Polybutadiene Network in a Styrene−Butadiene−Styrene Triblock Copolymer. NMR Observation

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ABSTRACT: The semilocal structure (space scale: ≈50 Å) of a styrene−butadiene−styrene triblock copolymer (SBS) was investigated by observing residual dipole−dipole interactions that govern the transverse relaxation of protons attached to the polymer. The molar masses were 10^4 and 5×10^4 g/mol for polystyrene (PS) and polybutadiene (PB), respectively. It is shown that, above the glass transition of PB, there exists a network structure; the comparison made with NMR properties of long PB chains, in the melt, suggests this structure is a network formed by entanglements. These chain coupling junctions are trapped by the presence of PS glassy domains where the interface plays the role of embedding points for PB block ends. The mean segmental spacing between chain coupling junctions was found to vary as c^{-1} where c is the concentration of PB in heptane, a selective solvent of PB. A probability distribution function of end-to-end vectors joining two consecutive coupling junctions, along a PB chain, is proposed to analyze relaxation curves. The estimated lifetime of PB coupling junctions is 1 ms, at 220 °C, the temperature of the order−disorder transition that occurs in SBS. With regard to the PS properties, the glass transition process, as observed from NMR, spread over the range 50 to 130 °C; this result is in agreement with all earlier NMR studies reported about the PS glass transition.

I. Introduction

A great deal of effort has been devoted to studying the morphology of diblock copolymers using transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and neutron scattering experiments. For pure diblocks, extensive studies both theoretical and experimental have given evidence for the existence of a morphological phase diagram. These investigations have been also extended to triblock copolymers.[1,2] In this work, attention was focused on properties of styrene−butadiene−styrene copolymers. The existence of cylindrical polystyrene domains, in such systems (KRATON 1102) studied above the glass transition temperature of polybutadiene, has been observed, using TEM and SAXS.[3,4] The experimental value of the diameter of cylinders is about 150 Å, while the mean spacing is about 300 Å.[5−7] The morphology was also investigated by NMR, using the spin-diffusion approach.[8] The mean distance between cylinders, Δ, is expected to vary as a fractional power of the molecular weight: $\Delta \approx \chi_{A,B}{}^{1/6}N^{2/3}$ ($\chi_{A,B}$ is the interaction parameter of monomeric units A and B, N is the number of skeletal bonds in one chain).[9] The order−disorder transition temperarure (≈220 ± 10 °C) has been estimated from rheological measurements[3] and compared with the theoretical value predicted from models proposed by Leibler[10] and Helfand and Wassserman.[11]

The purpose of this work was to characterize the statistical structure of SBS, using NMR as a technique of investigation. More precisely, attention was not focused on the morphology of the triblock copolymer, which is already well described over a space scale equal to about 500 Å. Semilocal investigations (≈50 Å), reported here, aim at proving the existence of a polybutadiene network formed from trapped entanglements; the network was probed, observing the transverse relaxation of protons attached to the SBS copolymer. NMR has proved to be a suitable technique for characterizing networks whether these exhibit temporary or permanent structures.

Investigations were focused on two significant temperature ranges: (i) Below and around the glass transition temperature of polystyrene where rigid glassy domains of PS act as anchoring points for polybutadiene chain ends; fixed ends give rise to a network structure. (ii) Above the glass transition temperature of PS, the progressive order−disorder transition that occurs in SBS was detected by NMR.

II. Experimental Section

Samples. The polymer used in this study is a S/B/S copolymer (poly(styrene−butadiene−styrene)), manufactured by Shell Chemical Co., and corresponding to the trade name KRATON 1102. Its molecular weight (M_w) is 70 000, with a polydispersity index equal to 1.1 (GPC). The mass fraction of styrene content and the polybutadiene chains microstructure were calculated from 300 MHz NMR spectra. The mass fraction of styrene is about 29%. The polybutadiene chains contain 9% of monomeric units in the vinyl-1,2 conformation. Concentrated solutions were prepared using a selective solvent for the PB block; deuterated heptane was purchased from Aldrich (deuteration rate: 99%). Four SBS weight fractions were considered, $\phi = 0.7$, 0.5, and 0.4. Thermograms were obtained using a Perkin-Elmer DSC 2C equipment.

NMR Measurements. All samples used for NMR measurements were kept in sealed NMR tubes, under vacuum, to avoid any effect of oxidation of chains on raising the sample temperature. Proton relaxation functions were observed by using an MSL Bruker spectrometer operating at 60 MHz. Relaxation curves were determined from free induction decays (FID) over a time interval going from 0 to about 150 μs and then from Hahn spin echoes (90°/x−τ−180°/y pulse sequence) for longer times. Pseudosolid spin echoes were formed by applying the following pulse sequence to the spin system: 90°/x−τ−180°/x−τ−90°/y −[τ_1−180°/x−τ_1−180°/−x]$_n$.[12]

NMR measurements were recorded as a temperature function between 193 and 503 K for the bulk sample and at room temperature for the concentrated solutions.

