NMR Evidence for Residual Dipolar Interactions in SBS Systems: Influence of a Plasticizer on the Network Structure

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Received January 3, 2003; Revised Manuscript Received March 10, 2003

ABSTRACT: Evidence for residual dipolar interactions in the polybutadiene domains of two poly(styrene−butadiene−styrene) block copolymers is shown at temperatures ranging from ambient to 90 °C. The two copolymers differ for the presence of a plasticizer, selectively compatible with the polybutadiene blocks. The evidence results from the analysis of ^{1}H transverse magnetization decays, ^{1}H pseudo-solid echoes, and ^{13}C edited ^{1}H spectra. ^{1}H transverse magnetization decay data can be interpreted using a simplified network model, which provides the number N of statistical segments between cross-links. The analysis of decays and ^{1}H pseudo-solid echoes shows that the plasticizer induces a lowering of the entanglement density. These results are consistent with the information obtained from the ^{13}C edited ^{1}H spectra.

Introduction

Chemically and physically cross-linked elastomers have long been intensively studied in order to gain insight into their “semilocal” space scale structure (10−100 Å), which is responsible for some of their mechanical properties. NMR, in particular, although more commonly used to characterize local structure (about 5 Å), has proved to be useful for obtaining semilocal information in partially ordered systems.[1]

Local chain order in cross-linked elastomers arises from the presence of constraints which restrict the chain motions, making them anisotropic. Consequently, anisotropic spin interactions, such as dipole−dipole couplings, are not fully averaged out, and the system displays solidlike properties.

In this paper, evidence for residual dipolar couplings is shown for the polybutadiene domains in two poly(styrene−butadiene−styrene) block copolymers (SBS) differing for the presence of a paraffinic oil, selectively compatible with the polybutadiene blocks. Plasticization of SBS with oils is highly desirable in some applications in the food, pharmaceutical, and medical industries in order to increase the flexibility and workability of the polymeric system. Studies on SBS block copolymers concerning both mechanical and swelling properties have been reported, suggesting that SBS may be modeled as a collection of polystyrene domains, behaving as physical cross-links in a polybutadiene matrix.[2] In the present case, further evidence of the feasibility of such a model is provided by the measurement of the residual dipole−dipole interaction by means of different NMR techniques. Moreover, within this model, the addition of a plasticizer is expected to decrease the residual dipolar interaction; this is a common effect observed when a good solvent is progressively added to long polymeric chains, in consequence of the lowering of entanglement concentration.[3]

In the present work, residual dipolar couplings associated with polybutadiene domains have been probed with different NMR experiments: ^{1}H transverse magnetization decay, ^{1}H pseudo-solid echoes, and ^{13}C edited ^{1}H spectra. The first two are quite well-established low-resolution experiments for the investigation of residual dipolar couplings. A prediction of ^{1}H transverse magnetization decay data has been proposed within the assumptions of an already developed model.[1] The fitting of the decay with the model function provides “semilocal” structural parameters, which are related to the residual dipolar interaction. On the other hand, symmetric properties of ^{1}H pseudo-solid echoes data[3,4] are generally invoked to prove that transverse magnetization decay is completely dominated by residual dipolar interactions. The third type of experiment has only been recently applied to cross-linked systems,[5] although it was earlier introduced for the investigation of quite different materials, such as hydrogenated silicon[6] and coal structures.[7] This experiment allows residual heteronuclear ^{13}C−^{1}H dipolar interactions to be estimated.

NMR Evidence for Residual Dipolar Interactions

^{1}H Transverse Magnetization Decay. It is well-known that the presence of residual homonuclear dipolar couplings affects the transverse magnetization decay $M(t)$ according to the following expression:[1]

$$M(t) \cong M_0\langle\cos[\omega_{ij}t]\rangle = M_0\left\langle\cos\left[\int_0^t \frac{3}{2}\,\Delta_{ij}\,\frac{3\cos^2\theta_{ij}(t') - 1}{2}\,\mathrm{d}t'\right]\right\rangle \quad (1)$$

where the effects due to the fluctuating part of the dipolar Hamiltonian have been neglected. Δ_{ij} stands for $(\mu_0/4\pi)(\gamma^2\hbar/r_{ij}^3)$, with γ the magnetogyric ratio for the interacting nuclei, r_{ij} the distance between nuclei i and j, and θ_{ij} the instantaneous angle between the vector $\vec{r}_{ij}$ joining the two nuclei and the magnetic field. The angular brackets indicate an average over all the $\vec{r}_{ij}$ vectors in the polymer, thus averaging over all available configurations for the bond vectors. The averaging to the isotropic value of zero is prevented in the case constraints, for example due to entanglements or cross-links, are present.

