Homogeneity Properties of NMR Rates Measured in Molten Polybutadiene. Temperature Dependence of Segmental Chain Motions

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ABSTRACT: Spin-lattice relaxation rates and NOE factors were measured in molten polybutadiene samples by observing protons and ^{13}C nuclei. It is shown that these NMR parameters obey a homogeneity property with respect to the reduced variable ω_0/ν_r where ω_0 is the Larmor frequency and ν_r is a relaxational frequency of segmental motions. Without any specific model, this characteristic parameter is found to reflect a free volume law dependence upon the temperature, in agreement with previously reported data derived from mechanical measurements. The basic assumption of homogeneity property is reinforced by observing the lowering effect of the glass transition temperature induced by a chain microstructure change.

I. Introduction

This work deals with the characterization of segmental chain motions occurring in a high molecular weight molten polymer. Properties of these motions were investigated from measurements of spin-lattice relaxation rates of protons and ^{13}C nuclei, performed in two polybutadiene samples. The attention was mainly focused upon the dynamics of these motions, observing the effects induced by temperature variations. It was not attempted to disclose the real nature of these random molecular processes. The purpose of the present study was 2-fold:

(i) We first attempted to characterize the collective dynamics of monomeric units within short segments, without using any specific model. The interpretation of experimental results relied upon a single hypothesis concerning the spin-lattice relaxation rate, T_1^{-1}, a linear function of the spectral densities associated with diffusional motions of segments. The expression $\omega_0 T_1^{-1}$ (ω_0 is the Larmor frequency) was supposed to obey a homogeneity property with respect to the Larmor frequency ω_0 on the one hand and with respect to the main relaxational frequency $\nu_r = \tau_r^{-1}$, characterizing the observed molecular motions, on the other hand. Starting from

$$\omega_0 T_1^{-1} = f(\omega_0, \nu_r)$$

the homogeneity property means that the value of the product $\omega_0 T_1^{-1}$ is unchanged by multiplying both ω_0 and ν_r by any positive number q. The homogeneity property is represented by the equality

$$\omega_0 T_1^{-1}(q\omega_0, q\nu_r) = f(\omega_0, \nu_r) \tag{1}$$

It is easily seen that this property well applies to simple spectral densities of energy describing diffusional motions of small molecules.[1] In these cases, the typical expression of a spectral density $J(\omega_0,\nu_r)$ is

$$\omega_0 J(\omega_0,\nu_r) \simeq \nu_r^{-1}/(1 + \omega_0^2/\nu_r^2)$$

and $\omega_0 J(\omega_0 \nu_r)$ obeys the homogeneity property (eq 1).

The homogeneity condition has been already used to characterize dynamical properties of chain segments in a polymer solution; the characterization was derived from the effects induced by variations of the polymer concentration and the Larmor frequency.[2] In the present work, both the Larmor frequency and the polymer temperature were varied to evidence the hypothesis concerning the homogeneity property. Larmor frequencies ranged from 1.6 × 10^8 to 6.3 × 10^8 rd s^{-1}. Consequently, correlation times, $\tau_r = \nu_r^{-1}$, characterized from NMR were not shorter than about 10^{-10} s. These characteristic times may be correlated with elementary jumps inducing rotational isomerization processes; we also considered that motions observed from NMR may be partly averaged along chain segments; accordingly, they should exhibit a degree of universality higher than that corresponding to single elementary jumps. It was the reason why the search for a homogeneity property associated with spectral densities describing observed random motions was the main purpose of this work. This property was found to apply to the nuclear Overhauser effect, too.

(ii) Then, we attempted to correlate NMR parameters characterizing the observed dynamical processes with those derived from viscoelastic measurements performed in similar samples, in another laboratory.[3]

Variations of spin-lattice relaxation rates, observed as a function of both the temperature and the Larmor frequency have been widely used to characterize local motions of polymer chains in solution. Properties of the relaxation rates have been analyzed from the autocorrelation function of orientation of vectors joining nuclei located on a given monomeric unit. Spectral densities of energy, specific to polymer chains, have been calculated by considering conformational jumps involving three bonds.[4,5] A review about models is given in the ref 6.

In the case of molten polymers, the resolution of resonance spectra is poor because of the dipolar broadening mechanism. Also, in the case of protons, dipole-dipole interactions established between nuclear spins located on different chain segments may contribute to the spin-lattice relaxation process. This contribution is not easily discriminated from that arising from interactions established between nuclear spins located within one given chain segment. These difficult problems, encountered in describing the spin-lattice relaxation mechanism in a melt, have been overcome by using spectral densities, which characterize an isotropic process of local reorientation and which are associated with a broad spectrum of relaxation times.[7-9] The mean correlation time, τ, determined from measurements performed in several polymers behaves according to the William-Landel-Ferry (WLF) law, with respect to temperature variations.[9] Recently, it has been proposed to describe the orienta-

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tional diffusion of skeletal bonds from two types of motions: isotropic rotations and a nonisotropic libration. Three correlation times were associated with this description to analyze the spin-lattice relaxation process occurring in a natural rubber.[10] It is now currently considered that monomeric units undergo nonisotropic rotations in a melt observed within a time scale shorter than the disentanglement relaxation time.[11,12] More recently, it has been proposed to interpret ^{13}C spin-lattice relaxation properties in polymer chains by using a single model, whether they are in a melt or in a solution.[13] From such a model, the libration motion of a skeletal bond is associated with a segmental mobility effect described from the damped propagation of an isomerization process.[13-15] The autocorrelation function of orientation calculated to describe the segmental mobility accounts for results observed from nonisotropy of decays of fluorescence polarization.[16-18] It applies to polymer chains in solution or in a melt as well.[17,18] The temperature dependence of the correlation time governing conformational jumps is in agreement with the WLF law.[13-15,18] However, the absolute value of the correlation time measured from NMR is about 100 times smaller than that derived from fluorescence measurements.[19]