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III. NMR Approach

The method of observation of the properties of the structure of SBS by NMR makes use of the transverse magnetic relaxation of protons attached to the copolymer. The polymeric system observed below the glass transition temperature of polystyrene and above that of polybutadiene is expected to exhibit a two-component transverse magnetic relaxation of protons. There is a fast decay associated with protons attached to polystyrene in the glassy state; this relaxation is specific to a solid state. The relaxation process is usually described according to a Gaussian time function. The second component is assocated with protons attached to polybutadiene; the copolymer can be pictured as a network in which nodes are defined by glassy polystyrene domains. The behavior of the relaxation function is specific to polymeric networks; the time scale is about 10 ms. The principle of the NMR approach to semilocal properties of polymeric gels has been already considered elsewhere; it is briefly outlined in this section, where it is shown that the existence of a network structure is detected from the relaxation of the transverse magnetization of protons attached to polymer chains.[12]

III.1. Residual Spin−Spin Interactions. A chain segment comprising N skeletal bonds is determined by two fixed nodes. The spin−spin Hamiltonian associated with nuclear spins located along the chain segment is first defined in the absence of any random motions of monomeric units; let H_D denote this Hamiltonian. Now observing fluctuations that occur in the chain segment above the glass transition temperature, random rotations of monomeric units are expected to be nonisotropic because of the existence of fixed ends; these rotations induce, in turn, a nonzero average of spin−spin interactions of protons. The strength of the averaged magnetic interactions, considered along this segment, is a function both of the mean distance, r, between the two nodes and of the number N. The estimate of the reduced Hamiltonian resulting from segmental fluctuations may be roughly written as $[rb/\sigma(N)^2]^2H_D$; $\sigma(N)^2$ is the mean square end-to-end vector of the segment and the mean skeletal bond length is designated by b. The existence of fixed chain ends affects the proton transverse relaxation; the description of this effect amounts to considering a partial weakening of spin−spin interactions and, correspondingly, a lengthening of the time scale of the proton transverse relaxation. In this work, the effect of residual spin−spin interactions on NMR was analyzed in two ways. The first analysis makes use of the mathematical expression derived for the relaxation function of one proton pair attached to a chain segment and submitted to a nonisotropic random rotation; it provides a picture of the statistical structure of the network formed by the copolymer. The second analysis is based on an integral treatment of relaxation curves, already applied to the NMR characterization of network structures;[12] such an analysis is independent of any model, and it reinforces the first analysis.

III.2. Noninteracting Protons Pairs. The proton transverse relaxation in polybutadiene is described by assuming that the spin system is an ensemble of proton pairs that represent methylene, $-(CH_2)-$ and methyne, $-(CH{=}CH)-$) groups, both present in the polymer. All magnetic interactions between different pairs are neglected, considering internal dipole−dipole interactions within each pair, only. The transverse magnetic relaxation associated with one proton pair linked to a Gaussian chain segment, built from N links and characterized by a fixed end-to-end vector, **r**, has already been calculated. The Gaussian distribution function of end-to-end vectors,

$$\pi(\mathbf{r}) = (2\pi\sigma^2/3)^{-3/2}\exp(-3r^2/2\sigma^2) \qquad (1)$$

with $\sigma^2 = NC_\infty b^2$ ($C_\infty b$ is the persistence length of the chain) leads to the following expression for the relaxation function:

$$M_x^R(t) = \frac{\sqrt{1 + 3(t^\dagger)^2 + B(t^\dagger)}}{\sqrt{2}B(t^\dagger)} \qquad (2)$$

where:

$$B(t^\dagger) = \sqrt{1 + 3(t^\dagger)^2 + 4(t^\dagger)^6} \qquad (3)$$

and

$$t^\dagger = 0.5t\Delta_G/NC_\infty \qquad (4)$$

the numerical value of Δ_G is the dipole−dipole interaction of protons within a $-(CH_2)-$ pair: 1.3×10^5 rad·s^{-1}. The transverse magnetic relaxation function associated with the two different proton pairs is then written as

$$M_x^{th}(t^\dagger) = \frac{1}{3}M_x^R(\alpha t^\dagger) + \frac{2}{3}M_x^R(t^\dagger) \qquad (5)$$

with $\alpha = (d_1/d_2)^3$; $d_1 = 1.78$ Å is the distance between two protons within a methylene pair while $d_2 = 2.43$ Å is the distance within a methine pair; the power 3 comes from the dependence of the dipole−dipole interaction on the distance between the dipoles.

III.3. NMR Structural Parameter. It is assumed that a relaxation function $m_x(t,\mathbf{r},N)$ is ascribed to each chain segment connecting two consecutive nodes. Each relaxation function is governed by the reduced Hamiltonian, $[rb/\sigma(N)^2]^2H_D$; the ratio $[rb/\sigma(N)^2]^2$ plays the role of a time scaling factor, which depends on the distribution of mean distances between two consecutive nodes. The relaxation function $M_x(t)$, observed over the whole sample results from an average carried out by using the probability distribution function of the mean end-to-end vector, **r**. Let $G(\mathbf{r}/\sigma(N))$ denote this probability distribution function; it is associated with the statistical structure of the polymeric network, and it is introduced to express the irreversible behavior of the transverse magnetization observed over the whole polymeric sample. The magnetization is thus written as

$$M_x^R(t,\sigma(N)) = \int \mathrm{d}\rho\ m_x(t,\rho b/\sigma(N))\ G(\rho) \qquad (6)$$

the normalized ρ vector is defined as $\rho = \mathbf{r}/\sigma(N)$). The relaxation function depends on $\sigma(N)$; it is treated by considering two tractable integrals

$$\Phi_1 = \int_0^\infty t^{-1/2}M_x^R(t)\ \mathrm{d}t \qquad (7)$$

and

$$\Phi_3 = \int_0^\infty t^{-1/2}(\mathrm{d}M_x^R(t)/\mathrm{d}t)\ \mathrm{d}t \qquad (8)$$