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10.1021/ma034004a CCC: $25.00

Cohen-Addad,[1] exploiting the scale invariance concept,[8] proposed an expression for the residual dipolar interaction ω_{ij} of a couple of spins belonging to a cross-linked chain as a function of the average number of skeletal bonds N between two successive junctions. The polymeric chain is modeled as a collection of submolecules defined by two cross-links, each skeletal bond carrying a couple of nuclei located along the bond. All magnetic interactions between couples of spins placed on different bonds are neglected, only dipolar interactions within each pair being considered. This approximation is based on the assumption that fast local conformational changes effectively average the couplings between remote groups. Within this model, the rescaled residual homonuclear dipolar interaction ω_{ij} results in[9,10]

$$\omega_{ij} = \frac{3}{2}\Delta_{ij}\frac{k}{N^2a^2}\vec{R}^2\frac{3\cos^2\Theta - 1}{2} = \frac{3}{2}\Delta_{ij}\frac{k}{N^2a^2}\frac{2z^2 - x^2 - y^2}{2} \qquad (2)$$

where a is the length of a skeletal bond, Θ is the angle between the end-to-end vector $\vec{R}$ associated with the submolecule and the magnetic field, and x, y, z are the components of the end-to-end vector. The parameter k is a numerical constant which depends on the model used to describe the chain statistics; for a freely jointed chain it assumes the value $^3/_5$.[11,12]

Thus, the contribution of residual dipolar interactions to the transverse magnetization decay $M(t)$ can be rewritten as[13]

$$M(t) \cong M_0\left\langle \cos\left[\frac{3}{2}\Delta_{ij}\frac{k}{N^2a^2}\int_0^t \frac{2z^2(t') - x^2(t') - y^2(t')}{2}\,\mathrm{d}t'\right]\right\rangle \qquad (3)$$

where the angular brackets now indicate an average calculated over all the $\vec{R}$ vectors, thus averaging over all dynamical configurations of the end-to-end vector. Assuming a Gaussian distribution of the $\vec{R}$ vectors, the following expression has been obtained:[13]

$$M(t) = \mathrm{Re}\left[M_0\left(1 - ik\frac{\Delta_{ij}}{N}t\right)^{-1/2}\left(1 + i\frac{k}{2}\frac{\Delta_{ij}}{N}t\right)^{-1}\right] \qquad (4)$$

It has been emphasized that, if a value of k is assumed on the basis of the model chosen to describe the chain statistics, N should not be strictly identified with the number of skeletal bonds between cross-links, but only qualitatively related to it. In fact, this parameter is also affected by local geometry and dynamics as well as limited chain flexibility.[14,15] It has been observed that, even in the simplest case of a polyethylene chain, the freely jointed chain model is not adequate.[16] k values which give a better reproduction of experimental data have been calculated for different cases using RIS Monte Carlo simulations.[16,17]

Cohen-Addad's model has been adapted for the analysis of the proton transverse relaxation in the polybutadiene domains of an SBS block copolymer.[18] The polybutadiene blocks were modeled as a network, where the cross-links of the network are constituted both by the interface between the polybutadiene chains and the glassy polystyrene domains and by the entanglements within the polybutadiene chains. Taking into account the composition of a monomer, the total magnetization decay $M^{\mathrm{PB}}(t)$ has been expressed as a combination of the contributions expressed by eq 4 from the proton pairs in the $-\mathrm{CH_2}-$ and $-\mathrm{CH{=}CH}-$ moieties:

$$M^{\mathrm{PB}}(t) = \frac{2}{3}M^{\mathrm{CH_2}}(t) + \frac{1}{3}M^{\mathrm{CH}}(t) \qquad (5)$$

where Δ_{ij} is 1.36×10^5 rad s^{-1} (corresponding to a proton distance of 1.78 Å, which is the average distance between protons within a methylene pair[18]) and 5.34×10^4 rad s^{-1} (corresponding to a proton distance of 2.43 Å, which corresponds to the average distance within a methine pair[18]) for $M^{\mathrm{CH_2}}$ and M^{CH}, respectively. Different k values have been used for the two moieties, i.e., -0.55 and -0.73 obtained for the methylene and methine protons of polybutadiene, respectively, using the RIS Monte Carlo method.[17]