It is worth emphasizing that these elementary motions involved in the mechanism of the glass transition can be characterized from the maximum value of the spin-lattice relaxation rate and also from the relaxation process in the rotating frame,[20,21] in that case, the reference frequency used to characterize the basic relaxational frequency, υ_r, of segments is not the Larmor frequency, $\omega_o \simeq 10^8$ rd s^{-1}, anymore but $\omega_1 \simeq 10^5$ rd s^{-1}, defined from the amplitude of the radio-frequency field. This gives a broad frequency range of investigations. However, it is difficult to disclose the exact nature of motions involved in a nuclear magnetic relaxation process although correlation functions associated with transient phenomena can always be given the reasonable expression of a decaying function. The present approach relies upon a generalization of the relationship ω_o/υ_r = constant observed at the maximum value of the relaxation rate; it is now supposed to apply to any value of the product $\omega_o T_1^{-1}$. It is assumed that all relaxational frequencies that may be involved in segmental motions are proportional to a basic relaxational frequency, υ_r, determined in this way.

Finally, the last aspect of this work concerns the characterization of local motions which further govern long-range fluctuations occurring in entangled polymer chains.[22,23] The present data may serve as basic dynamical parameters entering into the description of chain disentanglement. This kinetics of chain disentanglement can be observed either from relaxation rates measured in the frame rotating at the Larmor frequency[24] or from the relaxation of the transverse magnetization.[25]

II. Experimental Section

II.1. Samples. Two polybutadiene samples were studied: they had slightly different chain microstructures. The first sample, hereafter denoted PB 21, was characterized by the following isomeric conformations: cis-1,4 (34%), trans-1,4 (45%), and 1,2-vinyl (21%); the second sample, hereafter denoted PB 8, contained the following isomeric conformations: cis-1,4 (38%), trans-1,4 (54%), and 1,2-vinyl (8%). The weight average molecular weight of both samples was $M_w = 1.3 \times 10^5$ g mol^{-1}, and the polydispersity index was $I = 1.15$.

The samples were supplied and characterized by the Manufacture des Pneumatiques Michelin (France). Polymer melts were enclosed in NMR tubes (diameter 8 mm), sealed under a primary vacuum. Each NMR tube was inserted into a coaxial tube (diameter 10 mm) filled with a deuterated solvent (toluene) to lock the steady magnetic field.

II.2. Measurements. An inversion-recovery sequence (π, τ, $\pi/2$) was used to measure spin-lattice relaxation rates. Values of the relaxation rates were obtained from a three-parameter fit, including the amplitude of the magnetization, the spin-lattice relaxation time, and the value of the inversion angle. The standard deviation was smaller than 3% for all measurements; values of T_1 could be obtained within an accuracy of 7% by performing several measurements. The sample temperature was measured at the sample position; it was defined within an accuracy of 1 deg.

(i) Proton spin-lattice relaxation rates were measured at 60 and 100 MHz, using a CXP Bruker spectrometer, and at 32 MHz, using a home-built spectrometer.

(ii) Bruker spectrometers WP 100, WM 250, and AM 400 operating at 25.15, 62.9, and 100.6 MHz, respectively, were used to measure relaxation rates of ^{13}C nuclei.

The classical technique of random-noise proton decoupling was applied during $7T_1$ and also during signal acquisition delays to measure spin-lattice relaxation rates with a nuclear Overhauser enhancement. Nonenhanced spectra were obtained by only shifting the frequency decoupling during the $7T_1$ delays between acquisition times; the decoupling power was kept constant to avoid temperature fluctuations in the sample. We report in this paper the NMR properties concerning the most abundant methine and methylene groups on the chain backbone; triads including 1,2-vinyl groups are not described here.

III. Homogeneity Property of the Spin-Lattice Relaxation Rate

It is well-known that the spin-lattice relaxation rate is determined by the Fourier transform of the autocorrelation function of spin-spin interactions $g(t,\nu_r)$; roughly:

$$1/T_1 \propto R_e \int_0^\infty g(t,\nu_r) e^{-im\omega_o t}\,\mathrm{d}t \qquad m = 0\text{–}2 \tag{2}$$

ω_o is the Larmor frequency.

We supposed that the dynamics of molecular processes observed from NMR is governed by a single basic relaxational frequency, ν_r. Accordingly, the autocorrelation function is expressed as

$$g(t,\nu_r) = h(t\nu_r)$$

Then, the spin-lattice relaxation rate has the properties

$$\omega_o/T_1 \propto R_e \int_0^\infty h(u\nu_r/\omega_o) e^{-imu}\,\mathrm{d}u \tag{3}$$

with $u = \omega_o t$ or

$$\nu_r/T_1 \propto R_e \int_0^\infty h(v) e^{-im\omega_o v/\nu_r}\,\mathrm{d}v \tag{3'}$$

with $v = t\nu_r$.

Therefore, the ratios ω_o/T_1 and ν_r/T_1 are homogeneous functions of the reduced variable ω_o/ν_r, in accordance with formula 1.

More precisely, we consider first a given amplitude of the product $\omega_o T_1^{-1}(\omega_o,\nu_r(T))$ corresponding to the Larmor frequency, ω_o, and the temperature, T; if ω_o is multiplied by q, then the amplitude of the product $q\omega_o T_1^{-1}(q\omega_o,\nu_r(T'))$ is equal to the amplitude of $\omega_o T_1^{-1}(\omega_o,\nu_r(T))$, if and only if $\nu_r(T') = q\nu_r(T)$. This equality gives a relationship between $\nu_r(T)$ and $\nu_r(T')$. The Larmor frequency is thus used as a reference of relaxation frequencies, ν_o. The homogeneity property was supposed to hold over the whole range of temperature explored in this study. The value of the reduced variable ω_o/ν_r was set equal to 0.6 at the temperature of the maximum value of the spin-lattice relaxation rate. The principle of the analysis of the homogeneity property is described in the Appendix.

