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Carbon-13 NMR Investigation of Local Dynamics in Bulk Polymers at Temperatures Well above the Glass-Transition Temperature. 3. *cis*-1,4-Polybutadiene and *cis*-1,4-Polyisoprene

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ABSTRACT: Carbon-13 spin–lattice relaxation time measurements have been performed at two experimental frequencies on the considered polymers in the bulk state at temperatures well above the glass-transition temperatures and in solution. The data have been analyzed by using the orientation autocorrelation functions developed for polymers and a modified function proposed for poly(vinyl methyl ether) in a previous paper.[1] As observed in the latter compound and other polymers, a fast motion of the internuclear vector has to be considered. In the present case it can be assigned either to specific conformational jumps of the polydiene chain or to librations of limited but significant extent about the rest position. However, the high frequency of these processes and their generality are in favor of the second interpretation. Moreover the temperature dependence of the segmental motions proves that they are involved in the glass–rubber transition phenomenon.

Detailed analysis of carbon-13 nuclear magnetic relaxation in bulk poly(vinyl methyl ether), poly(propylene oxide), and cross-linked poly(ethylene oxides) at temperatures well above the glass–rubber transition temperature T_g have been reported in the first two papers of this series.[1,2] It has been shown that the well-known autocorrelation functions derived from models of conformational jumps in polymer chains,[3-5] which have proven to be relevant in describing fluorescence anisotropy decay data,[6] cannot account for the particularly high value of the minimum of the ^{13}C spin–lattice relaxation time T_1 observed as a function of temperature. Such behavior indicates that, besides the conformational jumps which induce a damped orientation diffusion along the chain, there exists an additional fast process which is not observed in the fluorescence depolarization experiments. In the previous papers, this fast process was assigned to a libration of limited but significant extent of the internuclear vectors about their rest position.[1,2]

It seems of interest to examine whether the autocorrelation function, which has been derived from the study of poly(vinyl methyl ether) and poly(propylene oxide),[1,2] can also be used to represent NMR data determined on other polymer melts having a quite different chemical chain structure such as polydienes. Polydiene melts have already been the subject of several NMR investigations and indication of fast anisotropic processes can be found in some papers. For example, in the case of *cis*-1,4-polybutadiene, it has been shown that the static dipolar interaction is almost entirely but not totally averaged by rapid modes.[7-10] A detailed analysis of the ^{1}H and ^{13}C NMR line widths of this polymer under various experimental conditions has led to the conclusion that the residual dipolar line broadening at room temperature is due to a weak anisotropy of the segmental motions which cannot totally reorient the internuclear vectors.[10] ^{13}C spin–lattice and spin–spin relaxation times and nuclear Overhauser enhancement in bulk polydienes have been determined by several authors. Results have been interpreted either in terms of a distribution of isotropic correlation times[11,12] or of a three correlation time autocorrelation function.[13] A more molecular approach has been described by Gronski[14] based on specific conformational jumps in polydienes. In fact, none of these T_1 fitting procedures is entirely satisfactory: although a distribution of correlation times is a good means for representing experimental results, it cannot lead to any physical description of the involved phenomena. At the present time, even though the Gronski model[14] has proven to be very useful to represent relative values of T_1, it does not account for absolute values.

Therefore, the purpose of this work is to examine to what extent the molecular approach which we have used for interpreting carbon-13 nuclear relaxation measurements on other bulk polymers at temperatures well above the glass-transition temperature can be generalized to polydienes. In this paper we will restrict our investigations to polybutadiene and polyisoprene of regular microstructure.

Experimental Section

The polybutadiene under study was Bayer Uran with microstructure 98.8% cis-1,4, 0.5% trans-1,4, 0.7% 1,2. Its molecular weight characteristics were M_n = 320 000 and M_p = 1 060 000. Its glass-transition temperature, as measured by DSC at a heating rate of 5 °/min, was −110 °C. The polyisoprene sample was Shell IR 307 with microstructure 92% cis-1,4, 5% trans, 3% 3,4. Its glass-transition temperature was −60 °C.

NMR experiments were carried out either on bulk polydienes or on 15% (w/w) deuteriochloroform or deuteriated 1,1,2,2-tetrachloroethane polymer solutions. Solution and bulk polymer samples were carefully degassed and the tubes were sealed under vacuum. In the case of the bulk sample, the lock signal was obtained from an external DMSO-d_6 tube.

^{13}C NMR spectra, 25.15 and 62.5 MHz, were recorded on a Jeol PS100 spectrometer and a Bruker WP250 spectrometer, respectively, by using the technique of proton noise decoupling. Spin–lattice relaxation times T_1 were measured by using the standard (180°, *t*, 90°) technique, with repetition times between pulse sequences greater than five times the longest T_1 of the considered nuclei. T_1 values were determined from exponential regression of the carbon-13 magnetization as a function of *t*. The relative accuracy for each T_1 measurement has been estimated to be better than 7%.