^{1}H Pseudo-Solid Echoes. Evidence of residual dipolar interactions in relatively mobile systems can be obtained from the observation of pseudo-solid echoes.[1] The sequence applied is $90_y{-}\tau_1/2{-}180_y{-}\tau_1/2{-}90_{-x}{-}\tau_2/2{-}180_y{-}\tau_2/2$,[3] where the 180° pulses refocus the magnetization and are introduced in order to overcome sample inhomogeneities. The amplitude of the magnetization along the x axis at time $t = \tau_1 + \tau_2$ gives the corresponding value of the pseudo-solid envelope, as shown for example in Figure 5 for the system under investigation.

It has been shown that, when transverse relaxation is entirely governed by residual dipolar interactions, the pseudo-solid echo envelopes exhibit several peculiar features.[1,3] For our purposes it is sufficient to focus on two of these features, that is: (a) the slope of the echo envelope at times slightly higher than τ_1 (τ_{1+}) is equal to the slope of the relaxation decay at times slightly lower (τ_{1-}) but with opposite sign; (b) two pseudo-solid echoes recorded using τ_1 equal to $\tau + \Delta\tau$ and $\tau - \Delta\tau$, respectively, will intersect at time $t = 2\tau$.

^{13}C Edited ^{1}H Spectra. Residual heteronuclear dipolar interactions can be estimated applying a 2D WISE experiment.[5,19] The experiment starts with a 90° pulse applied to protons, followed by a variable delay t_1. By means of a Hartmann−Hahn cross-polarization pulse of duration t_{CP} from protons to carbons, carbon magnetization is created and detected in t_2 in the presence of proton decoupling. Carbon magnetization is thus amplitude-modulated by the proton magnetization remaining at time t_1.[7,20] The intensity of carbon signal as a function of t_1 is thus a representation of the proton free induction decay (FID). Provided that short t_1 values and contact times are used in order to avoid ^{1}H spin diffusion, only ^{1}H nuclei directly bonded to ^{13}C nuclei are observed.

If the ^{13}C−^{1}H heteronuclear dipolar interaction dominates the evolution of the proton magnetization during t_1, the 2D spectrum resulting after 2D Fourier transformation shows proton dipolar spectra in the ω_1 dimension separated in the ω_2 dimension according to the chemical shift of the ^{13}C to which the protons are bonded. Under magic angle spinning dipolar spectra show well-separated dipolar spinning sidebands.

In the approximation that the ^{13}C−^{1}H heteronuclear dipolar interaction dominates both the evolution of the proton magnetization during t_1 and the cross-polarization dynamics during the fixed contact time t_{CP}, the proton magnetization transferred to the ^{13}C nuclei of the interacting spin pair at time $t_1 + t_{CP}$ in a powder sample under MAS as a function of the variable time t_1 is given by the following expression:[19]

$$M(t_1) = \langle \cos \phi(t_1)(1 - \cos \phi(t_{CP}))e^{-t_1/T_{2^*}} \rangle \tag{6}$$

where

$$\phi(t_1) = \int_0^{t_1} \omega^{MAS}(t)\, dt \tag{7}$$

$$\phi(t_{CP}) = \int_{t_1}^{t_1+t_{CP}} \omega^{MAS}(t)\, dt \tag{8}$$

with[21]

$$\omega^{MAS}(t) = \langle \omega_{^1H^{13}C} \rangle \left[\frac{1}{2} \sin^2 \beta \cos(2\omega_R t + 2\gamma) - \frac{1}{\sqrt{2}} \sin 2\beta \cos(\omega_R t + \gamma) \right] \tag{9}$$

where ω_R is the rotor frequency, $\langle \omega_{^1H^{13}C} \rangle$ is the residual heteronuclear dipolar coupling constant, and β and γ are the Euler angles denoting the relative orientation of the dipolar interaction PAS frame with respect to the rotor axis. T_2* has been introduced in eq 6 in order to take proton transverse relaxation into account.