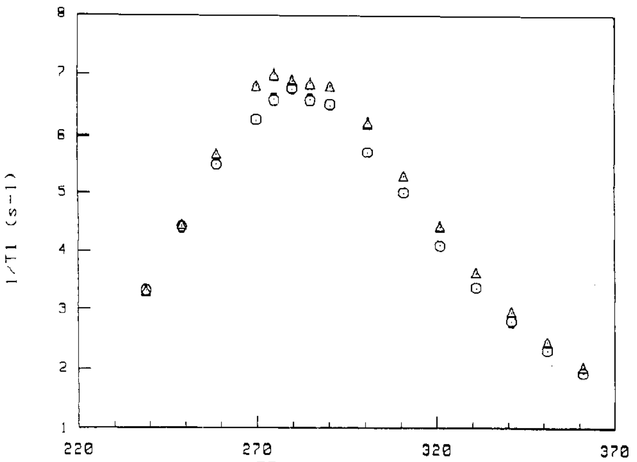


Figure 1. Spin-lattice relaxation rates of protons attached to methylene groups (▲) and to methine groups (○). The Larmor frequency is 100 MHz (PB 21 sample).

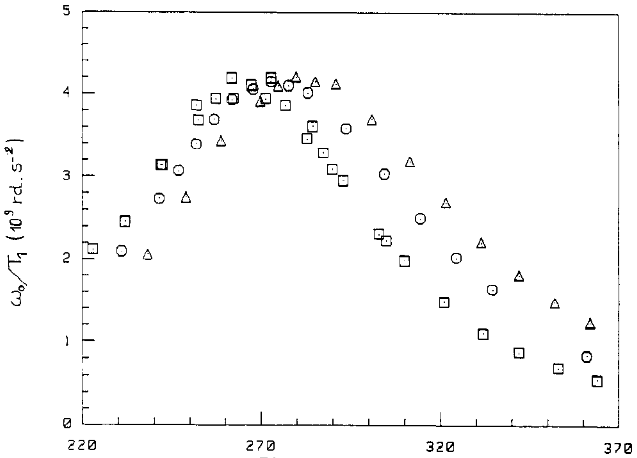


Figure 2. Normalized relaxation rates, ω_0/T_1, of the whole proton system observed at 32 MHz (□), 60 MHz (○), and 100 MHz (▲) (PB 21 sample).

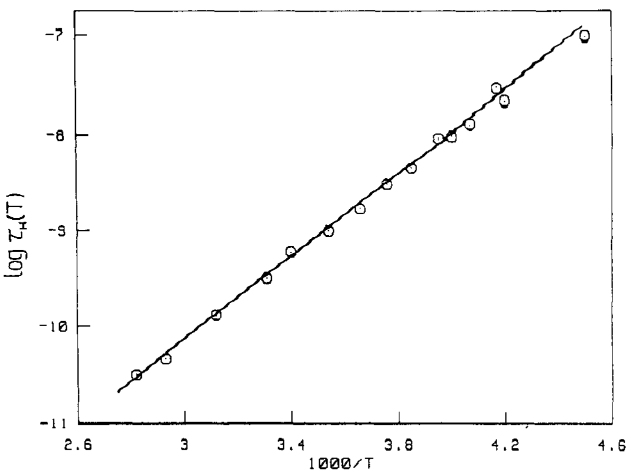


Figure 3. Correlation time, $\tau_H(T)$, represented as a function of the temperature.

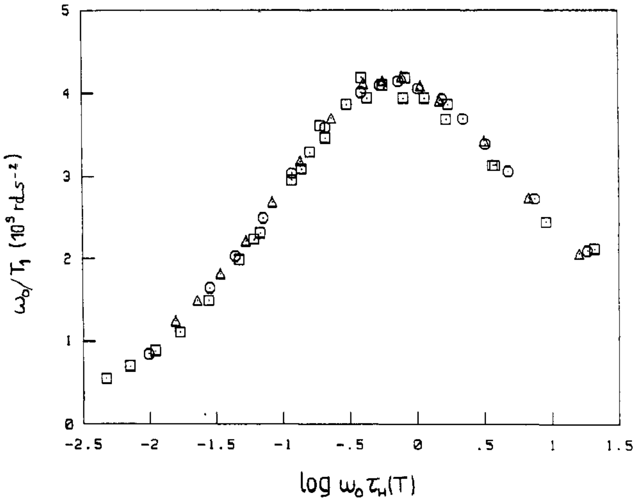


Figure 4. Normalized relaxation rate of the whole proton system represented as a function of the reduced variable, $\omega_o\tau_H(T)$.

IV. Proton Relaxation. Temperature-Frequency Relationship

First of all, Figure 1 shows that relaxation rates of protons attached to methine or methylene groups, respectively, are about equal to each other. So we considered that all protons could be characterized by a single relaxation time, T_1. Normalized relaxation rates ω_0/T_1 corresponding to three difference Larmor frequencies are reported in Figure 2 as a function of the temperature. It is noticed that the three maximum values are equal to one another. Furthermore, a dependence of the spin-lattice relaxation rate upon the Larmor frequency was observed over the whole temperature range, i.e., above and below the temperature corresponding to the maximum value.

The homogeneity property was applied to the analysis of the normalized spin-lattice relaxation rates, ω_0/T_1. Molecular motions observed from NMR were supposed to be governed by a single basic correlation time $\tau_H(T) = \nu_H^{-1}(T)$ obtained through the analysis described in the Appendix. The temperature dependence of the correlation time, $\tau_H(T)$, shown in Figure 3, was used to superpose the three curves shown in Figure 2: the normalized relaxation rates were reported as a function of the reduced variable, $\omega_o\tau_H(T)$. The result of the superposition is shown in Figure 4. The value of the correlation time was determined from the relationship $\omega_o\tau_H \simeq 0.6$ at the maximum of the spin-lattice relaxation rate: $\tau_H = 10^{-9}$ s at 281 K and $\omega_o = 6.3 \times 10^8$ rd s^{-1}.