The two specific integrals involve the moments of the G(ρ) function; they are defined in the following way

$$m_\beta = \int_0^\infty (\rho)^\beta\, G(\rho)\, \mathrm{d}\rho \tag{9}$$

($\beta = 1, 2$). Each moment m_β is intrinsic because it is defined in terms of the reduced vectorial variable, ρ; it reflects the shape of the distribution function $G(\mathbf{r}/\sigma(N))$. It has been already shown that the ratio defined by

$$\chi_c = \Phi_3/\Phi_1 \tag{10}$$

is equal to

$$\chi_c = \Delta G \Lambda m_3/\langle\sigma(N)^2\rangle m_1 \tag{11}$$

It has been called NMR structural parameter; ΔG is considered as an intrinsic nuclear magnetic quantity specific to the polymer observed; it is distinguished from the parameter, Δ_G, introduced in eq 4. Its exact numerical value is not easily predicted; however, it can be determined experimentally. The factor Λ accounts for the chain stiffness; it has been shown to be determined by the orientational correlations of three skeletal bonds along one chain.[12] Equation 11 shows that the inverse of the NMR structural parameter χ_c must be a simple function of the mean number of bonds in the network chain segments. This NMR parameter is used in the next sections to probe the mean segmental mesh size in SBS. The product defined by

$$\pi_c = \Phi_3\Phi_1 \tag{12}$$

is called the NMR distribution width; it is expressed as

$$\pi_c \approx m_1 m_3/m_2^{\,2} \tag{13}$$

The NMR distribution width is used to reveal variations in the statistics that describes polymeric gels (Gaussian or excluded volume statistics).

IV. Thermal Behavior

In this section, attention is first focused on polystyrene properties as observed from NMR; investigations concern the glass transition of domains. The network structure formed by polybutadiene chains is then probed from residual spin−spin interactions, according to the description outlined in section III. Proton relaxation curves were recorded as a function of temperature over the range −80 to +230 °C.

IV.1. Polystyrene Microphase. At −80 °C, the whole transverse relaxation curve was described according to a Gaussian curve, with a relaxation time $T_2^G = 12.9\ \mu$s; at this temperature, which is near the glass transition of polybutadiene ($T_g = -95$ °C), the whole block copolymer is detected from NMR, as a solid because random rotations of monomeric units are not fast enough to induce a motional averaging effect of spin−spin interactions.

Relaxation curves observed over the temperature range −50 to +50 °C exhibit two well-defined components, characterized by very different time scales of relaxation; a typical curve, observed at room temperature, is drawn in Figure 1a. The transverse magnetic relaxation function is thus analyzed as the sum of two components. The fast decay is associated with polystyrene in the glassy state; the long decay speads over about 5 ms and is ascribed to polybutadiene. It is represented by a polynome, called $P_x(t)$ and used as a trial function. The numerical fit concerns first the long decay; it yields the initial amplitude of the polynome $P_x(0)$. The polynome is then subtracted from the whole experimental relaxation curve; the resulting curve is in agreement with a Gaussian function in which $T_2 = 12.9\ \mu$s. The relaxation function is finally expressed as the sum of two terms

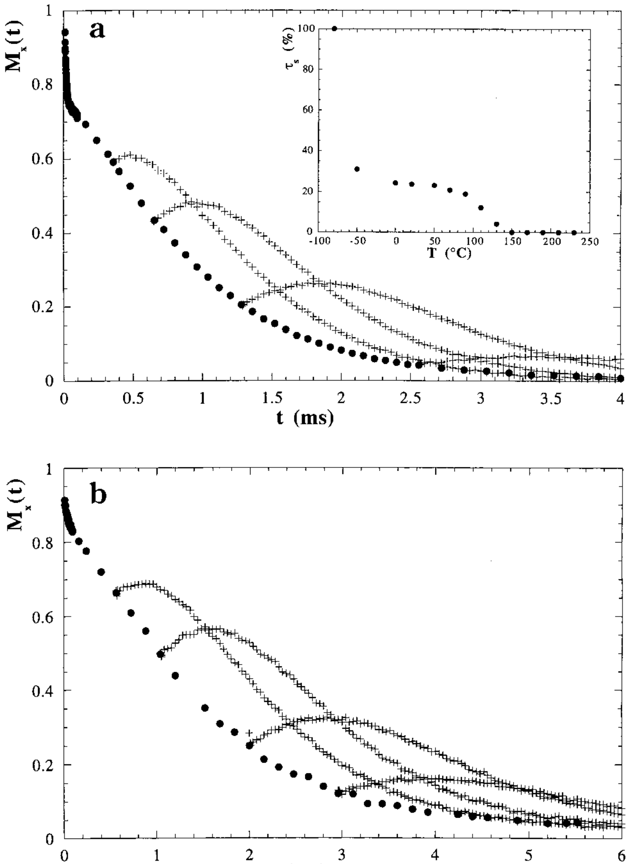

Figure 1. Transverse magnetic relaxation function (●) and pseudosolid spin echoes (+) recorded from SBS: (a) at room temperature; (b) at 130 °C. The temperature dependence of the fraction of protons, τ_s, attached to rigid domains is also shown.

