS) measurements, from which an interlayer of finite thickness has been derived in which both components are homogeneously intermixed[4,5]. A finite width is also predicted from thermodynamic considerations[6,7]. As far as the value of the experimentally determined interlayer width is concerned, there are considerable differences in the literature[4,5], which are mainly caused by the intricacies in evaluating the low-intensity tail of the true SAXS intensity distribution at large angles in the presence of diffuse liquid-like scattering. There have also been attempts to characterize the shape of the segmental density profile functions in the interfacial region. The shape of the dynamic mechanical functions of a series of poly(styrene-*b*-diene–styrene) block copolymers with a continuous elastomer phase has been quantitatively interpreted by assuming asymmetric segmental density profiles rich in styrene in the interfacial region[8], and even more complicated distribution functions have been discussed in conjunction with dynamical mechanic measurements[9]. An attractive feature of these approaches is that they are able to explain the T_g depression of the polystyrene phase at a nearly constant T_g of the rubber phase even at low molecular weights. Recently it has been proposed that the interface may have a statistical structure, i.e. it is characterized by a continuous average density profile

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† Dedicated to Professor Walther Burchard on the occasion of his 60th birthday

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parallel to the interface but is perfectly sharp on a local scale normal to the phase boundary[10].

If the local structure of the interface in block copolymers is to be analysed, it appears natural to use a molecular probe technique susceptible to the local surroundings in the interfacial region. Besides non-selective ^{1}H n.m.r. measurements[11], ^{2}H n.m.r. is a particularly useful technique for this purpose because selectively deuterated segments can be introduced at each side of the block boundary, and therefore the interfacial region can be probed from both sides of the interface[12]. The interaction of the quadrupolar moment of the deuteron with the electric field gradient tensor is of entirely intramolecular nature, and therefore the ^{2}H n.m.r. lineshape depends only on the dynamics of the bonds to which the deuteron is attached[13]. The ^{2}H n.m.r. technique based on dynamical differences therefore complements SAXS based on electron density differences. Not only can the interfacial region be monitored but also inner parts of the microphases by variation of the length of the labelled segments. Thus a detailed picture of the thermal behaviour of the microphases and of interfacial effects can be expected from a ^{2}H n.m.r. study of block copolymers.

EXPERIMENTAL

Poly(styrene-*b*-isoprene) block copolymers (50 wt% styrene, 50 wt% *cis*-1,4-isoprene) were synthesized by sequential anionic polymerization in cyclohexane. In two samples ($M_n = 10\,000$ and $20\,000$) 40 isoprene units at the block boundary were deuterated in the 1,4-position (samples SI_DI). Two other samples containing 40 or 10 1,2-d_3 deuterated styrene units at the block boundary had molecular weights of 10 000 and 15 000 (SS_DI). Deuterated polystyrene ($M_n = 4000$), 1,4-polyisoprene ($M_n = 25\,000$) and 1,4-polybutadiene ($M_n = 100\,000$) were prepared as reference systems. ^{2}H n.m.r. spectra were taken with a Bruker CXP 300 n.m.r. spectrometer at 46 MHz with $\pi/2$ pulses of 2.8 μs. The pulse delay of the solid echo sequence for the spectra was 10 μs, if not indicated otherwise. T_1 measurements were performed by the saturation recovery sequence. Absolute C_p measurements were carried out by a Perkin–Elmer DSC-7 according to established procedures[14].

RESULTS

Thermal behaviour as observed by d.s.c. and n.m.r.

The T_g values of the deuterated block copolymers and the homopolymers used as reference systems, determined by d.s.c., are given in *Table 1*. If the heating rate is extrapolated to zero, only the T_g of the isoprene phase can be determined. At a molecular weight of 20 000 of the block copolymers it is indistinguishable from the T_g of polyisoprene. At high heating rate both the isoprene and the styrene transitions are detected, showing that both the higher- and lower-molecular-weight block copolymers are two-phase systems. As generally observed in low-molecular-weight block copolymers, a significant depression of the hard-phase T_g is observed. *Table 1* also contains the heat capacity changes at the glass transitions. The temperature variation of C_p for the block copolymers is shown in *Figure 1*. Contrary to published data obtained by the unreliable baseline method[3], claiming identical C_p for the isoprene transition in block copolymers of low molecular weight and polyisoprene, the ΔC_p value of our absolute C_p measurement yields a value about 20% lower than in the case of the homopolymer.

Table 1 Glass transition temperatures and heat capacities of deuterated samples

Sample	M_n (g mol^{-1})	T_g^I (K)	T_g^S (K)	ΔC_p^I (J K^{-1} mol^{-1})	ΔC_p^S (J K^{-1} mol^{-1})
PI_D	25 000	206^a	–	30.1^c	–
PS_D	4 000	–	349^a	–	30.5^c
SI_DI	20 000	207^a	–	–	–
		219^b	330^b	–	–
SS_DI	15 000	–	–	24.9^c	27.5
	10 000	223^b	297^b	24.7^c	–

^{a} Extrapolated to zero heating rate
^{b} Heating rate 40°C min^{-1}
^{c} Heating rate 30°C min^{-1}

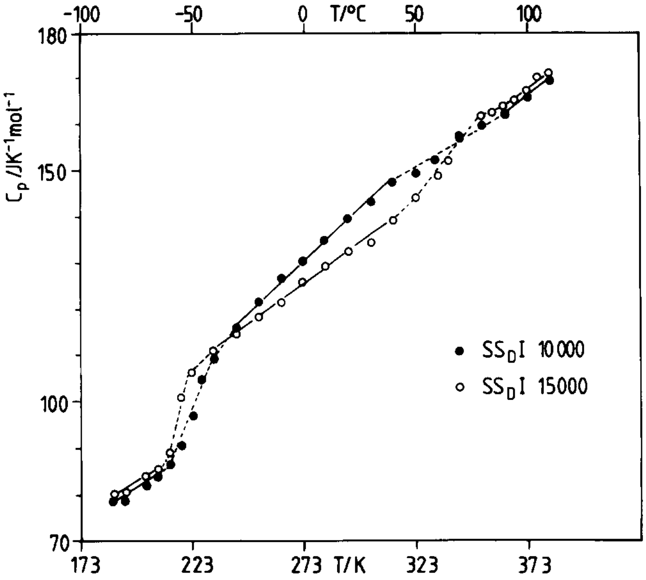

Figure 1 ΔC_p measurements of block copolymers SS_DI 10 000 and SS_DI 15 000

In *Figure 2* the temperature variation of the relative ^{2}H n.m.r. intensities are shown for the two reference homopolymers PI_D 25 000, PS_D 5000 and the block copolymers SI_DI 10 000 and SS_DI 10 000. The intensity of the spectra is normalized with respect to the intensity of the spectra of the rigid systems and is appropriately corrected according to the Boltzmann factors of the energy equilibrium levels. The curves reflect the changes of the main-chain dynamics on the ^{2}H n.m.r. frequency scale and are the ^{2}H n.m.r. counterpart of the quasi-static d.s.c. measurements shown in *Figure 1*. The intensity minimum appears at a temperature where the mean correlation time of the main-chain motion is of the order of the inverse width, 250 kHz, of the spectrum of the rigid system, i.e. 4×10^{-6} s. Thus the temperature of the intensity minimum can be considered as the dynamical glass transition temperature on the scale of the ^{2}H n.m.r. experiment occurring at a correspondingly high temperature. The intensity minimum of the isoprene-deuterated block copolymer SI_DI 10 000 is shifted towards higher temperature by ~10–15°C with respect to the reference polyisoprene, whereas the transition on the styrene side for SS_DI 10 000 shows a much greater low-temperature

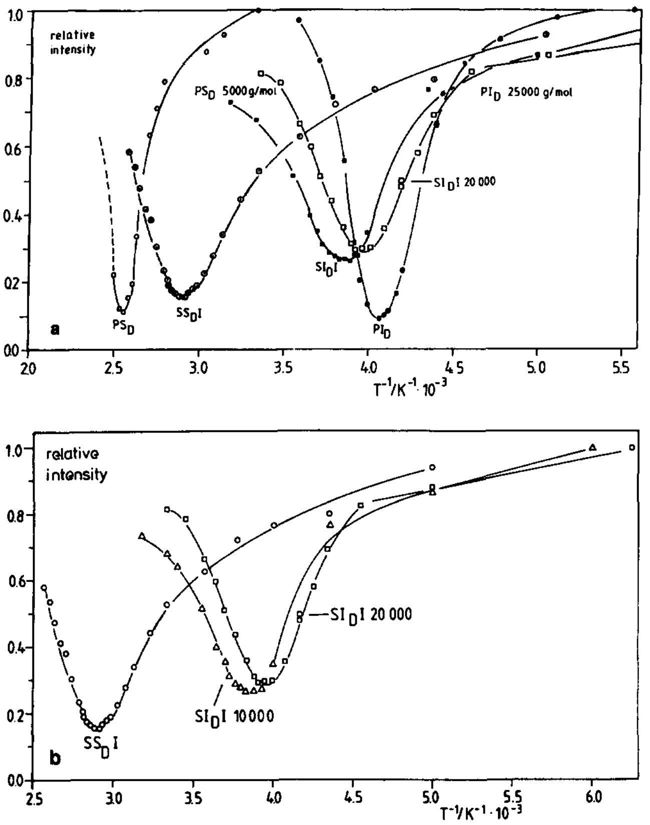

Figure 2 Relative intensity of the ^{2}H n.m.r. signal of polystyrene PS_D ($M_n = 4000\ g\ mol^{-1}$), polyisoprene ($M_n = 25\,000\ g\ mol^{-1}$), block copolymers SS_DI and SI_DI (both $M_n = 10\,000\ g\ mol^{-1}$) and block copolymer SI_DI 20000

shift of ~45°C with respect to polystyrene. In comparison with the d.s.c. experiment in *Figure 1* the styrene transition is much more distinct on the n.m.r. timescale and a stronger high-temperature shift of the isoprene transition of the block copolymer with respect to the homopolymer is observed. In addition to the temperature shift of the intensity minima of the block copolymers, the reduction of the intensities at the minima is less for the block copolymers than for the homopolymers. This indicates that the distribution of correlation times is broader in the block copolymers than in the homopolymers[13]. The distribution is broader on the isoprene than on the styrene side where the minimum intensity is closer to the height of the polystyrene minimum. In *Figure 2* the intensity distributions of the block copolymers of $M_n = 10\,000$ are shown together with the intensity variation of block copolymer SI_DI 20 000 having the same number of deuterated monomer units. The more perfect phase separation of this sample is indicated by the position of the intensity minimum closer to polyisoprene.