The value of the apparent activation energy derived from the slope of the straight line drawn in Figure 3 is $E_a = 9.6$ kcal mol^{-1}. This value is in agreement with that obtained from the analysis of fluorescence anisotropy decays concerning similar samples.[18] This apparent behavior, analogous to an Arrhenius law, may be considered as a rough approximation of a free-volume law described within the temperature range 250–350 K.[18] It is worth emphasizing that the homogeneity property is observed although all protons interact with one another through dipole–dipole interactions. In other words, dynamical properties observed from NMR do not concern only one monomeric unit within a single chain; they reflect the behavior of the whole medium defined by the polymer melt.

Furthermore, the spin–lattice relaxation process of protons is sensitive enough to detect slight differences induced by the temperature dependence of the local friction factor associated with two different microstructures. Figure 5 illustrates NMR results concerning PB 21 and PB 8 samples, respectively. The shift of the glass transition temperature is clearly perceived from the shift of the temperature of the maximum relaxation rate. The glass transition temperatures are 175 and 183 K for the samples PB 8 and PB 21, respectively.[3]

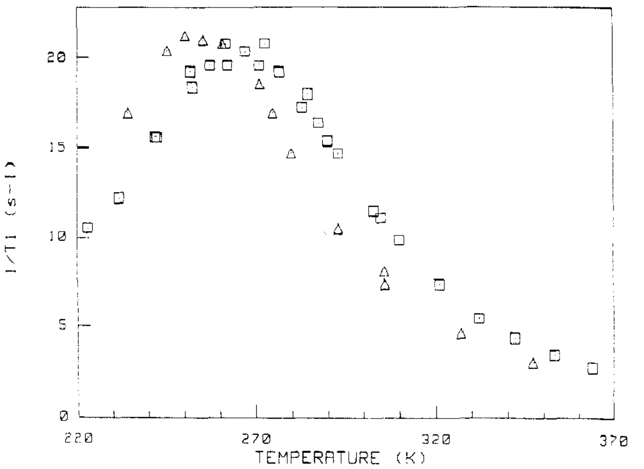


Figure 5. Effect of the chain microstructure upon the proton relaxation rate observed at 32 MHz (⊡, PB 21 sample; ◬, PB 8 sample).

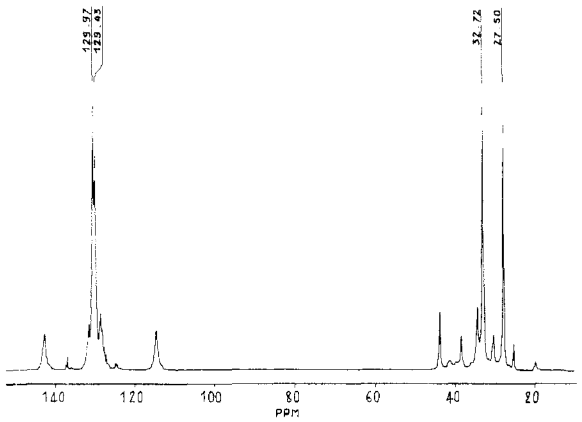


Figure 6. ^{13}C resonance spectrum of PB 21 sample observed in dilute solution, at room temperature. The Larmor frequency is 25.15 MHz. The labeled resonance lines concern this present study: methine group in trans (129.9 ppm) and cis conformation (129.4 ppm); methylene group in trans (32.7 ppm) and cis conformation (27.5 ppm).

V. ^{13}C Spin-Lattice Relaxation. Temperature–Frequency Relationship

In this section, the attention will be focused upon the segmental mobility of one chain although it is in physical interaction with all other neighboring chains. Spin–lattice relaxation rates and NOE factors of ^{13}C nuclei in natural abundance were measured as a function of the temperature, at different Larmor frequencies.

V.1. *trans*-Methylene Groups. V.1.a. Relaxation Rates and NOE Factors. The ^{13}C resonance spectrum of polybutadiene samples in dilute solution is shown in Figure 6. The attention was first focused on the spin–lattice relaxation rates measured from nuclei attached to the center of triads TTT, TTC, and CTC corresponding to trans isomeric conformations. The relaxation rate of ^{13}C nuclei corresponding to these methylene groups exhibits properties similar to those observed from protons:

(i) It depends upon the Larmon frequency, over the whole temperature range which was studied in this work.

(ii) The maximum value is a linear function of the inverse of the Larmor frequency.

(iii) The higher the Larmor frequency, the higher is the temperature corresponding to the maximum value.

Variations of the ratio $\omega_0/2T_1$ are illustrated in Figure 7. Similarly, the NOE factor is a function of both the temperature and the Larmor frequency. Figure 8 shows that it is a monotonous function of the temperature. This curve is analogous to that reported in ref 15. However, like in this reference, the experimental curve exhibits a slight deviation from the theoretical one, calculated according to the Hall–Helfand model based on a damped diffusion process along a chain segment. An illustration of this deviation will be given in section V.2.

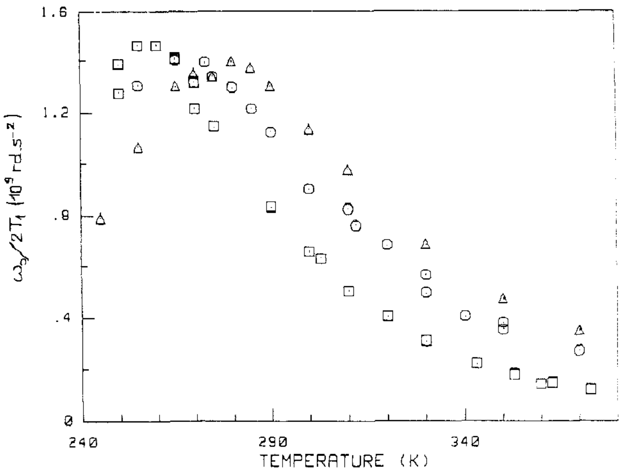


Figure 7. Normalized relaxation rate, $\omega_0/2T_1$, of ^{13}C nuclei belonging to methylene groups in a trans isomeric conformation. Larmor frequencies are 25.15 MHz (⊡), 62.9 MHz (⊙), and 100.6 MHz (◬) (PB 21 sample).