Isotropic chemical shift modulation of ^{1}H magnetization in t_1 is eliminated by working at the resonance frequency of the proton of the $^{13}C-^1H$ spin pair of interest. The Fourier transformation of the experimental signal $M(t_1)$ (eq 6) will lead to the proton dipolar spectrum.

All the information on the dipolar interaction is contained in the t_1 signal sampled over a single rotor period, and the evolution is exactly periodic with $2\pi/\omega_R$, apart from transverse relaxation. The T_2* effect can be eliminated after compensation of the experimental signal decay by multiplication with $\exp(t_1/T_2^*)$, such that the intensities at $t_1 = 0$ and $t_1 = 2\pi/\omega_R$ are equal. Therefore, in this work, only t_1 values within one rotor period were sampled, as proposed in a similar experiment.[22] After Fourier transformation, assuming a periodic continuation of the data points, "delta-peak" sidebands spaced by ω_R appear as the dipolar spectrum, with relative intensities depending on the residual dipolar interaction.

In the case of CH groups, heteronuclear dipolar interaction has been assumed to dominate the evolution of the magnetization. This approximation, already used for similar systems,[15] may be justified on the basis of the relative magnitude of the hetero- and homonuclear dipolar coupling constants ($\Delta_{^1H^{13}C} = 1.42 \times 10^5$ rad s^{-1} for $r_{^1H^{13}C} = 1.10$ Å and $\Delta_{^1H^1H} = 5.34 \times 10^4$ rad s^{-1} for $r_{^1H^1H} = 2.43$ Å, corresponding to the typical distances in $-CH{=}CH-$ methine groups[18]). Thus, the "delta-peak" sideband spectrum of the CH groups can be simulated using eq 6 with the adjustable parameter $\langle \omega_{^1H^{13}C} \rangle$.

Experimental Section

The two samples investigated (I and II) are poly(styrene−butadiene−styrene) block copolymers, without and with a paraffinic oil, respectively.

Sample I was obtained from II by extraction in CH_3CN. Its molecular weight (M_w) is 92 300, and the polydispersity index is equal to 1.3 (GPC). The composition in styrene and butadiene monomers was determined by solution NMR;[23,24] it resulted that the mole fraction of styrene is 23%, and the polybutadiene chains contain 9% of monomeric units in the vinyl-1,2 conformation.

Sample II is an oil extended poly(styrene−butadiene−styrene) block copolymer. It was manifactured by Shell Chemical Co. and corresponds to the trade name Kraton D-4123CS*. The content in paraffinic oil is 30 wt % (TGA).

Low-resolution ^{1}H NMR experiments were performed on a single-channel Varian XL-100 spectrometer interfaced with a DS-NMR Stelar acquisition system. The experiments were performed on-resonance, working at a reduced magnetic field, corresponding to a proton Larmor frequency of 25 MHz. The 90° pulse was 3 μs. The transverse relaxation curves were built using the FID from a quadrupolar echo sequence ($90_x - \tau - 90_y - \tau$)[25] for short times (i.e., below few hundreds of microseconds) and the FID from a Hahn spin echo ($90_x - \tau - 180_y - \tau$)[26] for longer times. The former sequence avoids the dead time effects which prevent a correct measurement of short components, while the second one eliminates effects due to field inhomogeneities, more relevant for long components. The experiments were performed at variable temperature, in the range from 25 to 90 °C, well above the glass transition temperature of polybutadiene and below that of polystyrene.

Pseudo-solid spin echoes were recorded by applying the pulse sequence $90_y - \tau_1/2 - 180_x - \tau_1/2 - 90_x - \tau_2/2 - 180_x - \tau_2/2$.[3] The measurements were performed at room temperature.

High-resolution NMR experiments were performed on a Bruker AMX-300 WB equipped with a 4 mm CP-MAS probe. The operating frequencies were 300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively. The 90° pulse was 3.8 μs. The rotor frequency was set to 1000 Hz, the contact time 500 μs, and t_1 sampled every 40 μs. The experiments were performed at room temperature.