^{2}H n.m.r. spectra

In *Figure 3* the normalized spectra of block copolymer SI_DI 10 000 are compared with the spectra of polyisoprene. The shape of the homopolymer spectra undergoes a homogeneous narrowing from a Pake spectrum at low temperature through a bell-shaped spectrum at intermediate exchange rate in the vicinity of the intensity minimum (246 K) to a motionally narrowed Lorentzian lineshape of ~2 kHz width at room temperature. The same spectral changes also occur in the case of polystyrene and polybutadiene shifted to corresponding higher and lower temperatures, respectively[15]. Therefore the ^{2}H n.m.r. solid echo technique is not able to distinguish structure-specific details of the main-chain motion in these polymers. The small peak in the centre of the main resonance in the region of intermediate exchange does not originate from a peculiar motional mechanism specific for polyisoprene but is simply an effect of the end-groups. They become visible only near the intensity minimum where the intensity of the main chain is damped to a much higher extent in the solid echo spectra than the intensity of the mobile end-groups[11]. This effect is absent in samples of high molecular weight[15]. This demonstrates the necessity of partial deuteration of the blocks excluding chain ends because otherwise end-group effects may conceal the dynamical heterogeneity originating from the phase boundary. The effect also demonstrates the difficulties of intensity resolution of the ^{2}H n.m.r. solid echo technique in dynamically heterogeneous systems.

In contrast to the homopolymer the spectra of the isoprene-deuterated block copolymer exhibited a two-component behaviour. At about 259 K at the intensity minimum of *Figure 2* the major volume fraction of deuterated material located in the isoprene microphase has reached the critical intermediate exchange rate and gives rise to the same bell-shaped spectrum as in homopolyisoprene at 246 K. The partial spectrum of this material is superimposed on a box-like spectrum of ~130 kHz half-width representing those isoprene segments whose mobility is restricted by styrene hard segments in the phase boundary region. In a subsequent broad temperature interval of ~15°C towards higher temperature, the intensity of the 'interphase material' of reduced mobility decreases at the expense of the growing intensity of the mobile part. During this 'interphase transition' as viewed from the isoprene side the shape and width of the box-like interphase resonance stays approximately constant, a feature that will be important for the quantitative decomposition of the spectra discussed below.

The dynamical behaviour as viewed from the other side of the phase boundary is shown by the temperature variation of the spectra of block copolymer SS_DI 10 000 having the same number of deuterated monomer units. The spectra are shown in *Figure 4* and are compared with the SI_DI spectra shown before. Again, two dynamical regimes can be distinguished. However, the roles of mobile and rigid components are interchanged with respect to the isoprene side. The mobile component first showing up at about 325 K apparently originates from mobile styrene segments at the interface. This component is superimposed on a Pake-like pattern, which is attributed to the quasi-rigid core of the hard domains. Again a broad temperature interval of ~25°C follows where both components coexist. The gradual growing of the narrow component at the expense of the broad one as well as the corresponding transformation on the isoprene side appears to be in agreement with the model of a gradual softening of the hard domains proceeding from the outside of the phase boundary towards the centre of the hard domains. The continuously decreasing quadrupolar splitting of the rigid styrene component indicates that the motion of styrene segments inside the domains also changes during 'the interphase transition' as viewed from the styrene side.

Comparing the spectra of the isoprene- and styrene-

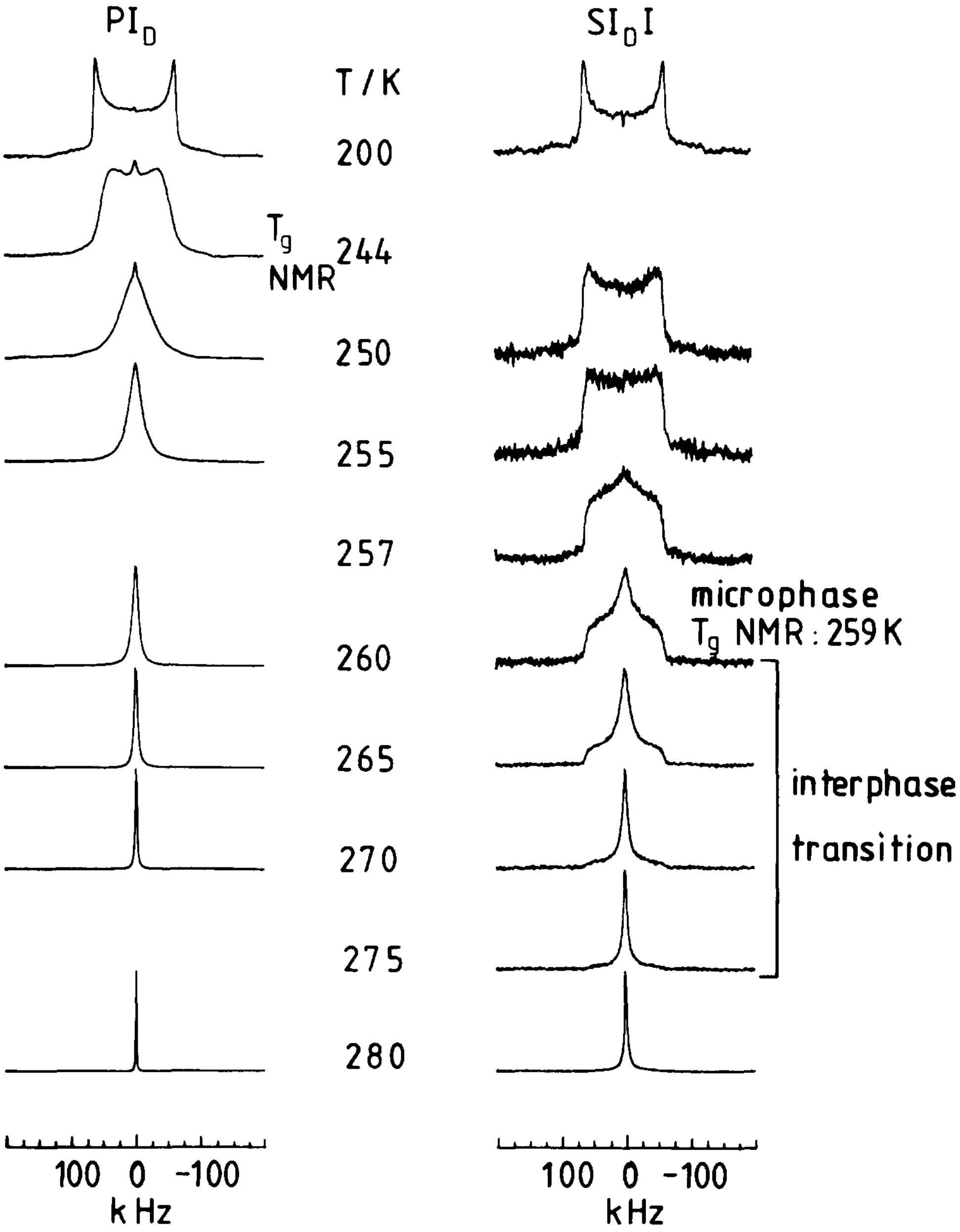

Figure 3 ^2H n.m.r. spectra, normalized to equal height, of polyisoprene and of block copolymer SI$_D$I 10000

deuterated block copolymers in *Figure 4* one might gain the impression that there is very little motional coupling between soft and hard segments. In the case of an intermixed interfacial layer the converse is expected. For instance, at 300 K a highly motionally narrowed isoprene spectrum contrasts a Pake-like spectrum on the styrene side where no styrene segments of comparable mobility are visible that could be assigned to styrene segments motionally coupled to isoprene segments in their neighbourhood. However, small amounts of styrene material, in particular with frequencies of motion in the intermediate exchange region, may not be detected because of the length of the deuterated styrene segment. The same argument holds for the isoprene side, where a small amount of material of restricted mobility may be obscured by the main resonance because of an unfavourable high reduction factor. In *Figure 5* the amplified SI$_D$I spectrum at 280 K of *Figure 4* is shown. Also given is an amplified spectrum of a block copolymer with a molecular weight of 20000 having the same deuteration length of 40 monomer units. A very weak broadened resonance becomes visible at the base of the sample with lower molecular weight, its shape being similar to the bell-shaped spectrum of deuterated polyisoprene in *Figure 3* near the intensity minimum. According to the intensity distribution of PI$_D$ in *Figure 2*, the true intensity of the broadened component must be higher by a factor of ~10. In the equally amplified spectrum of the sample with double molecular weight, the resonance of isoprene units of restricted mobility is broader, more intense and has a similar box-like appearance as in the 'interphase transition' region of SI$_D$I 10000 in *Figure 3*.

On the styrene side a small component of styrene segments of enhanced mobility of similar width as the broad component on the isoprene side cannot be detected by simple signal amplification because it will be buried under the Pake-like signal of the quasi-rigid core. The