$$M_x(t) = g(0)\exp(-t^2/2T_2^{\,2}) + P_x(t) \tag{14}$$

This analysis provides the numerical value of the initial magnetization, $M_x(0) = g(0) + P_x(0)$, which cannot be measured directly, on account of the dead time of observation resulting from the applied radio frequency pulse. The fraction of protons, $\tau_s = g(0)/M_x(0)$, participating in the fast decay, was determined as a temperature function; τ_s was found to be a slightly decreasing function of temperature while a lengthening effect of T_2 was observed.

It is of interest to compare the fraction of protons, τ_s, participating in the fast component of the relaxation with the fraction of protons belonging to polystyrene chains. The latter, calculated from the mass percentage of polystyrene in the block copolymer (29%), is equal to 23%. There is first a slow decrease of this fraction when the temperature is raised from −50 to +50 °C; at room temperature, these two fractions are nearly equal to each other (Figure 1). Below this temperature, the fraction of protons participating in the solidlike relaxation is higher than the percentage of protons corresponding to polystyrene microdomains. This result means that a fraction of protons, attached to polybutadiene monomeric units, participate in the solidlike relaxation curve. The simplest interpretation is to consider that these units are located at the interface of the PS cylinders; consequently, their random motions are strongly hindered and correspondingly, the proton relaxation exhibits a solidlike behavior.

IV.2. Glass Transition of Polystyrene Domains. A thorough calorimetric study of the molecular weight dependence of the glass transition of polystyrene, in bulk, has been already reported.[13] Considering narrow molecular weight distributions, the glass transition temperature of long polystyrene chains, in bulk, is usually observed at 100 °C ($M_n \approx 2 \times 10^5$); the glass transition temperature is lowered when polymeric chains are shortened; it is equal to 90 °C, for $M_n \approx 10^4$. Furthermore, an additional depression of the glass transition temperature has been observed on low molecular weight styrene−isoprene diblock copolymers studied by DSC.[14] For instance, the PS glass transition temperature is 65 °C, in a copolymer with a molecular weight equal to 12.6×10^3 (the PS fraction is 0.5 w/w); in that study, this lowering effect has been interpreted as a consequence of premature molecular motions, in polystyrene domains, induced by the PB segmental mobility. In this work, the glass transition temperature of polystyrene in SBS, determined from DSC, was 90 °C. The glass transition, as detected here, from the fraction of protons participating in the solidlike component of the magnetic relaxation curve, spread over a broad temperature interval; the fraction of protons, τ_s, was found to decrease to zero, over the range 50−150 °C. The width of the glass transition is in agreement with earlier NMR studies reported about the PS glass transition.[15,16] It is assumed that segmental fluctuations of polystyrene take place around 50 °C and they start affecting the outer part of the cylinders first.

The progressive onset of PS segmental fluctuations, induced on heating SBS, is detected from the motional averaging effect of spin−spin interactions, observed at temperatures higher than 50 °C. It is known that to detect the motional averaging process, from NMR, the rate of molecular fluctuations must be higher than the strength of nuclear magnetic interactions ($\mathrm{rad \cdot s^{-1}}$).[17] Also, this averaging process is known to affect, first, the tail of relaxation curves while the upper part of the decay is unaffected and still exhibits a pure solidlike behavior.[17] This property, specific to NMR, is well illustrated by comparing the relaxation curve recorded at 130 °C (Figure 1b) with the relaxation curve recorded at room temperature (Figure 1a); the relative amplitude of the long component of the relaxation curve is seen to increase when SBS is heated at 130 °C. This result shows that a small part of the PS relaxation curve must be included in the PB relaxation curve; the part of the PS relaxation added to the PB relaxation is increased when the temperature varies from 50 to 150 °C. Above 150 °C, the relaxation curves result from the full motional averaging effect of spin−spin interactions in polystyrene; PB and PS chains are both involved in the temporary network structure induced by entanglements. The observation of the motional averaging effect in polystyrene, at 150 °C, permits us to consider that the rates of fluctuations, in PS, are higher than about 10^5 $\mathrm{rad \cdot s^{-1}}$.