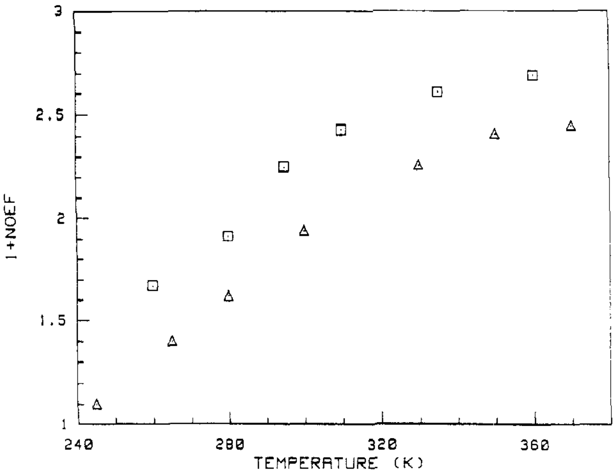


Figure 8. NOE factor measured from ^{13}C nuclei in methylene groups in a trans conformation. Larmor frequencies are 25.15 MHz (⊡) and 100.6 MHz (◬) (PB 21 sample).

V.1.b. Homogeneity Property. It was assumed that all molecular motions perceived from ^{13}C nuclei are governed by a single basic correlation time, $\tau_c(T)$. The homogeneity property was supposed to fully apply to the frequency–temperature dependence of measured relaxation rates reported in Figure 7. The analysis described in the Appendix was used to derive the variation of τ_c as a function of the temperature (Figure 9). This temperature dependence was compared with the WLF law defined by parameters obtained from already published mechanical measurements.[3] The dependence of viscoelastic properties upon the microstructure of polybutadiene chains has been carefully determined in the ref 3. The shift factor, a_T, describing the frequency–temperature superposition property has been shown to obey a single for-

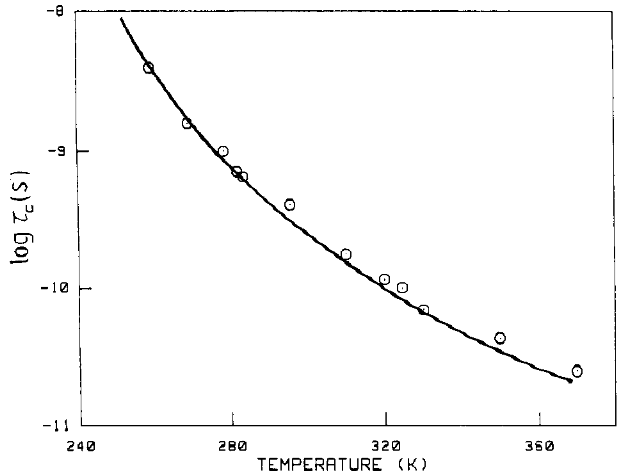


Figure 9. Correlation time, $\tau_c(T)$, derived from Figure 7 and compared with the curve drawn using formula 4.

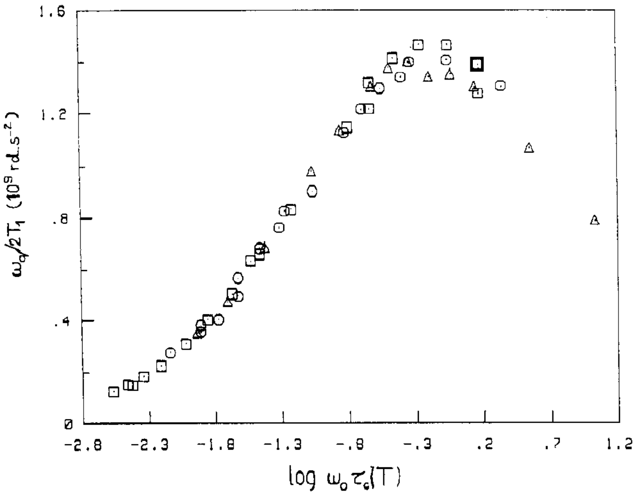


Figure 10. Normalized relaxation rate, $\omega_0/2T_1$, represented as a function of the reduced variable, $\omega_0\tau_c(T)$. Data correspond to Figure 7; $\tau_c(T)$ was calculated using formula 4.

mula, whatever the chain microstructure:

$$\log a_T = -\frac{5.78(T - T_G - 55)}{94.8 + (T - T_G - 55)} \qquad (4)$$

The glass transition temperature, T_G, strongly depends upon the vinyl content of the chain microstructure. Considering the PB 21 sample T_G was set equal to 183 K. The above formula was used in the present work to calculate $\tau_c(T) = a_T\tau_c(T_0)$. The value of $\tau_c(T_0)$ was determined from the maximum of the relaxation rate at the Larmor frequency $\omega_0/2\pi = 100$ MHz: $\tau_c = 10^{-9}$ s at $T_0 = 280$ K (Table I). Then, the homogeneous function $\omega_0/2T_1$ was drawn as a function of the calculated reduced variable, $\omega_0\tau_c(T)$ (Figure 10). It must be noticed that the range of variations of times τ_H and τ_c overlap.

V.2. *cis*-Methylene Groups. A homogeneous function, identical with that reported in Figure 10, was obtained from measurements of spin–lattice relaxation rates of ^{13}C nuclei associated with methylene groups in a cis isomeric conformation. In this case $\tau_c(T)$ was also calculated using eq 4 and with $\tau_c = 10^{-9}$ s at $T_0 = 275$ K (Table I). The normalized relaxation rate, $\omega_0/2T_1$, was drawn as a function of the corresponding reduced variable, $\omega_0\tau_c$(T) (Figure 12); it was found to be in coincidence with the *trans*-methylene curve.