Nuclear Overhauser enhancements were determined from comparison of proton-decoupled and proton-coupled ^{13}C NMR spectra recorded on the Bruker WP250 spectrometer.

Theoretical Background

With the assumption of a purely ^{13}C–^{1}H dipolar relaxation mechanism, the spin–lattice relaxation time T_1 and nuclear Overhauser enhancement (NOE) obtained from a ^{13}C experiment are given by the well-known expressions[15]

$$\frac{1}{T_1} = \frac{\hbar^2\gamma_C^2\gamma_H^2}{10}\frac{1}{r_{CH}^6}[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \quad (1)$$

$$\mathrm{NOE} = 1 + \frac{\gamma_H}{\gamma_C}\frac{6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)}{J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)} \quad (2)$$

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Table I
Expressions of the HH, VMB, and DLM Orientation Autocorrelation Functions

HH	$G(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1)$
VMB	$G(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)[I_0(t/\tau_1) + gI_1(t/\tau_1)]$
DLM	$G(t) = (1-a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) + a\exp(-t/\tau_0)$

where ω_H and ω_C are the ^{1}H and ^{13}C resonance frequencies, r_{CH} is the internuclear distance, and $J(\omega)$ is the spectral density function defined by

$$J(\omega) = \tfrac{1}{2}\int_{-\infty}^{+\infty} G(t)e^{i\omega t}\,dt \qquad (3)$$

Here, $G(t)$ is the normalized second-order spherical harmonic autocorrelation function.

The autocorrelation functions which have been developed for local dynamics in polymers have been reviewed in the first paper of this series.[1] The motional models for chain dynamics are based on conformational changes, characterized by a correlation time τ_1, which propagate along the chain according to a damped diffusional process. The damping is described by the correlation time τ_2. In the following, the expressions of $G(t)$ that we will use for the description of the local polymer chain dynamics will be either the Hall–Helfand (HH) expression for the autocorrelation function[3] or the Viovy–Monnerie–Brochon (VMB)[4] one. These expressions are given in Table I where I_0 and I_1 are the modified Bessel functions of order 0 and 1, respectively.

In the case of poly(vinyl methyl ether), either in bulk or in solution,[1] and for poly(propylene oxide),[2] it has been shown that the above autocorrelation functions for polymer chain motions cannot account for the high value of the spin–lattice relaxation time T_1 at the minimum observed as a function of temperature. Results obtained from these studies demonstrate that the internuclear vectors are involved in an additional fast anisotropic process which has been assigned to a libration of limited but significant extent about the rest position. This libration has been described in terms of an anisotropic reorientation occurring with a correlation time τ_0 inside a cone of half-angle θ. The amplitude of the libration mode is related to the steric hindrance at the considered site.[1,2] Assuming the independence of the segmental motions and of the libration process, this leads to the complete Dejean–Laupretre–Monnerie expression written as[1]

$$G(t) = (1-a)\exp\left(-\frac{t}{\tau_2}\right)\exp\left(-\frac{t}{\tau_1}\right)I_0\left(\frac{t}{\tau_1}\right) + a\exp\left(-\frac{t}{\tau_0}\right)\exp\left(-\frac{t}{\tau_2}\right)\exp\left(-\frac{t}{\tau_1}\right)I_0(t/\tau_1) \qquad (4)$$

where

$$(1-a) = [(\cos\theta - \cos^3\theta)/2(1-\cos\theta)]^2 \qquad (5)$$

Assuming that τ_0 is much shorter than τ_1 and τ_2, which has been verified in the case of bulk poly(vinyl methyl ether), the second term in the $G(t)$ expression can be simplified, yielding the expression later referred to as (DLM) and given in Table I.

$(T_1)^{-1}$ can then be written as

$$\left(\frac{1}{T_1}\right) = (1-a)\frac{\hbar\gamma_C^2\gamma_H^2}{10}\frac{1}{r_{CH}^6}[J_{HH}(\omega_H-\omega_C) + 3J_{HH}(\omega_C) + 6J_{HH}(\omega_H+\omega_C)] + a\frac{\hbar\gamma_C^2\gamma_H^2}{10}\frac{1}{r_{CH}^6}[J_0(\omega_H-\omega_C) + 3J_0(\omega_C) + 6J_0(\omega_H+\omega_C)] \qquad (6)$$

where

$$J_{HH}(\omega) = 1/(\alpha + i\beta)^{1/2} \qquad J_0(\omega) = \frac{\tau_0}{1+\omega^2\tau_0^2}$$