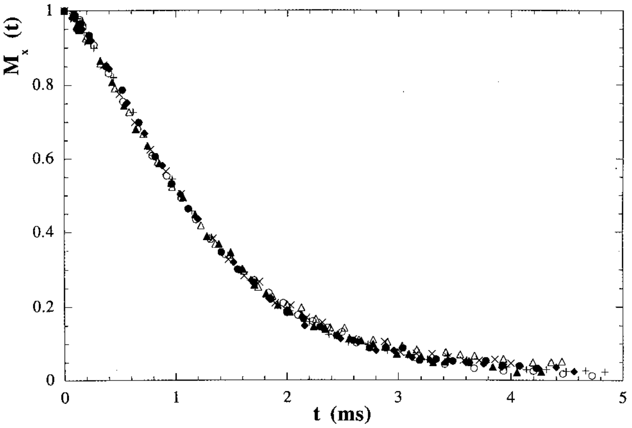

Figure 2. Property of superposition of the transverse relaxation functions, recorded from 0 to 130 °C. The reference is the curve recorded at 70 °C: (○) 0 °C; (▲) 21 °C; (+) 50 °C; (◆) 70 °C; (●) 90 °C; (×) 110 °C; (△) 130 °C.

IV.3. Polybutadiene Network Structure. Polybutadiene properties in SBS are reflected by the long component of proton relaxation curves. The analysis of these curves consists of four steps. The existence of a network is detected from residual spin−spin interactions in the first step; then it is shown, in the second step, that the mechanism of proton relaxation associated with the presence of a network is invariant except for the time scale, which is temperature and polymer concentration dependent. In the third step, a distribution function is proposed to provide a description of the observed network structure; finally, the NMR structural parameter is applied to the characterization of the proton relaxation over the temperature range −50 to +220 °C.

IV.3.a. Evidence for Residual Interactions. The evidence for residual tensorial spin−spin interactions is given by forming pseudosolid spin echoes from the relaxation function ascribed to polybutadiene chains (Figure 1a,b). Pseudosolid echoes are obtained by applying a specific pulse sequence to the spin system (section II). The observation of well-defined pseudosolid echoes indicates the presence of chain segments with fixed ends; anchoring points are determined both by entanglements and by the links of polybutadiene blocks to polystyrene blocks, at the interface of microdomains. The following analysis is based on the existence of residual dipole−dipole interactions of protons; it does not require the use of high-resolution NMR.

IV.3.b. Superposition Property. Long components of relaxation curves, recorded from 0 to 130 °C, were normalized; the curve observed at 70 °C was chosen as a reference. Then, relaxation cuves were found to obey a superposition property by applying a suitable factor to the time scale used to plot each curve (Figure 2). Such a property ensures the invariance of the physical mechanism that governs the magnetic relaxation, except for the time scale determined by a parameter that depends on both temperature and PB concentration. As shown from the existence of pseudosolid spin echoes, the relaxation process is primarily induced by residual spin−spin interactions.

IV.3.c. Network Function. Considering the invariance of the relaxation mechanism, within the temperature interval 0−130 °C, the model of noninteracting

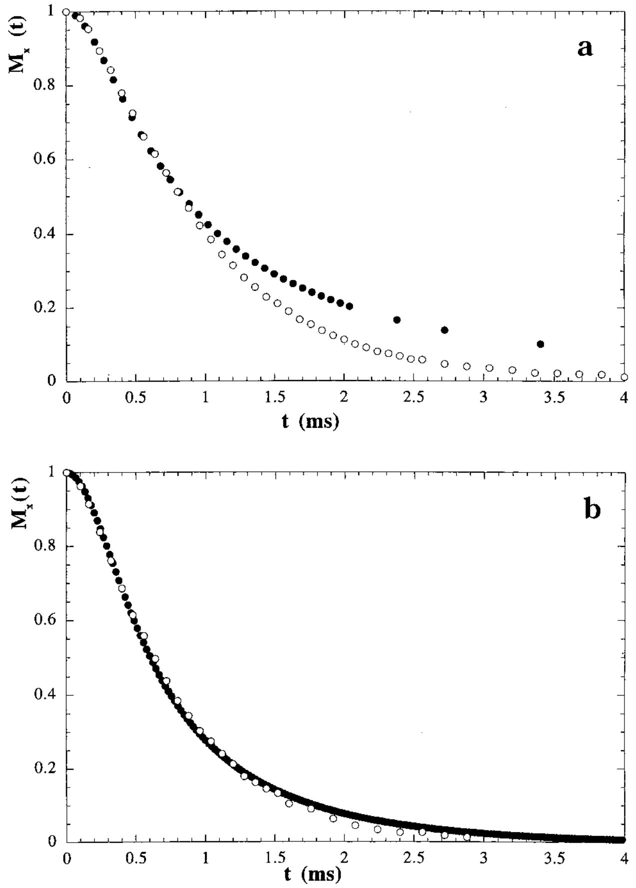

Figure 3. (a) Experimental relaxation curve, recorded at room temperature and compared with the numerical function calculated from eqs 2 and 5. (b) Experimental relaxation curve, recorded at room temperature and compared with the numerical function at 0 °C from eq 17. Key: (○) experimental points; (●) numerical points.