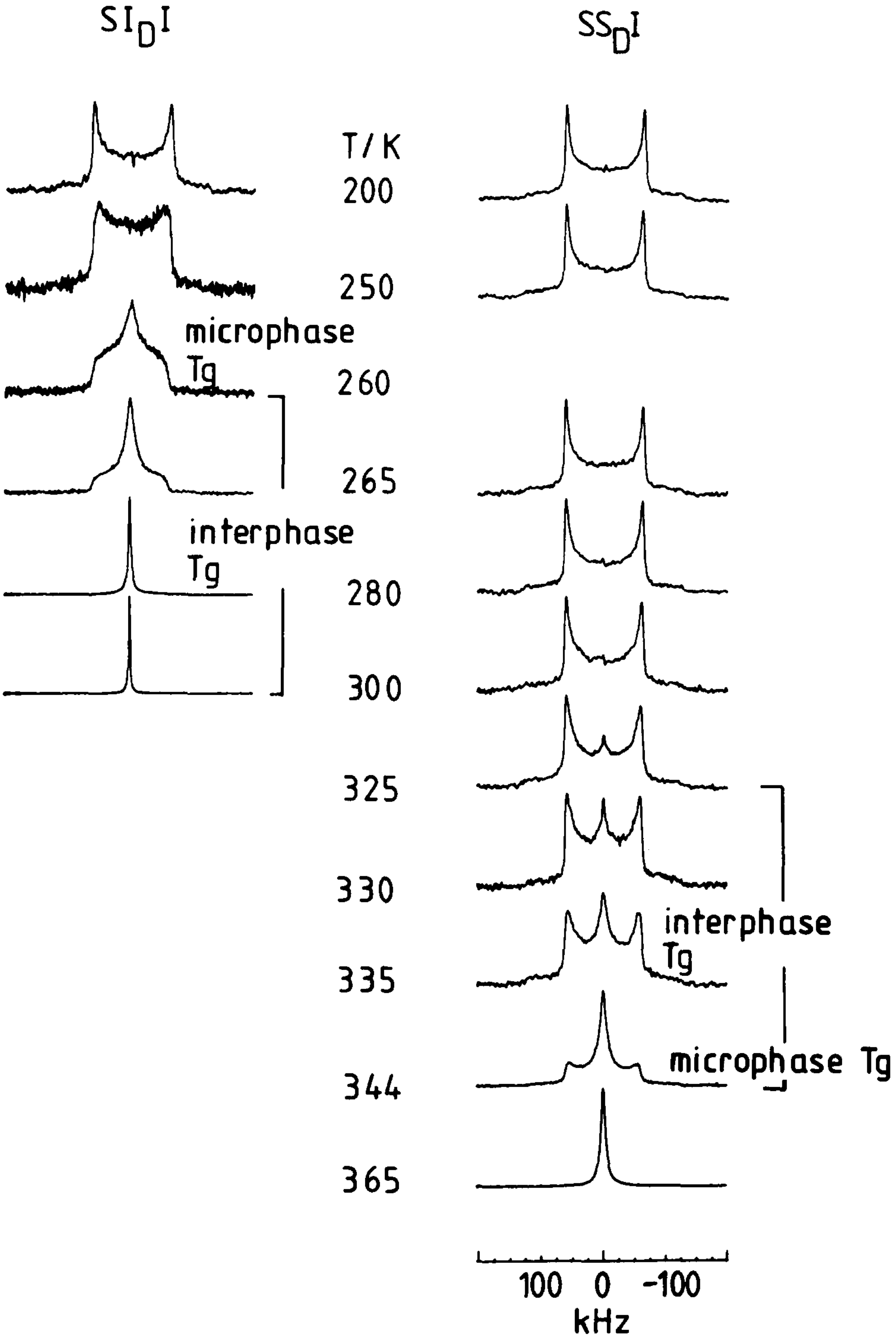

Figure 4 ^{2}H n.m.r. spectra, normalized to equal height, of block copolymers SI$_D$I 10000 and SS$_D$I 10000

fraction of quasi-rigid styrene material can be reduced by shortening the deuteration length. In *Figure 6* the spectra of block copolymer SS$_D$I 15000 carrying only 10 deuterated monomer units are contrasted to the spectra of SS$_D$I 10000 with 40 deuterated monomer units shown before. In the spectra of the sample with the shorter deuteration length, a narrow line of highly mobile styrene units can now be detected unambiguously at room temperature which cannot be observed in the spectrum with longer deuterated segments. This line has grown considerably at 325 K where a motionally narrowed line becomes visible for the first time in an unambiguous way in the sample with longer deuteration length in *Figure 4*. The relative amount of the mobile styrene units in the immediate neighbourhood of the block junction is four times greater at the shorter length of labelled units. Therefore, it can be discriminated against the excess of quasi-rigid material already at a lower temperature. However, the amount of these mobile styrene segments is very small. Since the linewidth of this signal is much smaller than the linewidth of the broad component on the isoprene-deuterated side in *Figure 3*, these mobile

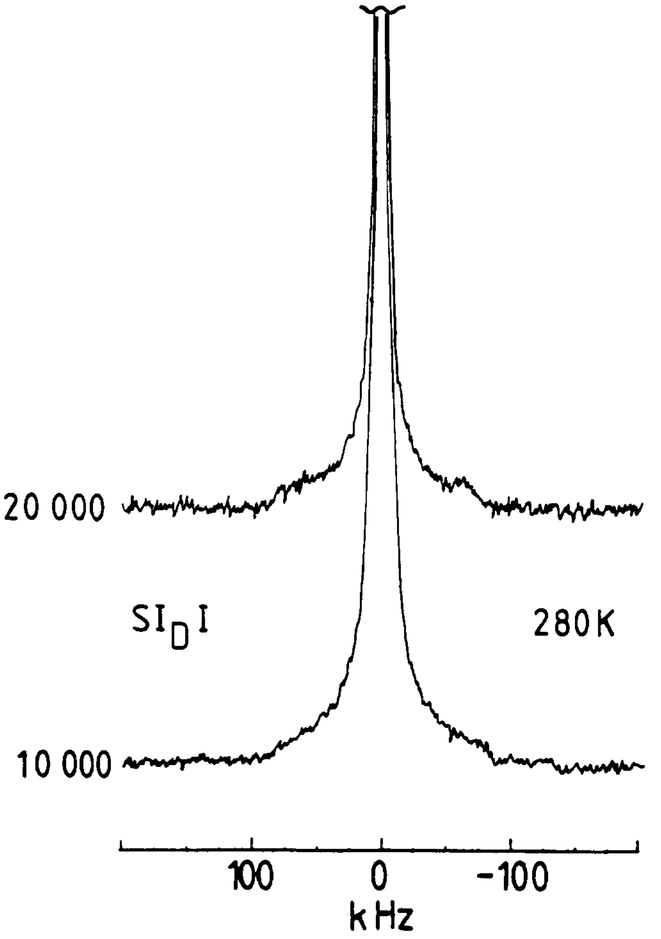

Figure 5 Amplified spectra of block copolymers SI_DI 10000 and SI_DI 20000 at 280 K

styrene segments obviously cannot be in close contact with the isoprene segments of restricted mobility of the broad component.

Determination of true intensities

The true intensities were evaluated on the basis of the observation that the ^2H n.m.r. lineshape changes associated with the main-chain motion are indistinguishable for polystyrene, polyisoprene and polybutadiene if compared at corresponding temperatures at a given mean correlation time of motion. This means that at a given temperature the block copolymer spectra in *Figures 3* and *4* can be considered as a superposition of the spectra of any of the homopolymers at equivalent temperatures. If a decomposition in terms of homopolymer spectra can be achieved, the true partial intensities can also be determined from the known intensity reduction factors of the homopolymers belonging to a given lineshape.

Although in the dynamically heterogeneous materials a continuous distribution of components in different spatial and dynamical situations will be present, the resolution of the block copolymer spectra in general only allows a decomposition into two components. The procedure is exemplified for the isoprene-deuterated block copolymer SI_DI 10000 in *Figure 3*. As already noted, the width of the broad box-like component in the interphase transition region stays approximately constant. The width of this component is the same as that of a polyisoprene spectrum at 235 K having a damping factor of 0.15. This spectrum is subtracted from the SI_DI spectra in the transition region. The results of this procedure are shown in *Figure 7*. The approximate reduction factors of the difference spectra are similarly obtained by comparison with homopolymer spectra of the same width. The decomposition works in the temperature interval from 257 to 274 K, beyond which the width of the broad component changes. In SI_DI 20000 the decomposition can be carried out up to 300 K (compare *Figure 5*). On the styrene-deuterated side a similar procedure was adopted by subtracting one or two motionally narrowed homopolymer spectra corresponding to the mobile styrene segments in the interphase.

In *Figure 8* the fraction x_{int} of isoprene of restricted mobility and of mobile styrene, both located in the interface region, is plotted for block copolymers with 40 deuterated monomer units at the block boundary. Both the apparent and the true fractions determined by the appropriate experimental damping factors are shown. The isoprene fraction is seriously underestimated without correction for the intensity loss. As suggested by the spectra in *Figure 6* there is only a negligible amount of mobile styrene segments in the interfacial region below room temperature. On the other hand, it is inferred from *Figure 8* and the spectra of SI_DI in *Figures 3* and *4* that in the range of the interphase transition the fraction $1-x_{\text{int}}$ of deuterated isoprene material of high cooperative mobility in the block copolymer SI_DI 10000 increases from 20% to about 50%. This estimation is based on the extrapolated upper line on the right-hand side of *Figure 8*, which would be obtained if the box-like lineshape of the interphase component, subtracted in *Figure 7*, persists at higher temperature. Since this component undergoes further motional narrowing above 274 K, as *Figure 5* shows, the actual amount of material transformed to the mobile phase is actually greater. This can also be seen by comparison with the interphase fraction of SI_DI 20000 which could be determined up to 300 K by the procedure described above.

Calculation of the spectra

To estimate the character and mean correlation times of the main-chain motion in the different dynamical regimes determined in the preceding section, an attempt has been made to simulate some of the spectra by a motional model. This can be done only in a simplified approximate way. Recent two-dimensional experiments have shown that the main-chain dynamics of glassy polymers is characterized by a broad distribution of small-angle fluctuations at temperatures near the glass transition[16]. With increasing temperature the amplitudes increase and eventually large-angle jumps indicate the onset of conformational transitions. Because of the cooperativity of the main-chain motion, the jumps do not occur between well defined positions and can therefore not be described by a multisite jump model.