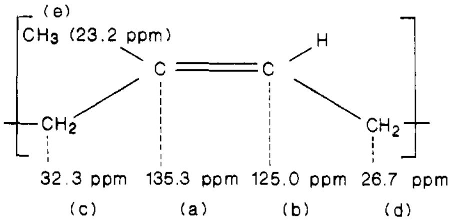
and

$$\alpha = \tau_2^{-2} + 2\tau_1^{-1}\tau_2^{-1} - \omega^2 \qquad \beta = -2\omega(\tau_1^{-1} + \tau_2^{-1})$$

Under the assumption of fast segmental motions, $\tau_0 \ll \tau_1$, τ_2 and $(\omega_H + \omega_C)\tau_1 < 1$, the second term can be neglected in expression 6. Under this condition, the T_1 value at the minimum is directly proportional to $1/(1-a)$ and therefore the height of the T_1 minimum is highly dependent on the amplitude of the libration mode, whereas, as shown by calculations reported in ref 1, the correlation time of the libration only influences the T_1 values in the "long time" part of the curves.

Results and Discussion

Nuclear Magnetic Relaxation in Bulk *cis*-1,4-Polybutadiene and Polyisoprene. The ^{13}C NMR spectra of bulk *cis*-1,4-polybutadiene recorded at temperatures well above the glass-transition temperature present two peaks at 129.5 and 27.5 ppm assigned to the ethylene and methylene carbons, respectively. In the case of *cis*-1,4-polyisoprene under comparable experimental conditions, five peaks are observed in the ^{13}C NMR spectrum. Their assignment is summarized in the following formula:



The dependence of (nT_1), where n is the number of protons directly bonded to the carbon of interest, as a function of the reciprocal of temperature T is plotted in Figures 1 and 2 for the CH and CH$_2$ carbons of polybutadiene, respectively, and in Figures 3–5 for the polyisoprene carbons. Results of nuclear Overhauser enhancement determinations are also shown in Figures 1–4.

Among the data reported in Figures 1–5, two important points have to be noticed. The first one concerns the fact that, as already noted by Gronski,[16] the experimental T_{1CH}/T_{1CH_2} ratios for the two polymers of interest are clearly different from the approximate value of 2 which can be anticipated from the number of protons directly bonded to each of the considered carbons. In the case of polybutadiene at 25.15 MHz, in spite of fluctuations of the T_{1CH}/T_{1CH_2} ratios due to experimental inaccuracy, this ratio has a mean value of 1.55 ± 0.1. At 62.5 MHz, this ratio gets smaller at lower temperatures. However, as the line broadening at low temperatures makes the T_1 measurements less precise, it is not possible to conclude a systematic decrease of T_{1CH}/T_{1CH_2} as a function of temperature. For temperatures in the range −25 to 85 °C, T_{1CH}/T_{1CH_2} is 1.45 ± 0.15, which shows that the mean values of the T_{1CH}/T_{1CH_2} ratios at 25.15 and 62.5 MHz are nearly equal.

In the case of bulk polyisoprene, the two methylene carbons are magnetically inequivalent due to the presence of the methyl group and they present slightly different T_1 values. The mean value of the T_{1CH}/T_{1CH_2} ratios for the methylene carbon vicinal to the methyl group are 1.49 at 62.5 MHz and 1.67 at 25.15 MHz. For the other methylene carbon of polyisoprene, these ratios are 1.35 at 62.5 MHz and 1.40 at 25.15 MHz.

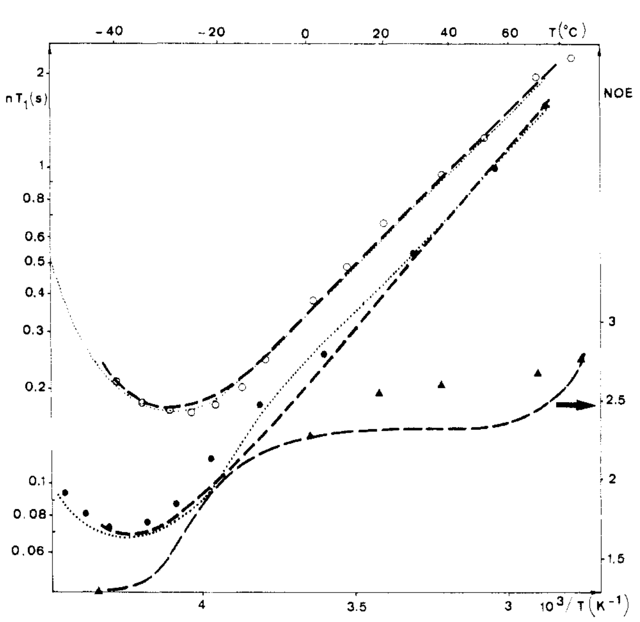


Figure 1. 62.5 (○) and 25.15 (●) MHz ^{13}C spin–lattice relaxation times (nT_1) and nuclear Overhauser enhancements NOE (▲) of the CH carbon in bulk *cis*-1,4-polybutadiene: (- - -) best fit calculated from the DLM autocorrelation function ($a = 0.27$, $\tau_1/\tau_0 = 150$, $\tau_2/\tau_1 = 500$, $r_{CH} = 1.08$ Å); (···) best fit calculated from expression 7 combining segmental motions and independent specific conformational jumps of polydienes ($\tau_1/\tau_i = 150$, $\tau_2/\tau_1 = 500$, $r_{CH} = 1.08$ Å).