proton pairs was applied to polybutadiene chains. The fit of the theoretical curve to experimental results is illustrated in Figure 3a, recorded at 20 °C; the time scale of the theoretical relaxation function (5), was adjusted to obtain the best fit to measurements. The tail of the theoretical curve which behaves like a $t^{-3/2}$ time function, does not fit the experimental points. At large time values, the decay of the experimental curve is much faster. This disagreement reveals a deviation of the distribution of the end-to-end vectors of network segments from the Gaussian statistics. The pure Gaussian distribution function is affected by the presence of polystyrene domains that result from the phase separation of the polymers. Polybutadiene chains must be considered as necessarily stretched because of the presence of the polystyrene cylinders; the distribution of these domains in space is characterized by a nonzero mean spacing. The assumption of a small stretching of polybutadiene chains, between domains, implies a nonzero average of the end-to-end vector, **r**. In other words, the maximum for the amplitude of the probability distribution function of **r** must not occur for components of **r** equal to zero. To take the permanent small stretching of chains into consideration, the following distribution function is proposed:

$$\pi^*(\mathbf{r}) = (2\pi\sigma^2/3)^{-3/2}(r^2/\sigma^2)\exp(-3r^2/2\sigma^2) \quad (15)$$

The maximum of the amplitude of the distribution

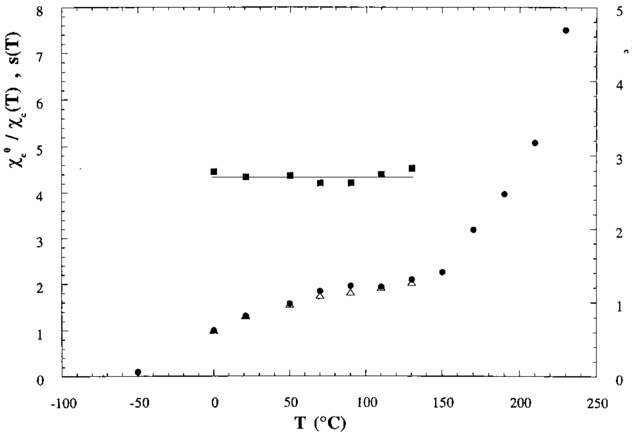

Figure 4. Temperature dependence of the ratio χ_c^0/χ_c, of the NMR width parameter π_c, and of the shift factor $s(T)$ as a temperature function: (●) χ_c^0/χ_c; (Δ) $s(T)$; (■) π_c.

function occurs now for components of **r** different from zero. The function $\pi^*(\mathbf{r})$ leads to

$$M_x^{th}(t) = \frac{1}{3}M_x^R(\alpha t) + \frac{2}{3}M_x^R(t) \quad (16)$$

with

$$M_x^R(t) = \mathrm{Re}\left\{\frac{2}{3}\left[\left(\frac{1}{1+it^\dagger}\right)^2\left(\frac{1}{1-it^\dagger}\right)^{1/2} + \frac{1}{2}\left(\frac{1}{1+it^\dagger}\right)\left(\frac{1}{1-it^\dagger}\right)^{3/2}\right]\right\} \quad (17)$$

where Re(A) means the real part of A. The theoretical curve was compared with the experimental results by setting the relaxation rate, defined according to eq 4, equal to 1.12×10^3 rad·s^{-1}, at 0 °C; in the general eq 4, N is replaced with n, the number of skeletal bonds, which reflects the mean segmental spacing between coupling junctions, along any polybutadiene chain. The comparison, made at 0 °C, is illustrated in Figure 3b: the theoretical curve was found to fit reasonably the experimental points. Similar fits were extended to relaxation curves recorded at several temperatures between 0 and 150 °C; they were achieved by applying a suitable shift factor, $s(T)$, to the time scale of the $M_x^R(t)$ function in order to put each experimental curve into coincidence with a theoretical relaxation curve. In all cases, the agreement between experimental results and the theoretical description was found to be reasonable; this result shows that the distribution function of end-to-end vectors of polybutadiene segments, in SBS, can be simply expressed according to the network function given by eq 15, provided a temperature shift factor $s(T)$ is introduced. Both the order of magnitude of the time scale of relaxation curves and the nature of the spin-system response reveal the presence of a network. The evolution of the shift factor, $s(T)$, is represented in Figure 4 as a temperature function. The existence of a shift factor is in agreement with previously reported results showing that the time scale of the proton transverse relaxation, observed in gels or in entangled melts, is a function both of the mean segmental spacing between cross-links or entanglements and of temperature; $s(T)$ accounts for segmental fluctuations between coupling junctions.[18,19]

IV.3.d. Trapped Polybutadiene Entanglements.

Relaxation curves were given a more general analysis

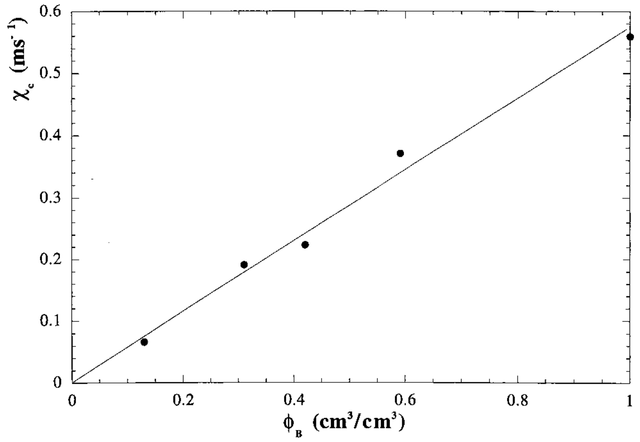

Figure 5. Variation of the structural parameter, χ_c, as a function of the polybutadriene concentration, in SBS heptane solutions, at room temperature.