The motional model used for the present calculations is depicted in *Figure 9*. It consists of a superposition of a three-site 120° jump on a cone with an opening angle β and a two-site jump connecting positions by the tetrahedral angle of 109°. The first process simulates small-angle diffusional motions of the CD main-chain bonds, whereas by the second conformational transitions, e.g. between *trans–gauche* rotational isomeric states, are simulated. The parameters of the model are the rate constants k_{fl} and k_{tg} for the small- and large-angle jumps,

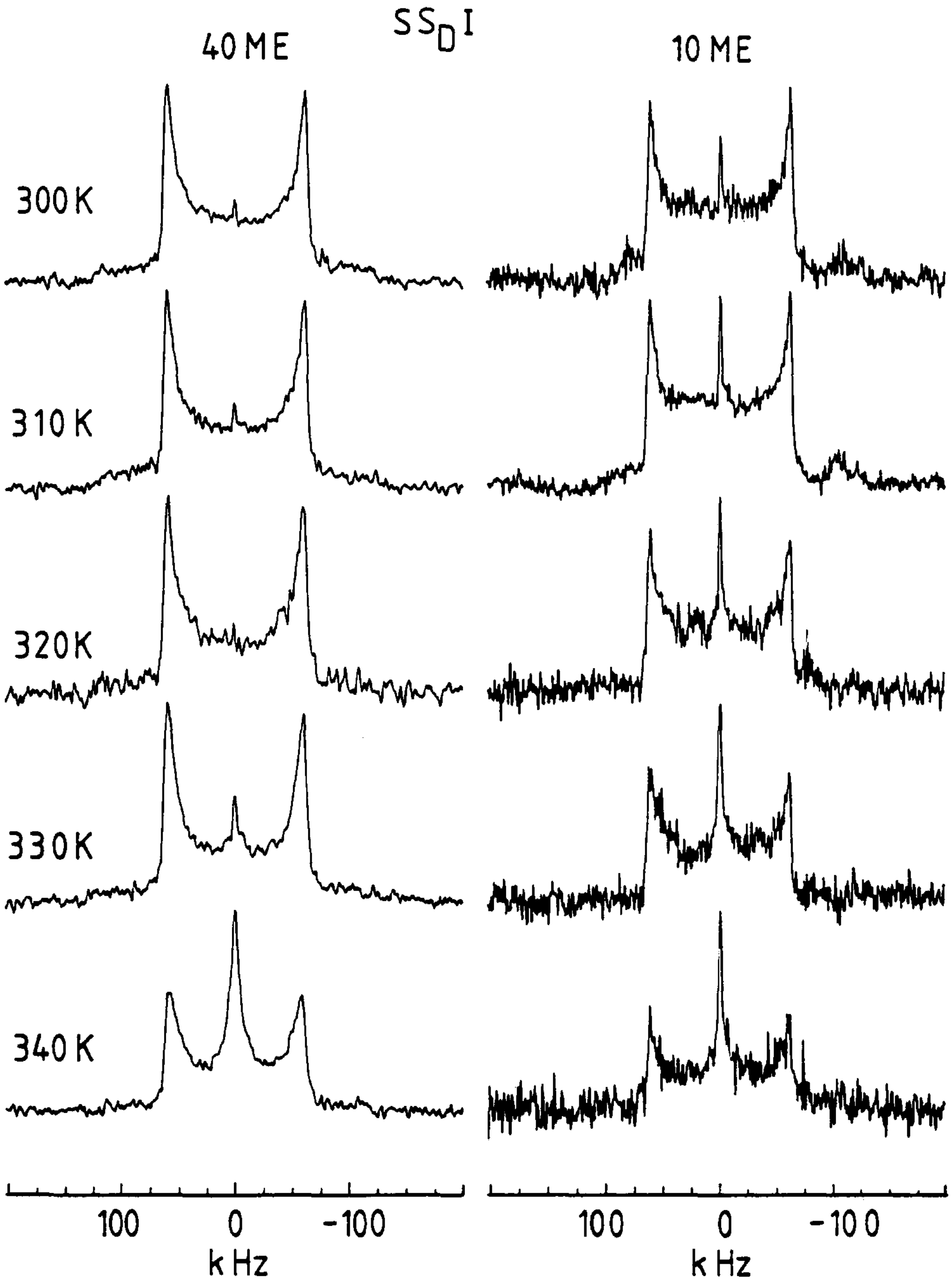

Figure 6 ^{2}H n.m.r. spectra of block copolymer 10000 with 40 deuterated isoprene units (40 ME) and of block copolymer SI$_D$I 15000 with 10 deuterated isoprene units (10 ME)

respectively, the cone angle β and the apparent population ratio of *gauche* and *trans* rotational states. The calculations were performed with a program for dynamical ^{2}H n.m.r. lineshape analysis by Wittebort[17]. One set of calculations were performed for spectra of block copolymer SS$_D$I 10000 at 310 K where the motionally narrowed component of mobile styrene is negligible. Experimental and calculated spectra are seen in *Figure 10* as functions of the pulse delay of the solid echo (SE) sequence. Owing to short T_2 the mobile styrene sequences contribute only to the spectral intensity at pulse delays $\tau_1 \leq 20\,\mu s$. At longer τ_1 values the spectra of the quasi-rigid core of the hard microdomains show a significant loss of intensity in the central region until at $\tau_1 = 100\,\mu s$ only the singularities are left. This behaviour is known to be typical for small-amplitude diffusional motions[13]. In fact, the pulse delay dependence of the spectra can be calculated satisfactorily by retaining only the small-angle jump process of the model of *Figure 9*. The width of the quadrupolar splitting is adjusted by the cone angle β; the shape of the spectrum and the height of the singularities are determined by the jump rate k_{f1}.

To obtain an estimation of the dynamical processes in the interphase region on the isoprene side of the phase boundary, some spectra on the low-temperature side of the intensity distribution of polybutadiene of molecular weight 100000 were calculated. Polybutadiene instead of polyisoprene was taken because of its higher molecular weight, which causes suppression of the end-group signals in the investigated region of intermediate exchange rates (see *Figure 3*).

In *Figure 11* experimental and calculated spectra are shown for two pulse delays at various temperatures including the theoretical spectra of the free induction

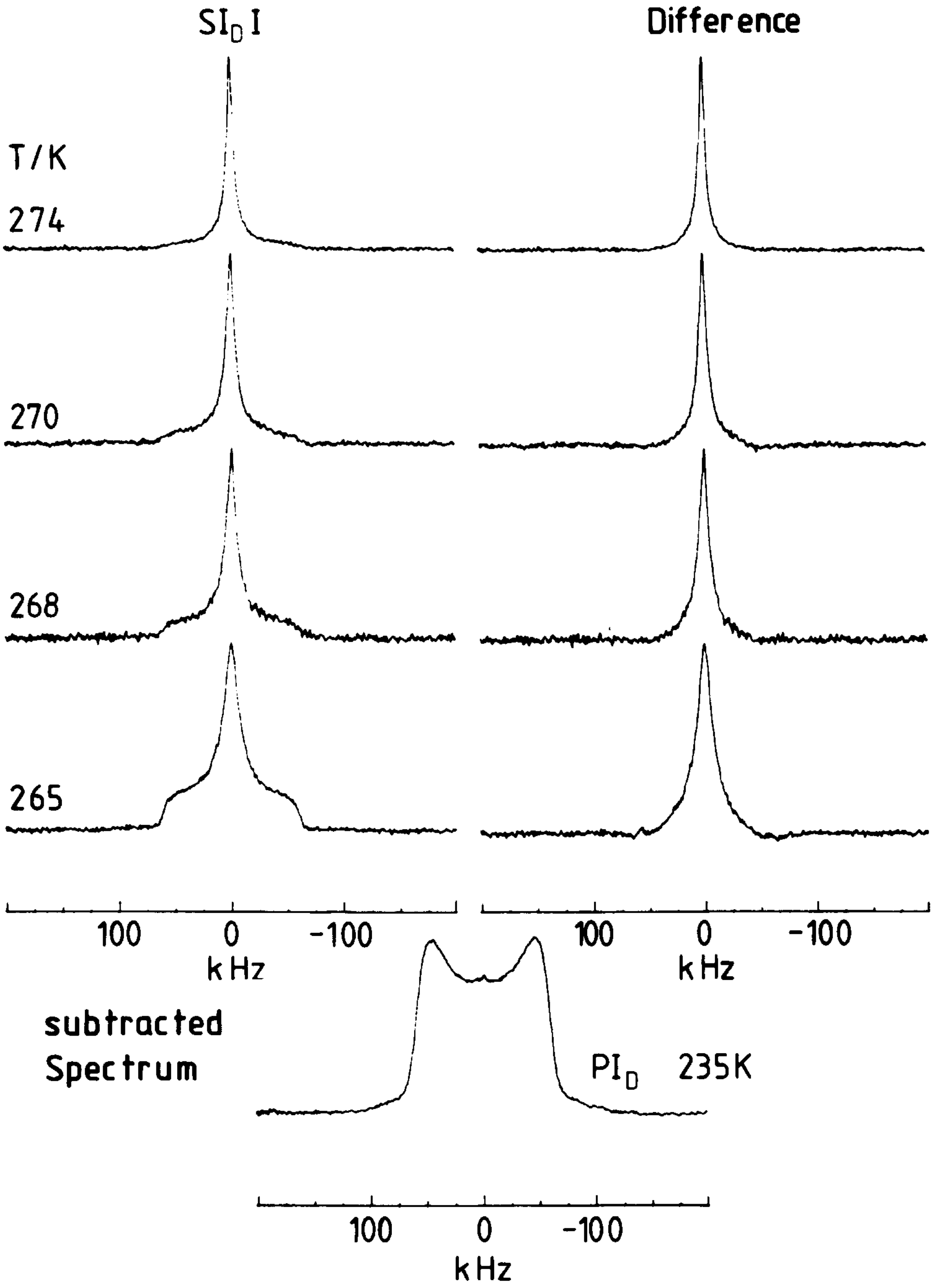

Figure 7 Decomposition procedure of the block copolymer spectra exemplified for block copolymer SI$_D$I 10000. The polyisoprene spectrum at 235 K, which has the same shape as the broad component of SI$_D$I, is subtracted from the block copolymer spectrum

decay (FID) in a one-pulse experiment, i.e. $\tau_1 = 0$. The shape and width of the spectrum at 193 K are identical with the spectrum of polyisoprene at 235 K in *Figure 7*, which was used as the spectrum representing the dynamical behaviour of isoprene segments in the interphase region. The simulation of the spectra in the vicinity of the intensity minimum occurring at 200 K in polybutadiene can only be achieved if conformational jumps are allowed in addition to small-angle fluctuations. The dynamical parameters of the best fits to the experimental spectra, collected in *Table 2*, show the expected temperature dependence: an increase of the amplitude of the small-angle fluctuation and an increase of the apparent '*gauche*' population. The rate of small-angle fluctuations, which can be interpreted as a cooperative diffusional process in the multidimensional potential of the rotational isomeric states of the chain, increases less with temperature with an apparent activation energy of 19.1 kJ mol^{-1} K^{-1} than the rate of the conformational jump process having an apparent activation energy of 35.9 kJ mol^{-1} K^{-1}. It has to be noted that the calculation fails to simulate the experimental intensity damping. The calculated intensities relative to the intensity at $\tau_1 = 0$ are always higher than the observed ones. The main reason for this shortcoming of the model is that the distribution of jump rates has not been taken into account.