The equations describing the transverse magnetization decay (eqs 10 and 11) and the rotational dipolar sideband patterns were calculated within the Mathematica 4 programming environment.[27] The parameters included in eqs 10 and 11 were optimized using a multiparameter nonlinear least-squares optimization routine based on the Levenberg−Marquardt algorithm. Rotational dipolar sideband patterns were simulated by numerically evaluating the integrals in eq 6, where the orientations on the unit sphere of a powder were generated using the Conroy method.[28]

Results and Discussion

^{1}H Transverse Magnetization Decay. Considering that our polymer is a styrene−butadiene−styrene block copolymer, the experimental ^{1}H transverse magnetization decays of sample I were fitted using a combination of eq 5, which takes into account the contribution of the relatively mobile polybutadiene blocks, and a Gaussian function, typically used for ordinary solids, for the rigid glassy polystyrene blocks, according to the following expression:

$$M_I^{tot}(t) = w_{PB} M^{PB}(t) + w_g e^{-(t/t_g)^2/2} \tag{10}$$

where w_i is the weight of the corresponding function, $M^{PB}(t)$ is the polybutadine contribution defined previously, and t_g is the decay time constant of the Gaussian function.

For sample II, an additional exponential function was used in order to describe the ^{1}H decay of the oil:

$$M_{II}^{tot}(t) = w_{PB} M^{PB}(t) + w_g e^{-(t/t_g)^2/2} + w_0 e^{-t/t_o} \tag{11}$$

with t_o the decay time constant of the oil magnetization.

It should be emphasized that this treatment implies the assumption that the presence of the oil does not change the nature of proton relaxation within the polymer, the magnetization decay in polybutadiene being still described by eq 5. This assumption is justified

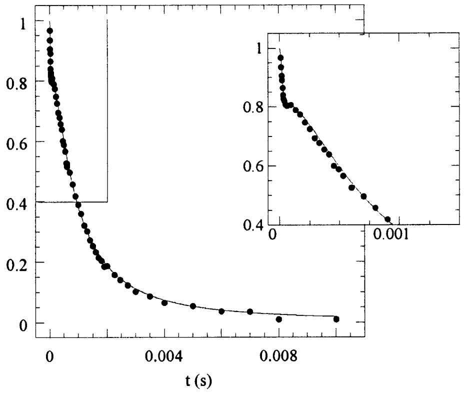

Figure 1. Comparison between the experimental decay (●) for sample I at 50 °C and the curve $M_{I}^{tot}(t)$ (−) calculated according to eq 10 using the best fit parameters ($w_g = 0.18$, $w_{PB} = 0.82$, $N = 30.9$, $t_g = 18\ \mu s$). The inset shows an expansion of the first part of the decay.

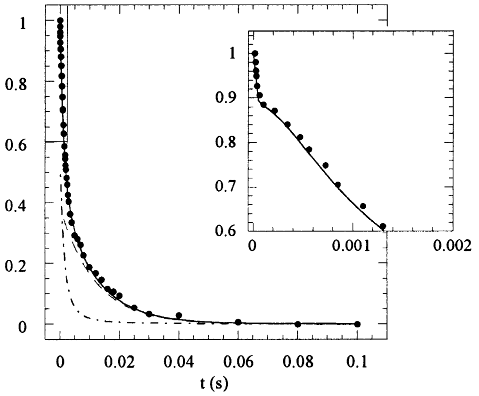

Figure 2. Comparison between the experimental decay (●) for sample II at 50 °C and the curve $M_{II}^{tot}(t)$ (−) calculated according to eq 11 using the best fit parameters ($w_g = 0.11$, $w_{PB} = 0.50$, $w_o = 0.39$, $N = 44.1$, $t_g = 20\ \mu s$, $t_o = 12$ ms). The contributions $w_{PB}M_{PB}(t)$ (alternate long short dashed line) and the weighted exponential function (long dashed line) are also shown. The contribution from the Gaussian function is not shown because it is relevant only for the first few points of the curve, as displayed in the inset showing an expansion of the first part of the decay.

on the basis of the results of pseudo-solid echo experiments, which will be shown in the following paragraph, and seems acceptable considering the success of the fitting.

A comparison between the experimental decay at 50 °C and the curve calculated using the best fit parameters is shown as an example in Figures 1 and 2, for samples I and II, respectively.