by using the NMR structural parameter, χ_c. The NMR width distribution, π_χ, of the so-called gel function, $G(\mathbf{r}/\sigma(N))$, was first calculated from the long component of the transverse relaxation curves; it was found to be constant (Figure 4). This result shows that, according to eq 13, the statistical framework of description of the polybutadiene network is invariant. Consequently, the parameter χ_c may be considered as a function of $\Lambda(T)/\sigma(n_0)^2$, only; $\Lambda(T)$ accounts for segmental fluctuations. The variation of the χ_c^0/χ_c is plotted in Figure 4 ($1/\chi_c^0 =$ 1 ms at 0 °C). A strong variation of this ratio is observed when the temperature is raised from −50 to +50 °C; then there is a smooth variation over the range 70−150 °C.

Both the nature of the spin-system response of protons and the order of magnitude of relaxation rates reveal the existence of a network; considering the length of polybutadiene blocks, on one hand, and already reported results of NMR measurements performed on vulcanized polybutadiene, on the other hand, it is assumed that the network structure results from the presence of trapped entanglements.[20] Variations of $s(T)$ and $1/\chi_c$ reflect the temperature dependence of segmental fluctuations that occur between entanglements.

IV.3.e. Addition of a Selective Solvent. The addition of a selective solvent (heptane) was used to reinforce the interpretation of NMR properties based on the assumption that entanglements are trapped by the formation of polystyrene domains. The NMR structural parameter, χ_c, is shown, in Figure 5, to vary as a linear function of the polybutadiene concentration, c, in SBS solutions ($0.1 \leq c \leq 1$ g/g); relaxation curves were recorded at 25 °C. The swelling effect of a temporary network structure, observed from NMR, is usually well distinguished from the swelling of a permanent gel. In the case of a network structure resulting from the random cross-linking of long chains, the NMR structural parameter has been clearly shown to be proportional to c^{-2}, while in the case of a swollen melt, the NMR structural parameter is proportional to c. The proportionality of χ_c to c results from eq 11 and from the usual concentration dependence of the mean segmental spacing, $N_e(c)$, between entanglements: $N_e(c) = N_e^0)/c^{21}$ N_e^0 determines the mean segmental spacing between entanglements, in the pure polymer; N is replaced with n/c in eq 11. It is considered that the existence of a network structure, formed by entanglements, is corroborated by Figure 5.

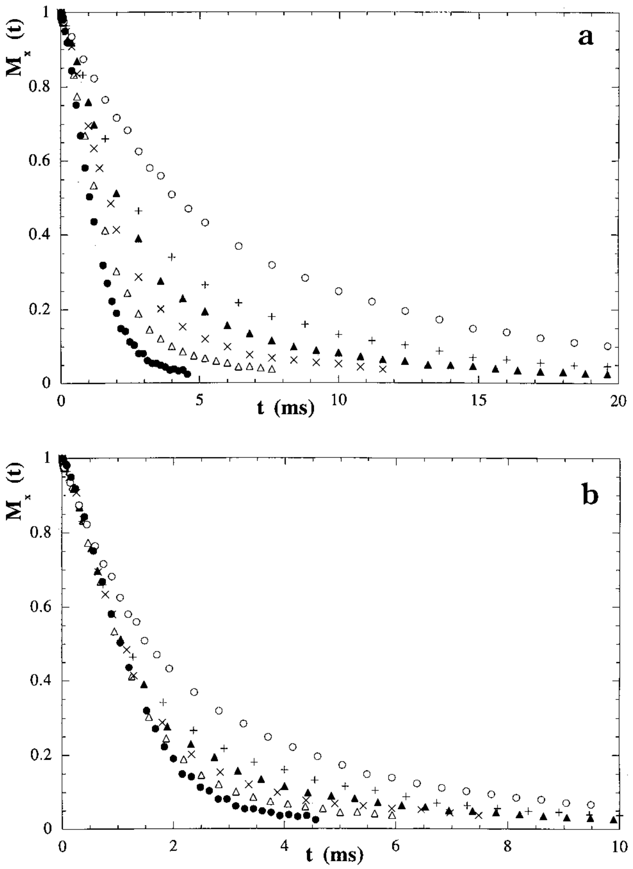

Figure 6. (a) Relaxation curves recorded from 150 to 230 °C. (b) Property of partial superposition of the relaxation curves recorded from 150 to 230 °C. The reference is the curve observed at 70 °C. Key: (●) 70 °C; (△) 150 °C; (×) 170 °C; (▲) 190 °C; (+) 210 °C; (○): 230 °C.

IV.4. Onset of the Network Dynamics in SBS. Above the glass transition temperature of polystyrene, the presence of domains results from the phase separation of polymers; the liquid polystyrene domains govern the three-dimensional organization of SBS until the order−disorder transition temperature is reached. Segmental fluctuations concern polybutadiene chains, on one hand, and polystyrene short chains, on the other hand; these are too short to be entangled. Polybutadiene block ends, located at the interface of polystyrene domains cannot be considered as embedding points anymore; they fluctuate, too. In this section, it is shown that the progressive increase of rates of segmental fluctuations leads to the order−disorder transition. Large amplitude fluctuations of chains take place around 230 °C.