Spin-lattice relaxation

In *Figure 12a* the spin-lattice relaxation of SS$_D$I 10000 is compared with the relaxation of polystyrene at 300 K. In contrast to the homopolymer, the relaxation rate of the block copolymer is faster by a factor of 10–50 and exhibits a two-component behaviour whereas the homopolymer relaxation can be approximated by a single T_1. The two-component behaviour is present over the temperature range from 250 K to 340 K, i.e. also at temperatures where only one component appears to be present according to the spectra in *Figure 4*. Contrary to the behaviour of the hard segments the spin-lattice relaxation of the soft segments, shown in *Figure 12b* at 260 K, cannot be decomposed in two components at any

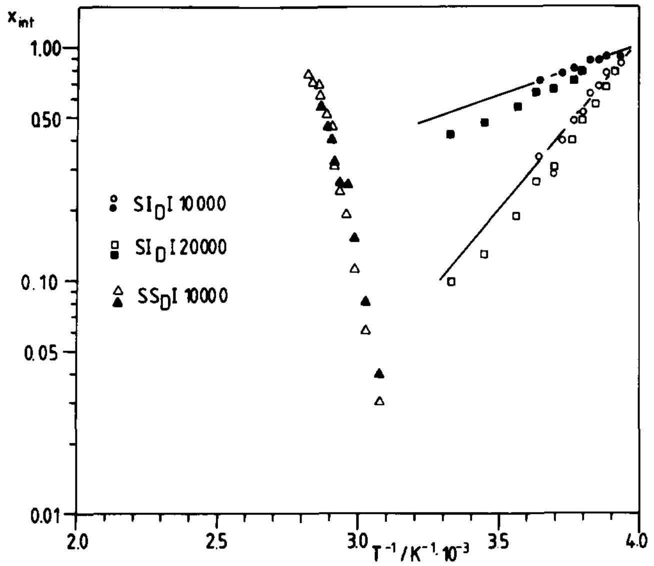

Figure 8 Fraction x_{int} of isoprene of restricted mobility in the interphase of block copolymer SI$_D$I 10000 (○, ●) and in block copolymer SI$_D$I 20000 (□, ■) and fraction of mobile styrene (△, ▲) in block copolymer SS$_D$I 10000. Open symbols refer to fractions determined without damping correction; filled symbols to fractions corrected for intensity damping

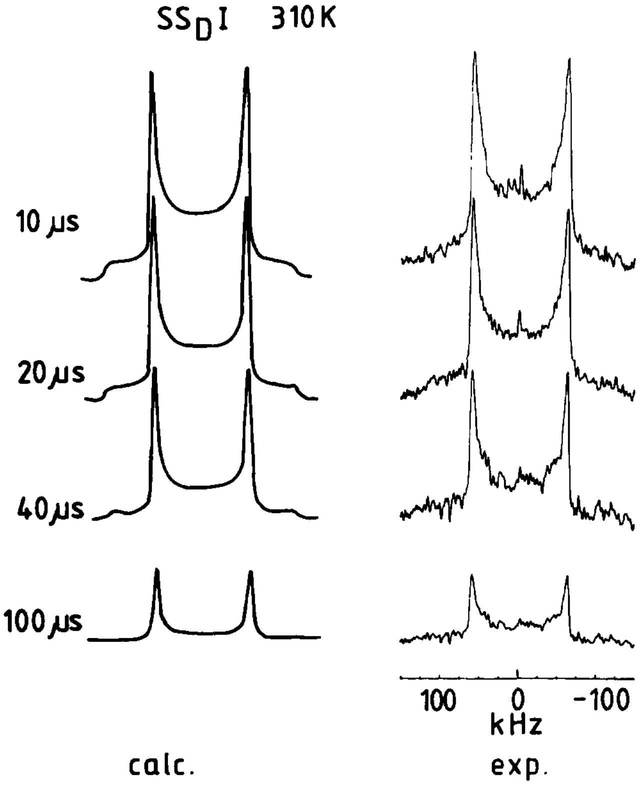

Figure 10 Experimental and calculated spectra of block copolymer SS$_D$I at 310 K for different pulse delays of the solid echo sequence. Simulation parameters are $k_{fl} = 6.3 \times 10^3$ Hz and $\beta = 10°$

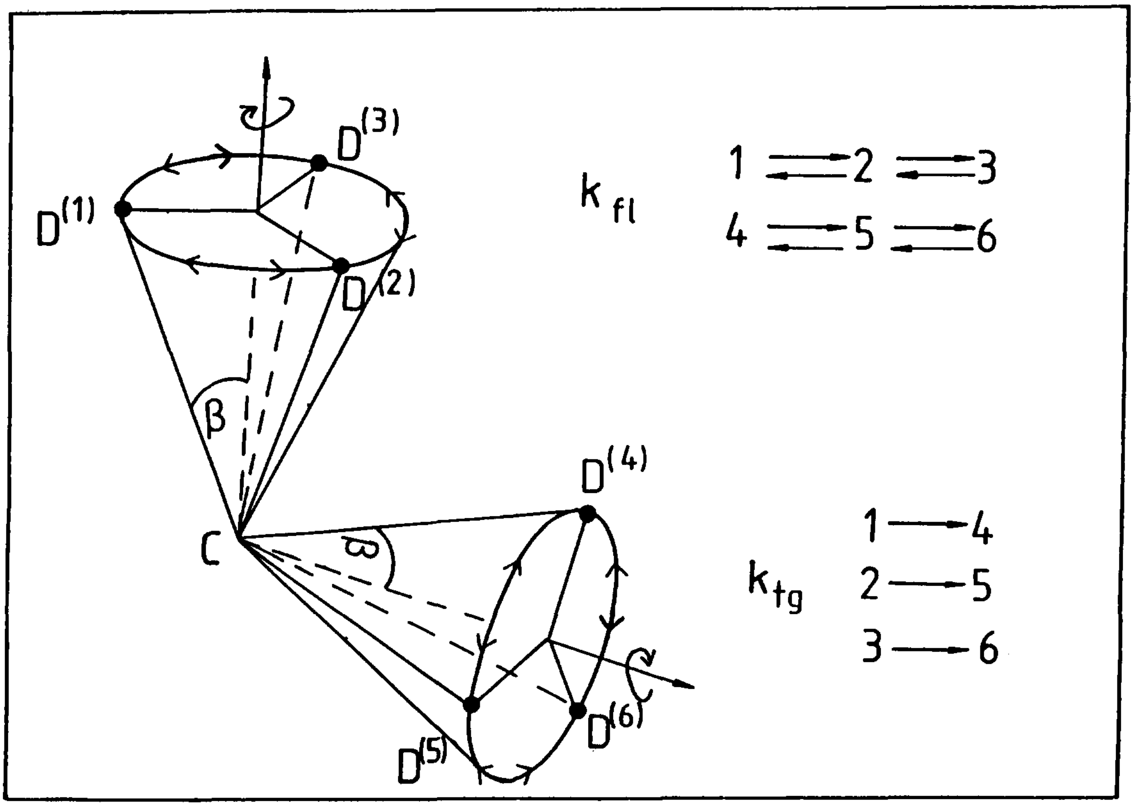

Figure 9 Motional model used for the calculation of the spectra

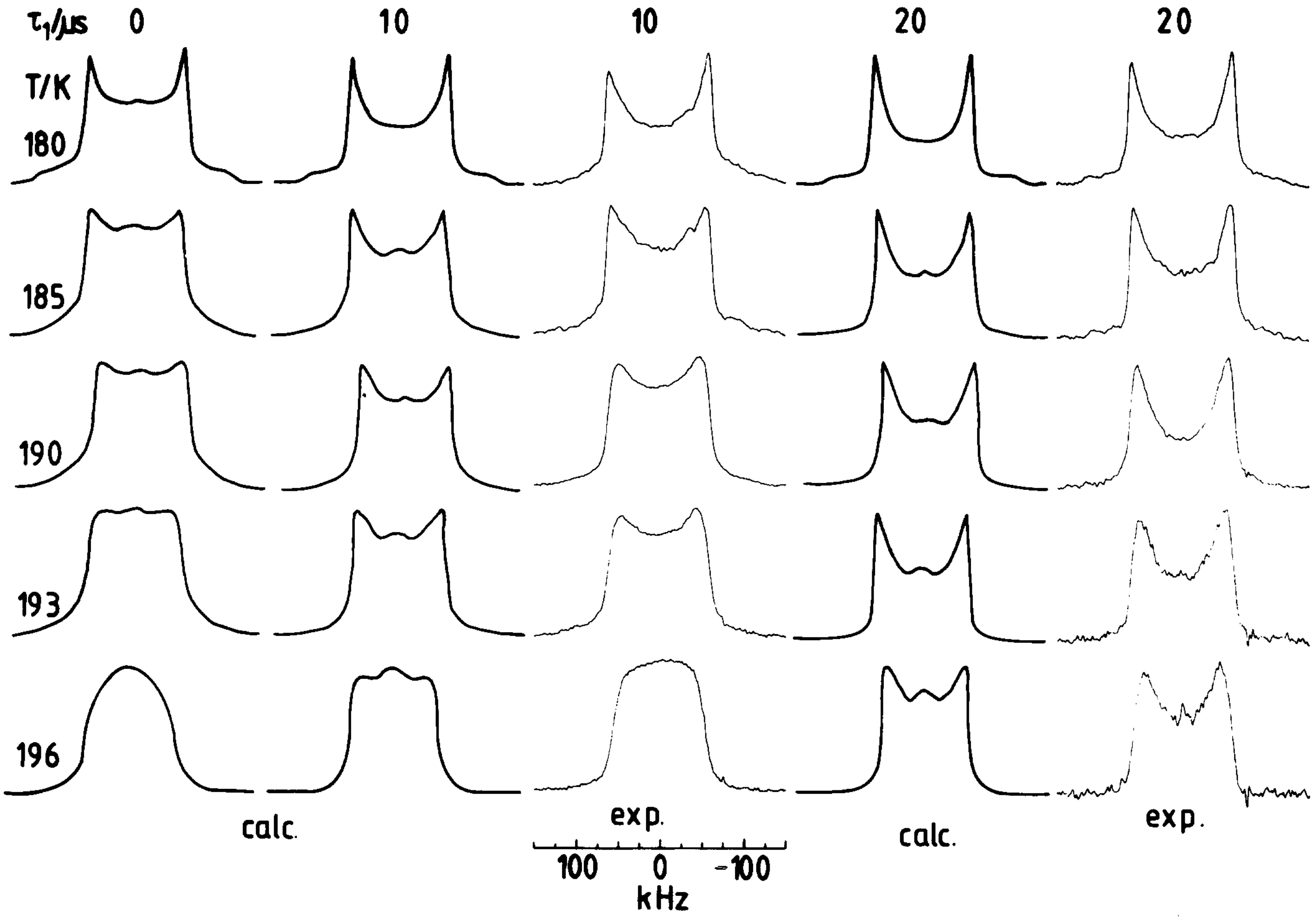

Figure 11 Experimental and calculated spectra of polybutadiene for pulse delays $\tau_1 = 10$ s and $\tau_2 = 20$ s. The theoretical spectrum of the FID in a one-pulse experiment ($\tau_1 = 0$) is also shown

Table 2 Dynamical parameters calculated from the simulations of the ^{2}H n.m.r. spectra of polybutadiene

T (K)	β (deg)	$k_{fl} \times 10^{-5}$	$k_{tg} \times 10^{-5}$	p_g
180	10	3.14	1.26	0.10
185	12	5.03	3.14	0.15
190	13.5	5.65	4.40	0.16
193	15	6.28	5.03	0.20
196	18	9.42	9.42	0.30

temperature even if the spectrum seems to indicate the presence of two components (see *Figure 3*). The different behaviour on both sides has to be taken into account when the structure of the interphase is discussed. The non-exponential T_1 behaviour of the block copolymers is also accompanied by a change of the spectral shapes as a function of the waiting time of the T_1 pulse sequence, proving the presence of a heterogeneous distribution of correlation times[13]. Also, in homopolymers the main-chain dynamics is generally characterized by a distribution of spin-lattice relaxation times[18]. However, the distribution is much broader in the block copolymers. Different lineshapes of fully and partially relaxed spectra in homopolymers are generally found only below the static glass transition temperature whereas lineshape changes in the block copolymers, e.g. SI$_D$I, are found far above the d.s.c. T_g of the isoprene phase[15].