The property of homogeneity also applies to NOE factors, defined from a ratio of spectral densities of energy. Figure 11 illustrates this property observed from ^{13}C nuclei belonging to methylene groups, in cis isomeric conformation; the reduced variable, $\omega_0\tau_c(T)$, was again calculated from formula 4 and $\tau_c = 10^{-9}$ s at $T_0 = 275$ K. This curve does not exhibit any plateau domain in the range of the small values of the correlation time, τ_c. This behavior is contrasted to that of a typical curve calculated using the spectral densities associated with the Hall and Helfand model, based on a damped diffusion process.[15] The theoretical curve in Figure 11 was calculated by using a ratio of correlation times, $\tau_D/\tau_c = 100$; τ_D characterizes the damping process.

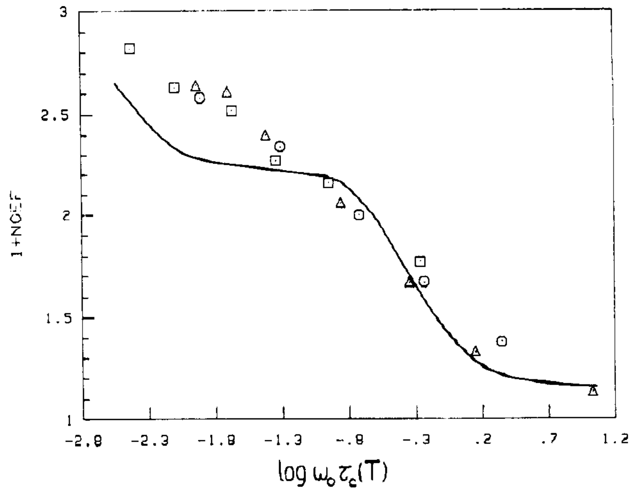


Figure 11. NOE factor represented as a function of the reduced variable, $\omega_0\tau_c(T)$. ^{13}C nuclei belong to methylene groups in a cis conformation. Larmor frequencies are 25.15 MHz (□), 62.9 MHz (○), and 100.6 MHz (△) (PB 21 sample). The continuous curve was calculated using a damped diffusion model (see text).

V.3. Methine Groups. Relaxation rates of ^{13}C nuclei belonging to methine groups of polybutadiene chains were also measured. At low temperature, the spectrum resolution was poor and spin–lattice relaxation times associated with cis and trans isomeric conformations could not be distinguished from each other. Normalized relaxation rates are reported in Figure 12 as a function of the reduced variable, $\omega_0\tau_c(T)$; $\tau_c(T)$ was calculated from formula 4 with $\tau_c = 10^{-9}$ s at $T_0 = 275$ K (Table I). Considering the trans isomeric conformation, it is shown that the ratio $T_1(\mathrm{CH})/T_1(\mathrm{CH_2})$ keeps the constant value 2, over the range of temperature going from 285 to 370 K. The ratio $T_1(\mathrm{CH})/T_1(\mathrm{CH_2})$ was found to be equal to 1.4, in the case of the cis isomeric conformation. The specific behavior of *cis*-methine groups is clearly perceived from Figure 12; it has been already observed in *cis*-1,4-polybutadiene and associated with specific crankshaft motions of the diene sequences.[8,15,26] Figure 12 also shows that *trans*-methine groups behave in a way similar to that of *trans*- and *cis*-methylene groups.

V.4. Effect of the Chain Microstructure. The effect of the chain microstructure on segmental motions occurring in a polybutadiene melt was observed from the relaxation rate of ^{13}C nuclei belonging to *trans*-methylene groups (Figure 13). The temperature associated with the maximum value of the relaxation rate is shifted toward a higher value when the amount of 1,2-vinyl monomeric units is increased. The temperature dependence of the correlation time associated with local motions occurring in the sample PB 8 was determined from formula 4 with $T_G = 175$ K. This value of the glass transition temperature, T_G, was derived from data reported in the ref 3. Then, the two curves reported in Figure 13 were drawn by using the reduced variable, $\omega_0\tau_c(T) = \omega_0 a_T\tau_c(T_0)$, cal-

Table I
Minimum Value of the Spin–Lattice Relaxation Time, T_1, for the ^{13}C Nucleus

		sample PB 21		sample PB 8	
isomeric conformn	ν_0, MHz	T_1(min), ms	T_0, K	T_1(min), ms	T_0, K
trans-methylene carbon	25.15	52.5 ± 1.5	259 ± 1	52 ± 1	251 ± 1.5
	62.9	138 ± 3	269 ± 1		
	100.6	225 ± 1	280 ± 1		
cis-methylene carbon	25.15	55 ± 1	255 ± 1	50 ± 1	251 ± 1.5
	62.9	133 ± 3	262 ± 1		
	100.6	215 ± 1	275 ± 1		
methine carbon[a] (C + T)	25.15	≃140	≃260	≃91	≃251 ± 1.5
	62.9	≃230	≃273		
	100.6	≃350	≃275		

[a] Poor resolution at low temperature induces the collapse of the two lines at the maximum of the relaxation rate.

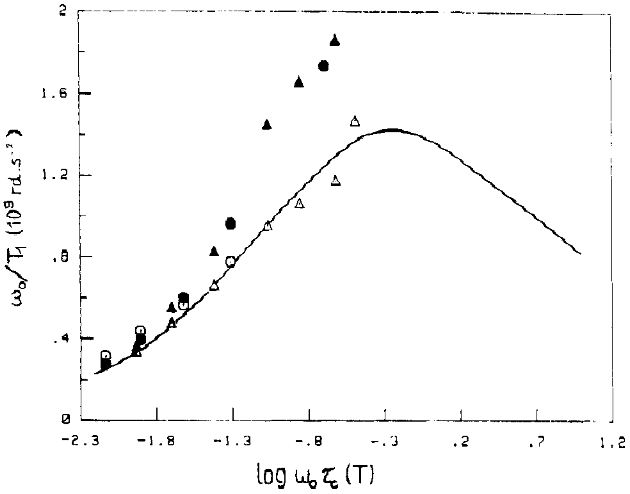


Figure 12. Normalized relaxation rate, ω_0/T_1, represented as a function of the reduced variable, $\omega_0\tau_c(T)$. ^{13}C nuclei belong to (a) methine groups in a cis conformation (●, 62.9 MHz; ▲, 100.6 MHz) and (b) methine groups in a trans conformation (⊙, 62.9 MHz; △, 100.6 MHz). The continuous curve represents the $\omega_0/2T_1$ values for methylene groups in cis and trans conformation (PB 21 sample).