IV.4.a. Partial Superposition Property. Normalized relaxation curves recorded between 150 and 230 °C are plotted in Figure 6a; these curves were compared with the long component of the transverse relaxation decay, observed at 70 °C, by applying a suitable factor to the time scale of each curve. The relaxation observed at 70 °C was chosen as a reference because it reflects only the polybutadiene network structure. It is seen, in Figure 6b, that the upper part of each relaxation curve obeys a property of superposition except for the curve recorded at 230 °C, which can be clearly distinguished from other relaxation curves. However, the amplitude of the upper part of the relaxation curve that obeys the property of partial superposition decreases, on heating the SBS sample. Correspondingly, the amplitude of the lower part of relaxation curves, which does not obey the property of superposition, is increased. The evolution of proton relaxation curves, observed on heating SBS, is interpreted in the following way. (i) It is assumed that the upper part of each relaxation curve corresponds to a function, determined by a mathematical expression, that is invariant except for the time scale. Therefore, starting from the reference (70 °C), it is considered that the upper part of each relaxation curve reflects the existence of spatial domains where the polybutadiene network is unaffected by the dynamics of polystyrene short chains. The mean size of these spatial domains is progressively reduced on heating SBS. (ii) The lower part of each relaxation curve is associated with properties both of polystyrene short chains that fluctuate rapidly because they are not entangled and of polybutadiene segments directly linked to them. The fraction of any polybutadiene chain affected by the dynamics of polystyrene is increased when the sample temperature is raised. Considering the criterion for observing the NMR motional averaging effect, the detection of a network structure, reflected by the upper part of the relaxation curves, indicates that the lifetime of PB coupling junctions is still longer than the time scale of relaxation (about 2 ms) associated with this upper part; this relaxation is still induced by residual spin−spin interactions.

IV.4.b. Approach to the Order−Disorder Transition. The NMR parameter χ_c was again used to characterize relaxation curves. This parameter encompasses, now, both structural and dynamical properties of SBS. It may be considered that $1/\chi_c$ is mainly sensitive to the lengthening of the time scale of relaxation of the transverse magnetization. The lenthening effect is induced by the increase of the rates of segmental fluctuations; this effect has not been, until now, satisfactorily described because of the complexity of the nature of the random motions that occur in polymeric systems. More generally, χ_c is equal to $1/T_2$ when the relaxation is described by an exponential function characterized by a time constant, T_2. The parameter χ_c is easily handled; it characterizes conveniently relaxation curves although it is not quantitatively related to the observed segmental dynamics. The ratio, χ_c^0/χ_c, plotted in Figure 4, was found to increase markedly, over the range 150−230 °C; the order−disorder transition temperature, estimated from viscoelastic measurements, is 220 °C. We interpret the increase of the NMR ratio as arising from the proximity of the order−disorder transition of SBS. This transition as detected from NMR, corresponds to an increase of the rates of fluctuations that occur within any SBS chain, considered as a whole.

V. Conclusion

In this work, the statistical structure formed in a styrene−butadiene−styrene triblock copolymer was probed, using the transverse magnetic relaxation of protons attached to the polymer chains. This study shows that in addition to the morphology already revealed from X-ray scattering (space scale ≈500 Å), there exists a polybutadiene network, clearly detected from the presence of residual dipole−dipole interactions of protons; from the comparison with relaxation properties observed on vulcanized or on strongly entangled chains, it is considered that the network is similar to the structure that could result from trapped entanglements. Below 150 °C, a proposed probability distribution function of end-to-end vectors joining two consecutive coupling junctions, along one chain, is applied to the analysis of relaxation curves. Polybutadiene block ends, fixed on the surface of glassy polystyrene domains, play the role of embedding points; correspondingly, the distribution function accounts for a small stretching of polybutadiene blocks. The hypothesis of a polybutadiene network, existing in SBS, was reinforced by observing the effect of dilation of the structure, induced by adding a selective solvent of polybutadiene. Above 150 °C, the relaxation curve of protons consists of two components; the tail is associated with the progressive motional averaging of residual dipole−dipole interactions. It reflects both the segmental dynamics of the short and nonentangled polystyrene chains in their domains and the dynamics of progressive disentanglement of polybutadiene embedded in a temporary network. The other component is well distinguished from the tail; it is still unaffected by the disentanglement process. Above 210 °C, the polybutadiene network is not detected from NMR, anymore; this observation shows that the lifetime of polybutadiene coupling junctions is shorter than about 1 ms. It is worth mentioning that the existence of a temporary network structure in a diblock copolymer (poly(ethylenepropylene)−poly(ethylethylene)) has been already shown, from measurements of the copolymer diffusion coefficient, using the forced Rayleigh light scattering method; the diffusion coefficient was found to exhibit a reptational behavior well above the order−disorder transition temperature while a deviation from this behavior occurs around this transition because the diffusion process interferes with the lamellar structure of the copolymer.[22]

The glass transition of polystyrene domains was found to spread over a temperature interval (≈80 K) analogous to the interval currently observed on homopolymers.

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