Dynamic profile functions

The mean correlation times derived from T_1 measurements and from the simulation of the spectra are plotted in *Figure 13* as a function of the volume fractions of the mobile or quasi-rigid parts of the respective microphases determined from the decomposition of the spectra, giving a rough representation of the dynamical profile and transition behaviour on both sides of the interface. The thick line in the centre represents the location of a hypothetical interface if it was completely sharp. To the left of the line the volume fractions and correlation times of the mobile and rigid parts of the 40 deuterated styrene segments in the SS$_D$I block copolymer are shown for three different temperatures. To the right the same is shown for the 40 deuterated isoprene units of the SI$_D$I block copolymer in the order of segments with restricted mobility followed by those of high mobility. The shaded areas compare the portion of isoprene segments of restricted mobility with the fraction of mobile styrene segments at 300 K. The volume fraction of mobile styrene segments is calculated from the corresponding volume fraction x_S^{int} in *Figure 8* by:

$$v_S^{int} = x_S^{int} v_D^{PS} \qquad (1)$$

$$v_S^{PS} = \frac{w_D^{PS} \bar{v}_D^{PS}}{w_D^{PS} \bar{v}_D^{PS} + w_H^{PS} \bar{v}_H^{PS}} \qquad (2)$$

v_D^{PS} is the volume fraction of deuterated polystyrene, $w_{D,H}^{PS}$

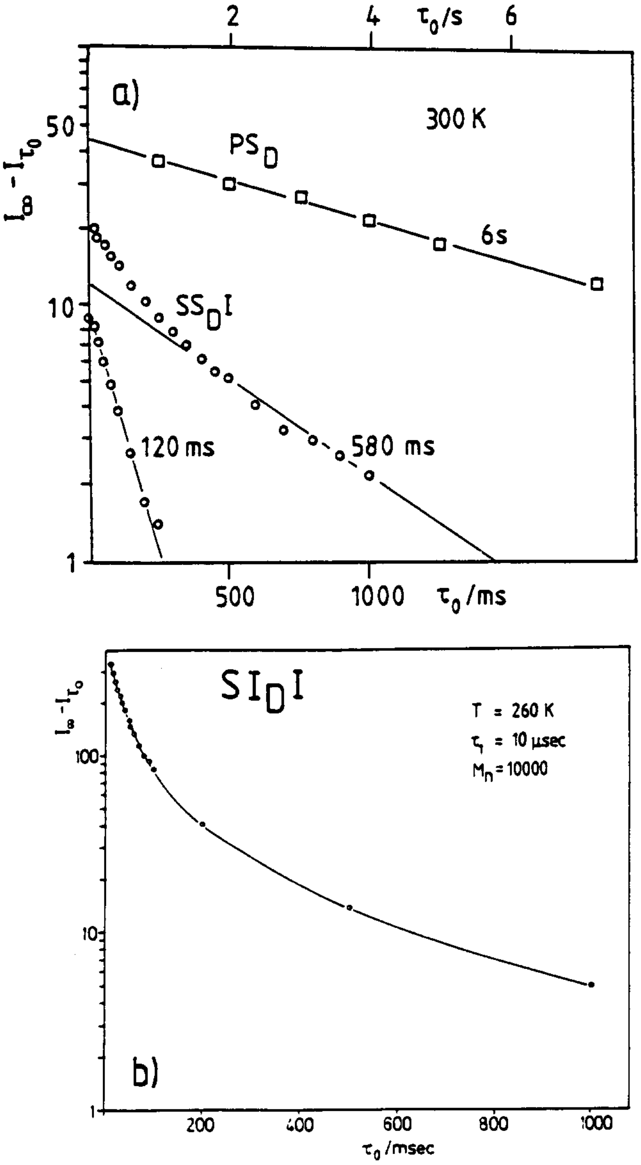

Figure 12 Spin-lattice relaxation of polystyrene and block copolymer SS_DI at 300 K (a) and of block copolymer SI_DI at 260 K (b)

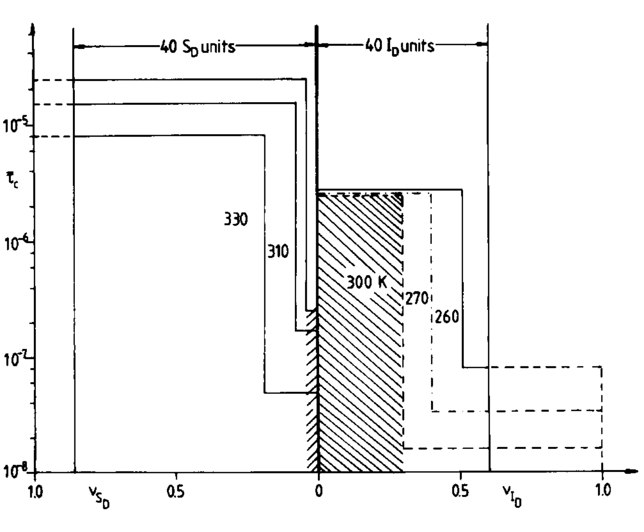

Figure 13 Dynamic profile functions of block copolymer SS_DI 10000 and SI_DI 10000 at various temperatures; for explanation, see text

are the weight fractions of deuterated (D) or protonated (H) PS material and $\bar{v}^{PS}_{D,H}$ are the specific volumes of deuterated and protonated material. The specific volumes are $\bar{v}^{PS}_{H(D)} = 0.953$ (0.985) cm^3 g^{-1} for polystyrene and $\bar{v}^{PI}_{H(D)} = 1.106$ (1.103) cm^3 g^{-1} for polyisoprene[19]. Similar equations to (1) and (2) hold for the volume fraction of isoprene in the regime of restricted motion at the phase boundary. The volume fractions of the complementary motional regimes are obtained by replacing x^{int} in equation (1) by $1-x^{int}$.

Mean correlation times τ_c have been determined in the following way. The τ_c value of v_S^{rigid} at 330 K has been approximated by the inverse of the mean jump rate k_{tg}^{-1} of the conformational jump process of the polybutadiene spectrum at 180 K in *Figure 11* having approximately the same lineshape as the rigid part of SS_DI at 340 K obtained after subtraction of the motionally narrowed component. The correlation time of the mobile component at the same temperature has been calculated from the fast component of the magnetization decay analogously to that shown in *Figure 12a* by approximating the relaxation rate by the expression for isotropic reorientation[20]. At temperatures smaller than 330 K the correlation times of the rigid fractions are greater than 10^{-5} s according to lineshape calculations for SS_DI at 310 K. The correlation time of the quasi-rigid interphase part on the isoprene side has been taken from the inverse of the mean conformational jump rate k_{tg} derived from the polybutadiene spectrum having the same lineshape as the polyisoprene spectrum at 235 K representing the interphase component of reduced mobility used in the decomposition shown in *Figure 7*. The mean correlation time of the interphase part of the isoprene microphase stays nearly constant in the temperature range considered. Finally, the mean correlation times of the mobile isoprene fraction originate from the short-time T_1 component of decay curves as in *Figure 12b*. On both sides of the interface the equivalent volume fractions of the deuterated block length is marked. It comprises about 85% of the styrene and 70% of the total isoprene phase.

The fractions of interphase material of restricted motion on the isoprene side of the interface and of the mobile fraction on the styrene side in *Figure 8* can also be expressed as equivalent dynamical interfacial thicknesses assuming a lamellar morphology and considering the molecular-weight dependence of domain dimensions of lamellar SI block copolymers from SAXS measurements[19]. The equivalent dynamical interfacial thicknesses are plotted in *Figure 14*. According to *Figure 13* the equivalent dynamical width of isoprene in the interphase contains isoprene with a mean correlation time of $\sim 2 \times 10^{-6}$ s, i.e. of the order of the inverse spectral width of the rigid system. The corresponding width of mobile styrene contains styrene with correlation times $< 10^{-7}$ s. The dynamical character of the thickness is apparent from the Arrhenius-type temperature dependence. The apparent activation energy is somewhat lower for the poorly phase-separated block copolymer with lower molecular weight $M_n = 10000$. This means that isoprene segments at the phase boundary are less hindered by neighbouring styrene segments in this block copolymer than the higher-molecular-weight sample with a more perfect degree of phase separation. The dynamical interphase thickness as seen from the isoprene side is ~ 10 Å at room temperature for the higher-molecular-weight sample ($M_n = 20000$) and ~ 14 Å for the

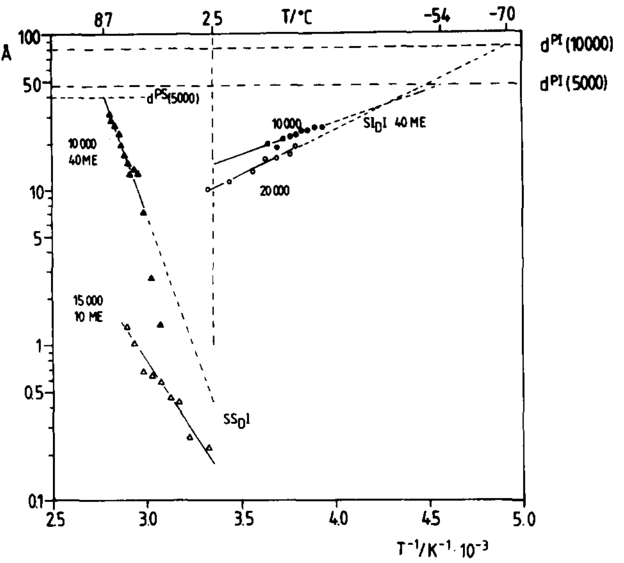

Figure 14 Equivalent dynamic interphase widths as determined from the ^2H n.m.r. spectra. Right-hand side: widths obtained from block copolymers SI_DI 10000 and 20000. Left-hand side: widths obtained from block copolymers SS_DI 10000 and 15000

low-molecular-weight sample ($M_n = 10000$), where the latter value is obtained by extrapolation. Since these values have been calculated from corresponding volume fractions of material of restricted mobility of the total isoprene phase, only half of the values have to be assigned to each interface because of the double-layer structure of the lamellae[19]. The dynamical widths are thus smaller than the widths of 10–20 Å determined by SAXS[4,5]. With decreasing temperature the equivalent dynamical thickness of the isoprene interphase increases until it is equal to the lamellar thickness d^{PI} of the isoprene phase. The temperature at which this occurs coincides approximately with the static T_g of the isoprene phase (see *Table 1*).