The success in fitting the experimental curves indicates that the approximations used in Cohen-Addad's model are reasonable for describing the magnetization decay in the polybutadiene block of the systems in question.

This is in agreement with results obtained for similar systems: in a series of random poly(styrene-*co*-butadiene) systems cross-linked at different degrees, ^{1}H relaxation curves were found to superimpose by applying a suitable factor to the time scale,[15] thus implying that the two-spin approximation was justified within the time range of the decay. Dipolar couplings between protons belonging to remote segments, which have been measured by double-quantum NMR experiments,[14] give a negligible contribution to the time evolution of the magnetization.

On the other hand, in an SBS block copolymer, ^{1}H relaxation data were successfully fitted only invoking a non-Gaussian distribution of the end-to-end vector $\vec{R}$,[18] while Gaussian statistics was used successfully in this work. This might reveal slightly different morphologies of the samples. In the case reported in the literature, polybutadiene chains had to be assumed stretched due to the presence of polystyrene blocks, while in ours the results are consistent with unstretched chains, which is possibly due to the slightly different styrene content of the samples.

In addition, in a random poly(styrene-*co*-butadiene),[14] the analysis of ^{1}H double-quantum NMR data revealed a difference between the dynamic order parameter of $-CH_2-$ and $-CH{=}CH-$ internuclear proton vectors with respect to the end-to-end vector $\vec{R}$, whereas in Cohen-Addad's model this order parameter is simply set to unity for both groups. In this work calculations were performed both using a single k value (set equal to 0.6, assumed for freely jointed chains) and using the two different k values calculated by RIS Monte Carlo methods for polybutadiene chains.[17] In the first case, different values of N for the two groups would have been expected given the difference in the order parameter; however, the data were well reproduced by using the same N value for the two groups, and the assumption of two different values gave values of N within experimental error with a higher correlation among the fitting parameters and hence higher errors. The fitting performed using the two different k values (i.e., -0.55 and -0.73 for the methylene and methine protons, respectively) yielded values of N differing by at most 10% with respect to those obtained using a single k value. The results obtained with the latter fitting procedure will be used in the following.

The fitting parameters w_i indicated in eqs 10 and 11 are not sensitive to temperature, with w_{PB} oscillating in the range 78%−86% in the temperature range 25−90 °C in sample I and w_{PB} and w_g varying between 47% and 50% and between 10% and 16%, respectively, in the same temperature range, in the case of sample II. These values are quite close to the stoichiometric value, the butadiene proton molar fraction being 0.72 and 0.44 in samples I and II, respectively, and the styrene proton one being 0.18 in sample II. The agreement between the w_i values and the proton molar fractions provide an indication of the effectiveness of the current data treatment.

The relaxation times relative to the polystyrene block (t_g of eqs 10 and 11) in both samples and relative to the oil (t_o of eq 11) in the case of sample II obtained from the fitting procedure are shown in Figure 3. The values are compatible with a rigid phase in the case of the polystyrene protons and a mobile phase for the oil; also, the trend with the temperature is as expected, indicating an increase in mobility with the temperature. The values of t_g in samples I and II are very similar and confirm that the oil interacts selectively with the polybutadiene blocks and does not influence the polystyrene blocks.

A comparison between the temperature trend of the parameter N obtained for samples I and II is shown in Figure 4.

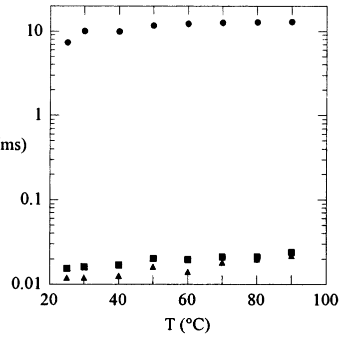

Figure 3. Temperature trend of the relaxation times of the Gaussian component (t_g) in sample I (▲) and in sample II (■) and of the exponential component (t_o) in sample II (●).

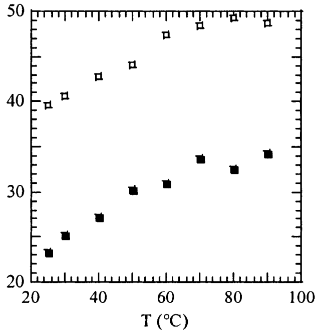

Figure 4. Temperature trend of parameter *N* for samples I (■) and II (□).