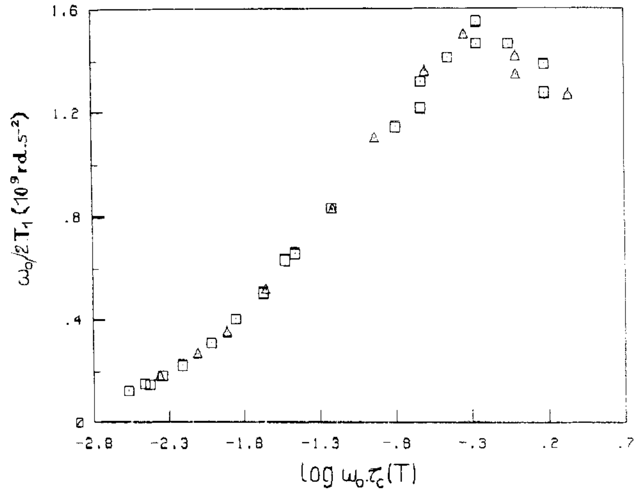


Figure 14. Relaxation rates of ^{13}C nuclei represented as a function of the reduced variable, $\omega_0\tau_c(T)$. (Data correspond to Figure 13.) The correlation time, $\tau_c(T)$, was calculated from formula 4 with T_G = 175 K for sample PB 8 and T_G = 183 K for sample PB 21.

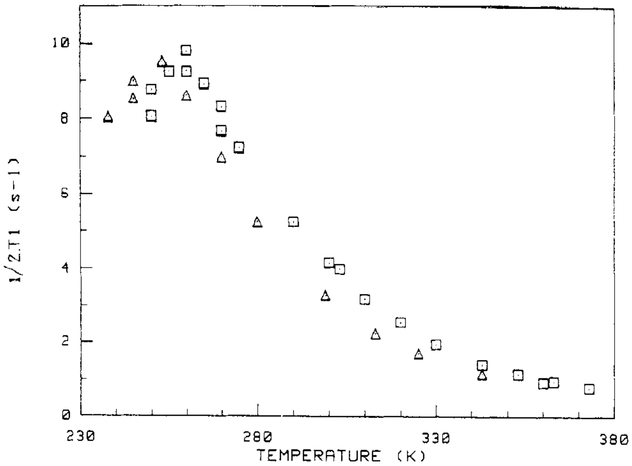


Figure 13. Effect of the chain microstructure on ^{13}C relaxation rates observed from methylene groups in a trans conformation; the Larmor frequency is 25.15 MHz: PB 21 sample, ☐; PB 8 sample, △.

culated from formula 4 with T_G = 175 K for sample PB 8 and T_G = 183 K for sample PB 21; $\tau_c(T_0)$ was set equal to 4 × 10^{-9} s at 251 and 259 K for PB 8 and PB 21 samples, respectively (Table I). Figure 14 illustrates the superposition property corresponding to the two different microstructures of polybutadiene chains.

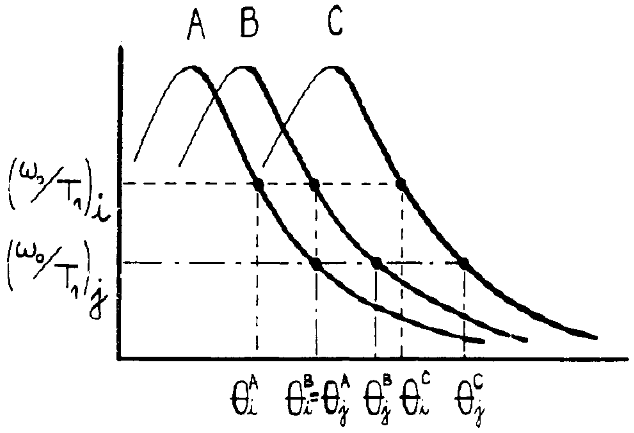
It is worth emphasizing that the maximum values of the relaxation rates occur at temperatures that depend upon both the chain microstructure and the isomeric conformation of the structural unit that is observed. This is illustrated in Table I; the maximum values of T_1^{-1} corresponding to *trans*-methylene ^{13}C nuclei occur at temperatures slightly shifted toward values higher than those corresponding to *cis*-methylene ^{13}C nuclei.

VI. Conclusion

It is well-known that spin–lattice relaxation processes reflect a quasi-resonant exchange of energy between the observed spin system and the surrounding molecular medium. Spin–lattice relaxation rates of protons and ^{13}C nuclei measured in polybutadiene present a Larmor frequency dependence in the low-temperature range and also in the high-temperature one, as is usual in polymer systems. This last result necessarily reveals a broad spectrum of correlation times associated with segmental chain motions. Correspondingly, spectral densities of energy of these random processes must be described by multicomponent functions. Although the thorough description of these segmental motions is quite complex, several models have been proposed until now. They rely upon a few characteristic times. The use of these models permits us to compare dynamical properties of polymer melts with one another. The approach proposed in this work is slightly different; it is based upon a temperature–frequency superposition property found to characterize relaxation rates as well as NOE factors. This result clearly indicates that all motions observed from NMR are governed by a single basic relaxation process. In other words, it must be considered that motions observed over a time interval longer than 10^{-10} s correspond to a time average occurring along chain segments. More precisely, the step by step isomerization process of monomeric units is not perceived from the present measurements, but the average along chain segments leads to a local universality, which is also perceived from viscoelasticity measurements.