The small equivalent widths determined by n.m.r. are partly a consequence of the approximations involved in their estimation. First, a constant composition of the interphase material is assumed because the two-component decomposition procedure does not allow one to estimate the compositional and motional gradient across the interface. Secondly, part of the interphase material contributing to the SAXS interphase width may be associated with the motionally narrowed component, which was totally assigned to the pure isoprene phase. The inadequacy of the two-component approximation for the characterization of a one-dimensional width of the interfacial layer is particularly apparent on the styrene side, where a negligible width is obtained from the mobile part of styrene. This shows that part of the interphase as seen from the styrene side has to be associated with the Pake-like resonance of the styrene-deuterated systems, which cannot be resolved into individual components.

DISCUSSION

Thermal transition behaviour of the isoprene microphase

First we discuss the thermal transition behaviour of the block copolymers in relation to molecular weight as observed by the C_p measurements in *Figure 1* and the n.m.r. intensity measurements in *Figures 2* and *3*. For the sample with higher molecular weight ($M_n = 20000$) there is no detectable T_g shift of the isoprene phase with respect to the homopolymer in the quasi-static d.s.c. experiment extrapolated to zero heating rate (*Table 1*). Also the width of the transition is the same. Both observations point to the existence of a pure isoprene phase. In the d.s.c. experiment the presence of motionally restricted soft segments at the interface is seen only in the lower-molecular-weight block copolymer by a slight increase and broadening of the isoprene transition. It is assumed that the measured thermal behaviour of SS_DI 10000 shown in *Figure 1* is similar to that of SI_DI of the same molecular weight. In contrast the ^2H n.m.r. experiment monitors the local dynamics preferentially near the interface by virtue of the selective deuteration at the block boundary. Therefore it is more sensitive to the interaction of soft and hard segments, as shown by the high-temperature shift of the dynamic glass transition of SI_DI 20000 in *Figure 2* with respect to PI_D. The shift is further enhanced (*Figure 2*) if the molecular weight of the block copolymer is lowered to the critical region of phase separation.

The presence of soft segments in contact with polystyrene leads to a reduction of the mean correlation time of the isoprene main-chain motion, i.e. to a high-temperature shift of the intensity minimum. The spatial distribution of part of the soft material at the phase boundary or in the hard microphase also gives rise to a broader distribution of correlation times than in the homopolymer, which explains the greater width of the intensity distribution and its vertical shift with respect to the homopolymer.

The difference of the ΔC_p values between the block copolymer and homopolyisoprene (*Table 1*) shows that $\sim 20\%$ of the total isoprene mass does not belong to the pure isoprene phase. This fraction can be situated in an interfacial layer where both components are intermixed or it may be distributed over the entire hard phase. Which of the two possibilities is correct will be discussed in connection with the transition behaviour of the PS phase below. In any case the ΔC_p difference excludes the model of a completely sharp interface, which was put forward previously on the basis of erroneous C_p measurements[3].

For the lower-molecular-weight block copolymer SS_DI 10000 there is also an indication of a minor mixing of polystyrene segments in the isoprene phase. This is shown by a small high-temperature shift of the isoprene T_g (*Table 1* and *Figure 1*). Direct evidence of the presence of some mixing of PS segments in the isoprene phase is obtained from the spectra of block copolymers SS_DI 10000 and 15000 with deuterated styrene segments at the block boundary in *Figure 6*. The narrow central line on top of the Pake-like spectra has a similar width as the narrow line in the isoprene-deuterated system at the same temperature (*Figure 4*). Therefore the narrow line in the SS_DI system can be interpreted as originating from isolated polystyrene segments in pure isoprene surrounding. From *Figures 13* and *14* it can be seen that the amount of these sequences is very small at 300 K. Furthermore it can be seen that isolated PS sequences in the isoprene microphase are not due to a dissolution of complete blocks but only to short PS sequences at the block boundary pointing into the isoprene microphase. This is inferred from the increased intensity of the narrow component of the block copolymer carrying only 10 deuterated styrene monomer units at the block boundary.

The presence of a small amount of isolated boundary PS sequences is accompanied by a reduction of the mean frequency of isoprene motion and a somewhat greater width of the frequency distribution in the lower-molecular-weight sample in *Figure 2*. Thus the phase mixing of isolated PS segments appears to be accompanied by a broader spatial extension of the interphase region. The increased width of motions on the ^{2}H n.m.r. frequency scale of the low-molecular-weight block copolymer also has its correspondence in the C_p behaviour of *Figure 1*. Succeeding the isoprene glass transition the heat capacity of the lower-molecular-weight sample ($M_n = 10\,000$) exceeds that of the higher-molecular-weight block copolymer ($M_n = 15\,000$), pointing to an excess of vibrational excitations in the polystyrene phase by virtue of extended contacts with polyisoprene in an intermixed region. The amount of isoprene material in the interphase region is the same in both the higher- and the lower-molecular-weight block copolymer judging from the same 20% C_p deficit at the isoprene transition with respect to polyisoprene (*Table 1*). Therefore the broadening of the interphase region with lower molecular weight can only be explained by a change of the shape of the distribution function of isoprene segments.

Since the mixing of styrene segments in the isoprene phase is negligible, this means that an increasing mixing of isoprene segments in the styrene phase occurs if the critical molecular weight of phase separation is approached, i.e. the distribution of isoprene across the phase boundary appears to become increasingly asymmetrical. The distribution is asymmetric in the sense that an initial fast drop of the isoprene concentration across the phase boundary is followed by a more slowly decreasing tail extending into the hard phase. Therefore the interphase is richer in styrene than in isoprene. The notion of an interphase becomes somewhat arbitrary in this case because it may encompass the entire hard microdomain. The mechanical dynamic behaviour of styrene–butadiene–styrene (SBS) block copolymers has also been explained by an asymmetrical density profile function[8,9].

Thermal behaviour of the styrene microphase

The styrene glass transition is very broad and can be detected only at high heating rates for the higher-molecular-weight block copolymers. In contrast to the d.s.c. experiment the PS glass transition on the ^{2}H n.m.r. frequency scale is clearly visible also in the case of the low-molecular-weight sample because on the scale of fast motions the system is always in equilibrium and heating rate effects are unimportant. The n.m.r. T_g is shifted by a much higher increment of $\sim$43°C towards low temperature than the isoprene transition is shifted towards high temperature. Obviously the mobility of the styrene phase is enhanced to a higher extent by interaction with mobile isoprene segments than the motion of mobile isoprene segments is reduced by the rigid styrene phase. On the other hand, the degree of motional coupling of isoprene to styrene segments is rather small since the intensity on the styrene side is reduced only by about 25% at the intensity minimum of the isoprene side of the block copolymer and vice versa (*Figure 2*). Both the asymmetry of the temperature shift of the intensity minimum and the small motional coupling can be explained by the asymmetry of the segment distribution. A small amount of isoprene segments in the tail of the isoprene segment density distribution mixed into the styrene phase leads only to a small shift of the mean frequency of motion of isoprene segments and to a small intensity reduction of the isoprene intensity in the region of the dynamic styrene glass transition. On the other hand, a small fraction of soft segments mixed into the hard phase can have a considerable plasticizing effect, i.e. a shift of the glass transition temperature. The n.m.r. intensity distributions also show a difference in the spread of motional frequencies on the isoprene and on the styrene side. The higher intensity minimum and the greater width of the isoprene intensity distribution as compared to the styrene intensity distribution points to a broader distribution of correlation times of isoprene than of styrene segments. Partly this may also be due to structure-specific differences, which are apparent already in the homopolymer intensity distributions (see *Figure 2*). The broad distribution of isoprene segments in the hard phase of the low-molecular-weight block copolymer gives rise to a continuous softening of the microdomains and a broad dispersion in the C_p curve (*Figure 1*). In the block copolymer of higher molecular weight ($M_n = 15\,000$) a distinct styrene glass transition can also be resolved giving a ΔC_p value only 10% lower than the value of homopolystyrene of molecular weight 4000. By virtue of the Simha–Boyer rule[21] and the molecular-weight dependence[8] of T_g, one concludes that about 90% of the polystyrene block is involved in the glass transition. The remaining part must belong exclusively to the interfacial region because the phase mixing of polystyrene into the isoprene phase is negligible.

The 10% of styrene and 20% of isoprene material not taking part in the main transitions could alternatively be distributed in an interphase spatially separating a pure isoprene and a pure styrene phase. In this case the T_g depression of the remaining pure styrene domains has to be explained entirely by surface effects or a negative hydrostatic pressure exerted by the thermal motions of the mobile phase. However, the already mentioned considerations and additional spectroscopic arguments that will be put forward in the course of the discussion do not support the explanation of the T_g depression as entirely due to surface effects. The first explanation in terms of an asymmetric density distribution and phase mixing also explains why at constant heating rate a continuous transition from the stepwise behaviour of the polystyrene transition at higher molecular weight to a broad structureless transition for low molecular weight occurs, as seen in *Figure 1*. With increasing phase mixing of isoprene in the polystyrene domains, when the compositional gradient is getting less and less sharp, local relaxations are able to adjust more rapidly at any part of the interphase to the quasi-equilibrium that was frozen during previous cooling.