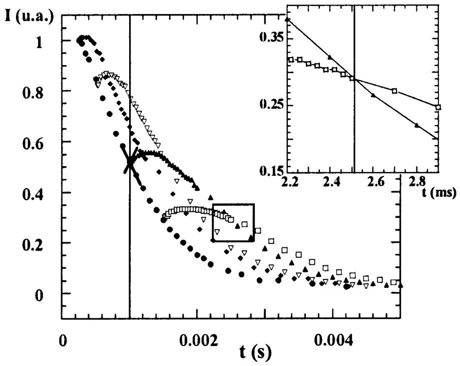

Figure 5. Proton transverse magnetization decay (■) and pseudo-solid spin echoes recorded for sample I at room temperature. The echoes have been recorded with $\tau_1/2$ equal to 0.12 (◆), 0.25 (▼), 0.5 (▲), and 0.75 ms (□). The slope of the proton transverse decay (■) at time τ_{1-} and of the pseudo-solid echo (▲) at τ_{1+} are indicated as an example of the first symmetry property (see text). An expansion of the intersection zone for the envelopes (▲) and (□) is shown as an example of the second symmetry property in the inset.

N is observed to increase with the temperature for the two samples in an essentially linear fashion, at least up to 70 °C; if the network is assumed to be characterized by a constant statistics, this behavior can be explained assuming a progressive disengagement of the entanglements in a temporary network.

N results to be sensibly higher in sample II with respect to sample I; this is related to a swelling effect involving both the disengagement of polybutadiene chain segments from one another and the swelling of each segment, again indicating the existence of a temporary network.

^{1}H Pseudo-Solid Echoes. Some pseudo-solid echo envelopes recorded using different τ_1 values at ambient temperature are shown in Figures 5 and 6 for samples I and II, respectively. Upon careful inspection, it can be realized that the trends shown for sample I fulfill the symmetry properties mentioned in the section describing the experiment, whereas they do not for sample II. In fact, for sample II, the magnitude of the slopes at τ_{1+} of the pseudo-solid echo envelopes are smaller than the slopes of the relaxation decay at τ_{1-}, and the echoes intersect at times slightly shorter than those predicted according to the second symmetry requirement indicated in the theory section.

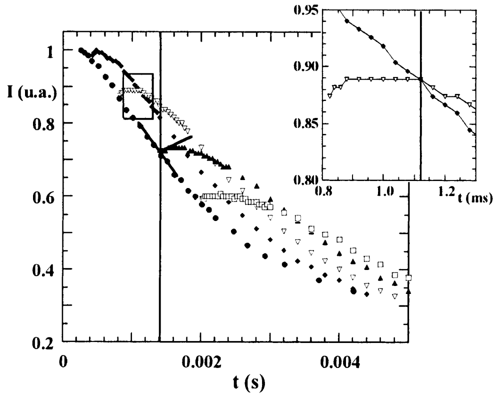

Figure 6. Proton transverse magnetization decay (■) and pseudo-solid spin echoes recorded for sample II at room temperature. The echoes have been recorded with $\tau_1/2$ equal to 0.2 (◆), 0.4 (▼), 0.7 (▲), and 1.0 ms (□). The slopes of the proton transverse decay (■) at time τ_{1-} and of the pseudo-solid echo (▲) at τ_{1+} are indicated as an example of the fact that the first symmetry requirement is not fulfilled (see text). An expansion of the intersection zone for the envelopes (◆) and (▼) is shown in the inset as an example. The intersection time, indicated by the vertical line, is shorter than the value of 1.2 ms expected on the basis of the second symmetry requirement (see text).

These results indicate that relaxation is entirely governed by residual dipolar interactions in sample I, but not in sample II. It must be pointed out that, in the latter sample, the signal comes from the protons of both the polymer and the oil, and the pseudo-solid echo behavior observed is consistent with transverse relaxation still dominated by residual dipolar interactions as far as the polymer is concerned, but also affected by the liquidlike relaxation of the protons of the plasticizer. This hypothesis is supported by the results reported in the previous section, where the ^{1}H experimental decay of sample II was reproduced by a curve resulting from a superposition of a solid- and a liquidlike contribution coming from the polymer and the plasticizer, respectively (eq 11).