Appendix

Frequency–Temperature Superposition Property. The frequency–temperature superposition property of the product $\omega_{\rm o}T_1^{-1}$ is analyzed according to the following schematic way.



Normalized relaxation rates measured at three Larmor frequencies $\omega_0^{\rm A}$, $\omega_0^{\rm B}$, and $\omega_0^{\rm C}$ are represented as a function of the temperature θ. It is assumed that curves A–C obey a property of homogeneity with respect to the Larmor frequency and with respect to the characteristic relaxational frequency, $\upsilon_{\rm r}(\theta)$, too. Then, a given amplitude $(\omega_0/T_1)_i$ of the curve A is assigned to the temperature $\theta_i^{\rm A}$. The same amplitude of the curve B is assigned to the temperature $\theta_i^{\rm B}$ such that

$$\omega_0^{\rm A}/\upsilon_{\rm r}(\theta_i^{\rm A}) = \omega_0^{\rm B}/\upsilon_{\rm r}(\theta_i^{\rm B}) \qquad \text{(A.1)}$$

This equality also applies to curve C, defining the temperature $\theta_i^{\rm C}$. Furthermore, the temperature $\theta_i^{\rm B}$ also defines the amplitude $(\omega_0/T_1)_j$ of the curve A. The homogeneity property is now applied from the temperature $\theta_j^{\rm A} = \theta_i^{\rm B}$:

$$\omega_0^{\rm A}/\upsilon_{\rm r}(\theta_j^{\rm A}) = \omega_0^{\rm B}/\upsilon_{\rm r}(\theta_j^{\rm B}) = \omega_0^{\rm C}/\upsilon_{\rm r}(\theta_j^{\rm C}) \qquad \text{(A.2)}$$

From eq A.1

$$\upsilon_{\rm r}(\theta_i^{\rm B}) = (\omega_0^{\rm B}/\omega_0^{\rm A})\upsilon_{\rm r}(\theta_i^{\rm A})$$

and

$$\upsilon_{\rm r}(\theta_i^{\rm C}) = (\omega_0^{\rm C}/\omega_0^{\rm A})\upsilon_{\rm r}(\theta_i^{\rm A})$$

Also, from eq A.2 and with $\upsilon_{\rm r}(\theta_j^{\rm A}) = \upsilon_{\rm r}(\theta_i^{\rm B})$

$$\upsilon_{\rm r}(\theta_i^{\rm B}) = (\omega_0^{\rm B}/\omega_0^{\rm A})^2\upsilon_{\rm r}(\theta_i^{\rm A})$$

and

$$\upsilon_{\rm r}(\theta_j^{\rm C}) = (\omega_0^{\rm C}/\omega_0^{\rm A})(\omega_0^{\rm B}/\omega_0^{\rm A})\upsilon_{\rm r}(\theta_i^{\rm A})$$

This analysis applied along the three curves $\omega_0^{\rm A} < \omega_0^{\rm B} < \omega_0^{\rm C}$. The reference temperature is determined from the maximum of the relaxation rate at a given frequency, assuming that the relation $\omega_0/\upsilon_{\rm r} = 0.6$ is valid.

References and Notes

(1) Abragam, A. Les principes du magnétisme nucléaire. PUF, 1961.
(2) Cohen-Added, J. P.; Messa, J. P. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, L193.
(3) Carella, J. M.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1984**, *17*, 2775.
(4) Valeur, B.; Jarry, J. P.; Geny, F.; Monnerie, L. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 667, 675, 2251.
(5) Jones, A. A.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 847.
(6) Heatley, F. *Prog. NMR Spectrosc.* **1979**, *13*, 47.
(7) McBrierty, V. J.; Douglass, D. C. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 295.
(8) Schaefer, J. *Macromolecules* **1973**, *6*, 882.
(9) Dekmezian, A.; Axelson, D. E.; Dechter, J. J.; Borah, B.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 367.
(10) Howarth, O. W. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 1219.
(11) Cohen-Addad, J. P. *J. Chem. Phys.* **1974**, *60*, 2440; **1982**, *76*, 2744.
(12) English, A. D. *Macromolecules* **1986**, *18*, 1130.
(13) Dejean de la Batie, R.; Lauprêtre, F.; Monnerie, L. *Macromolecules* **1988**, *21*, 2045.
(14) Dejean de la Batie, R.; Lauprêtre, F.; Monnerie, L. *Macromolecules* **1988**, *21*, 2052.
(15) Dejean de la Batie, R.; Lauprêtre, F.; Monnerie, L. *Macromolecules* **1989**, *22*, 122.
(16) Hall, C. K.; Helfand, E. J. *J. Chem. Phys.* **1982**, *77*, 3275.
(17) Viovy, J. L.; Monnerie, L.; Brochon, J. C. *Macromolecules* **1983**, *16*, 1845.
(18) Viovy, J. L.; Monnerie, L.; Merola, F. *Macromolecules* **1985**, *18*, 1130.
(19) Monnerie, L.; Viovy, J. L.; Dejean de la Batie, R.; Lauprêtre, F. *Polymer Motions in Dense System*; Springer-Verlag: Berlin, 1988.
(20) Schlichter, W. P.; Davis, D. D. *J. Appl. Phys.* **1963**, *34*, 98.
(21) Munie, G. C.; Jonas, J.; Rowland, T. J. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1061.
(22) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(23) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802.
(24) Kimmich, R.; Koch, L. *Colloid Polym. Sci.* **1980**, *258*, 261.
(25) Cohen-Addad, J. P. *J. Phys. (Les Ulis, Fr.)* **1982**, *43*, 1509.
(26) Gronski, W. *Makromol. Chem.* **1976**, *177*, 3017.

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