Nature of the interphase

One aspect of the n.m.r. experiments as compared to d.s.c. is that the observation time is longer by orders of magnitude than the relaxation processes in the range of 10^4–10^7 Hz. Therefore at any temperature a true snapshot of the dynamics of the quasi-equilibrium structure of the material in this frequency range is obtained. As demonstrated in *Figures 3* and *4* this leads to a resolution of relaxation processes of spatially separated regions in the dynamically heterogeneous block copolymers which cannot be resolved in the d.s.c. experiment.

Of main interest is the transformation of this dynamical regime of restricted motion to the mobile phase with increasing temperature. As pointed out above, the regime of restricted motion is characterized by a box-like spectrum the width of which stays nearly constant over a broad temperature interval. This observation was the basis for the decomposition into two components. The fact that the width of this partial spectrum does not change appreciably with temperature can be interpreted as follows. At an initial temperature, when this spectrum first appears, a high isoprene volume fraction of ~0.5 (*Figure 13*) is involved in small-amplitude diffusional motions and localized jumps comprising only a few bonds. The free volume available to these motions is restricted by nearby styrene segments, which are quasi-rigid on the ^{2}H n.m.r. timescale as seen by the Pake-like spectrum of the styrene-labelled block at the same temperature (*Figure 4*). The constancy of the lineshape of restricted isoprene motion points to the existence of isoprene segments for which the free volume changes only slowly with temperature. This can be explained by the tail of the asymmetric isoprene segment distribution in the inner core of the hard domains rich in styrene, where the free volume increase is essentially given by the thermal expansion of polystyrene. Towards the outer interfacial region the isoprene segment density increases more rapidly. This is reflected in the lineshape of the narrow component obtained by subtraction of the broad component in *Figure 8*. The narrow line has been shown to be represented to a good approximation by a corresponding line of the same width of the dynamically homogeneous homopolymer. However, one has to be aware that small fractions located in the interfacial region having high damping factors because their motional frequency is near to the critical frequency of 250 kHz may be masked by the major intensity of those parts of the pure isoprene phase with a low damping. The spectroscopic effect of the compositional and motional gradient in the interfacial region is then mainly contained in the base and the wings of the narrow resonance obtained by subtraction in *Figure 7* (see also *Figure 5*), which eludes a quantitative evaluation. Therefore the step-like behaviour of the correlation time profile in *Figure 13* obtained from the decomposition into two components gives only a crude representation of the true situation. The height of the horizontal lines only represent the upper and lower limits of the correlation times of the mobile parts and the part of restricted motion of isoprene and styrene.

There are clear indications that a compositional and motional gradient does exist. The spectra of the styrene-deuterated systems, in particular those with only 10 deuterated monomer units (*Figure 6*), show that the motionally narrowed component consists of a very narrow line superimposed on a broader line. Because of the greater fraction of mobile styrene segments relative to the block copolymer with greater deuteration length, more mobile parts of the boundary region with higher damping factors can be detected. In fact, the decomposition of the SS_DI spectra was generally only possible by subtracting two narrow homopolymer resonances of different width[15].

The existence of a distribution of correlation times due to a compositional and motional gradient at the interface is even more apparent in the spin-lattice relaxation (*Figure 12*). Both the isoprene- and the styrene-deuterated systems exhibit a distribution of spin-lattice relaxation times, which has to be explained by the existence of spatially separated regions of different dynamics and composition. Since temperature-dependent T_1 measurements have shown that in all cases the correlation time regime is on the low-temperature side of the T_1 minimum[15], a greater T_1 value corresponds to a region of reduced mobility. In the unrealistic case of a sharp interface separating pure polyisoprene from pure polystyrene microphases, one would expect a relaxation behaviour of the styrene-deuterated block copolymer similar to polystyrene. In this case the isoprene-deuterated block copolymer is expected to exhibit a non-exponential decay, as experimentally observed. In flexible chains attached to a silica surface, different $^1H-^{13}C$ cross-polarization time constants can be distinguished for C atoms as far as 9–10 bonds away from the surface, reflecting the increased freedom of motion with increasing distance from the rigid wall of silica[22]. However, the multi-exponential decay of the longitudinal magnetization observed for the SI_DI block copolymer can only be explained qualitatively by an analogous situation. Quantitatively the fraction of units with low mobility, i.e. long T_1 values, would be too large because T_1 differences are expected to be detectable only for the first 2–3 monomer units in the neighbourhood of a sharp interface. Under no circumstances can the T_1 behaviour on the styrene side be explained by this model, first because of the faster overall relaxation as compared to the homopolymer, and secondly because of the pronounced non-exponential relaxation. An additional feature is the bimodal behaviour of the spin-lattice relaxation of the styrene-deuterated block copolymer, which also contradicts the model of a sharp interface and pure domains.

The model of a continuously varying but symmetrical segment density could basically explain the continuous distribution of relaxation times on the isoprene side but not on the styrene side. If an asymmetrical distribution is assumed, for which other evidence was given above, both experimental observations can be accommodated. If we consider a low concentration of isoprene chains included in the inner core of the hard domains, it appears natural to assume that there is a corresponding distribution of spin-lattice relaxation times because the free volume will not be identical for all parts of these chains. Local fluctuations can be visualized by twists, folding and to some extent also contacts with other isoprene segments. Therefore, on a local level, similar as for chains attached to a rigid unit, local variations of mobility extending over a few bonds may occur for those polyisoprene chains of low mobility in the inner part of the hard microphase. The local motions of these isoprene chains enclosed in the hard matrix afford some conformational freedom as the model calculations of the spectrum of motionally restricted isoprene in SI_DI have shown. The long tail of the isoprene relaxation decay curve with low T_1 values can be assigned to these isoprene segments.

On the other side, the effect of phase mixing of a low concentration of isoprene segments in the hard core will lead only to a rather narrow distribution of relaxation times on the styrene side in the SS_DI block copolymer.

Because of the greater stiffness of the polystyrene chains, a weak increase of the free volume can induce only small-angle fluctuations of the bonds without conformational jumps, in agreement with the model calculations of the SS_DI spectrum corresponding to the hard core (*Figure 10*). This leads to a depression of the mean relaxation time as compared to the homopolymer and explains the component with long T_1, which therefore is assigned to polystyrene segments in the hard core weakly diluted by the long tail of the asymmetric isoprene segment distribution. The fast initial relaxation decay of the styrene-deuterated system is then assigned to the interfacial region, where the segmental densities of both styrene and isoprene segments change rapidly. By virtue of the motional gradient there should also be a T_1 distribution in this part of the material. Apparently the distribution is rather narrow and cannot be observed. This points to a very sharp decrease, i.e. a high degree of asymmetry of the segmental density distribution at the interface, or to other possible structural features to be discussed in the following.

The key problem concerning the nature of the interface is the question whether the quasi-rigid part of the isoprene spectrum originates from a state of continuous intermixture with styrene segments in the hard domains or in a boundary layer. The observation that cannot be explained easily in terms of a homogeneous intermixture of both components is the transformation of the isoprene interphase material of restricted motion into a highly mobile state of high correlation length with increasing temperature, which is not paralleled by a corresponding behaviour on the styrene side. This is expressed in a semiquantitative way by the correlation time profiles in *Figure 13* based on the two-component decomposition. Starting from a temperature of 300 K on the isoprene side a growing fraction of material in the interface region of restricted mobility is transformed into a state of highly correlated motion with correlation times smaller than 10^{-7} s, whereas on the styrene side the material is characterized by correlation times significantly greater than 10^{-5} s. Therefore no equivalent fraction seems to be transformed on the styrene side. At the high-temperature side of the transformation only a very small fraction of mobile styrene segments exists in a comparable state of high dynamic cooperativity.

At 300 K the linewidth of the mobile fraction into which the motionally restricted fraction is transformed is of similar order as that obtained from Monte Carlo simulations of the motion of polyethylene chains in amorphous regions under the assumption that 20 carbon atoms can move without restriction[23]. An equivalent segment of polyisoprene with the same number of carbon atoms would have a mean-square radius of gyration of ~ 15 Å, taking the characteristic ratio of *cis*-1,4-polyisoprene as $C_n = 4.7$[24]. This length then has to be considered as an estimation of the order of magnitude of the linear length scale of unrestricted motion at the phase boundary into which the material of restricted motion is transformed. If this is true, space of this order of magnitude must be provided as well in the vertical and the lateral direction of the phase boundary. A structural model that fulfils this requirement is that of a statistical boundary structure proposed recently[5]. The model is characterized by a fringed type of structure where like segments of isoprene and styrene are clustered in a statistical way. This structure can account for the observation that isoprene segments at the phase boundary are able to gain a high degree of cooperative mobility without the necessity that an equivalent amount of styrene has also to pass over into a state of similar cooperative mobility. In this interpretation the origin of a regime of restricted isoprene segmental motion is due first to fixation of the block junctions and secondly to the lateral restriction in the enclosures of the statistical boundary structure. The continuous distribution of correlation times as evidenced by the broad distribution of relaxation times in *Figure 12* has then to be explained by a continuously increasing mobility from the walls of the rugged interface in both the vertical and lateral directions of the phase boundary. The fact that with increasing temperature the spectral shape of the motionally restricted regime and consequently the mean correlation time of motion stay constant can then be viewed as a continuous increase of the amplitude of the small-angle jump process of the model calculations (*Table 2*) without affecting the lineshape significantly in a certain range. When the amplitudes reach a certain value, the segments jump over in an apparently discontinuous way to a highly cooperative state. The transition resembles a kind of phase transition in this picture. The bulk of styrene clusters on the other hand gain mobility at a much higher temperature except a very small portion of isolated segments pointing out of the isoprene domains. With increasing temperature, the styrene clusters are successively broken up, beginning with the smaller ones containing only relatively few units, whereas the core remains intact during the first stages of this process. Finally, entire domains disintegrate and a continuous passage to the cooperative motion of styrene segment occurs. The bimodal behaviour of the spin-lattice relaxation (*Figure 12a*) in this model could be associated with the motions of the outer parts of the statistical interface and the inner core of the hard domains, respectively.

CONCLUSIONS

The explanation of the experimental results in terms of a statistical boundary structure mainly relies on the two-component decomposition and the resulting apparently discontinuous dynamic behaviour. The limits and possible sources of errors involved in this approximation have been discussed. Weighing all experimental facts, the model of a continuous asymmetric distribution of segments in the interfacial region has the merit of being consistent with most of the observations. Although ^2H n.m.r. reveals many details of the heterogeneous dynamic behaviour of block copolymers, it is not possible to describe the dynamical gradient across the interface in a satisfactory quantitative way.

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