^{13}C Edited ^{1}H Spectra. The "delta-peak" sideband spectrum for the methine groups of the two samples, obtained according to the procedure outlined in the section describing the experiment, are shown in Figures 7 and 8 for samples I and II, respectively.

The experimental trends were successfully simulated by theoretical curves calculated as described previously, with the scaled heteronuclear dipolar interaction $\langle \omega_{^1H^{13}C} \rangle$ equal to $2\pi \cdot 700$ and $2\pi \cdot 500$ rad s^{-1} for samples I and II, respectively. In fact, in the hypothesis that Cohen-Addad's model holds also for the couple of nuclei ^{13}C and ^{1}H and assuming Gaussian statistics for the distribution of $\vec{R}$, according to eq 2 the ratio $\langle \omega_{^1H^{13}C} \rangle / \Delta_{^1H^{13}C}$ should be equal to k/N, which is comparable to the corresponding value obtained by means of transverse magnetization decay analysis. The ratio $\langle \omega_{^1H^{13}C} \rangle_I / \langle \omega_{^1H^{13}C} \rangle_{II} = 1.4$ obtained is, in fact, consistent with the

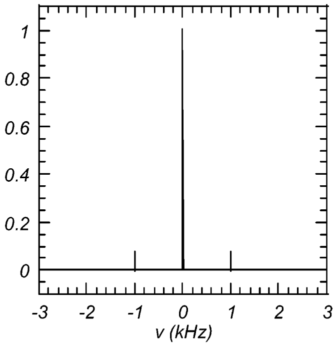

Figure 7. "Delta-peak" sideband spectrum of the methine protons in sample I at room temperature.

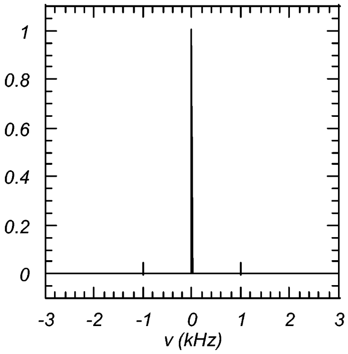

Figure 8. "Delta-peak" sideband spectrum of the methine protons in sample II at room temperature.

relative values of N^{-1} resulting from the transverse magnetization decay, at room temperature being $N_{\mathrm{I}}^{-1}/N_{\mathrm{II}}^{-1} = 1.6$. It must be pointed out, however, that the comparison should just be taken as a rough indication. In fact, the assumptions at the basis of Cohen-Addad's model, and therefore of eq 2, although used in cases similar to the ones under investigation,[15] are rather critical for the C−H interaction, since the C−H bond does not coincide with a skeletal bond.

Conclusions

NMR evidence for residual dipolar interactions in the polybutadiene domains of two SBS block copolymers differing for the presence of a plasticizer, selectively compatible with the polybutadiene blocks, is shown. The evidence results from the analysis of ^{1}H transverse magnetization decays, ^{1}H pseudo-solid echoes, and ^{13}C edited ^{1}H spectra. ^{1}H transverse magnetization decay data are interpreted using a simplified network model proposed by Cohen-Addad. The model implies the existence of residual interactions between couples of spins distributed on a polymeric chain and provides the number N of statistical segments between cross-links. The analysis of decays, together with ^{1}H pseudo-solid echoes, shows that the plasticizer, on one hand, preserves enough freedom to behave as a liquid and, on the other, induces partial release of the network. These results are consistent with the information obtained from the interpretation of the ^{13}C edited ^{1}H spectra where a decrease in the ^{13}C−^{1}H residual dipolar interaction of the order expected on the basis of the N values obtained from ^{1}H analysis is observed.

The collection of experimental evidence presented demonstrates that the assumptions of Cohen-Addad's model, although apparently rather crude to describe polymeric chains in real samples, reasonably account for the observables we focused on.

Acknowledgment. We acknowledge Dr. M. Geppi for kindly letting us use the Varian XL-100 spectrometer and Dr. L. Calucci for many helpful discussions. We also thank Dr. E. Passaglia for providing the samples.

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MA034004A