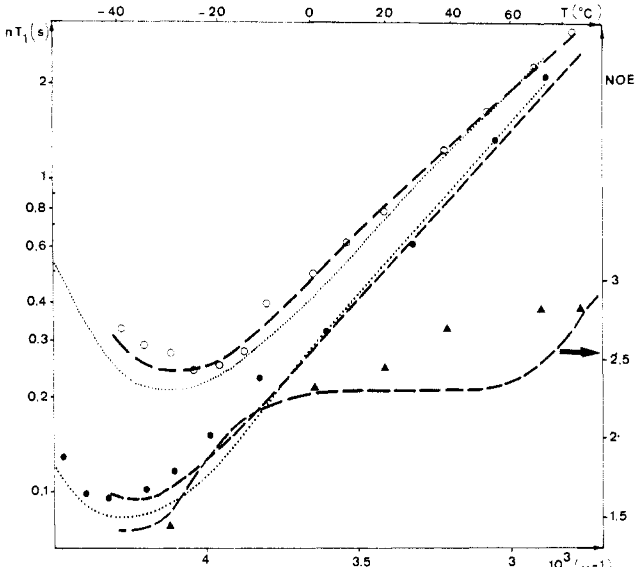


Figure 2. 62.5 (○) and 25.15 (●) MHz ^{13}C spin–lattice relaxation times (nT_1) and nuclear Overhauser enhancements NOE (▲) of the CH_2 carbon in bulk *cis*-1,4-polybutadiene: (- - -) best fit calculated from the DLM autocorrelation function ($a = 0.46$, $\tau_1/\tau_0 = 150$, $\tau_2/\tau_1 = 500$, $r_{CH} = 1.09$ Å); (···) best fit calculated from expression 7 combining segmental motions and independent specific conformational jumps of polydienes ($\tau_1/\tau_i = 150$, $\tau_2/\tau_1 = 500$, $r_{CH} = 1.09$ Å).

Very similar values of these ratios were observed in the case of bulk poly(propylene oxide)[2] whereas ratios of about 2 were determined for poly(vinyl methyl ether).[1] They indicate that the local motions observed by NMR in polybutadiene, polyisoprene, and poly(propylene oxide) are not identical for the internuclear vectors associated with the CH and CH_2 vectors. A deeper discussion of this effect requires a precise knowledge of the CH bond lengths in the CH and CH_2 groups. In the following discussion the CH bond lengths will be taken as 1.08 Å and 1.09 Å for the CH and CH_2 groups, respectively.[17]

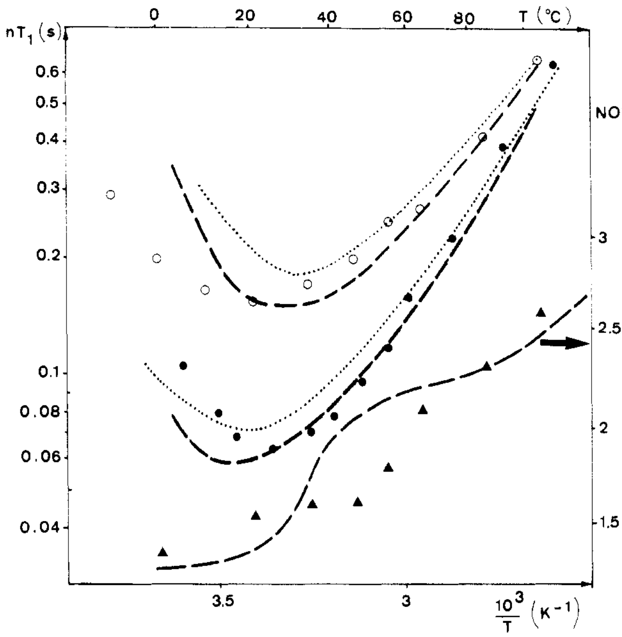


Figure 3. 62.5 (○) and 25.15 (●) MHz ^{13}C spin–lattice relaxation times (nT_1) and nuclear Overhauser enhancements NOE (▲) of the CH carbon in bulk *cis*-1,4-polyisoprene: (- - -) best fit calculated from the DLM autocorrelation function ($a = 0.17$, $\tau_1/\tau_0 = 150$, $\tau_2/\tau_1 = 40$, $r_{CH} = 1.08$ Å); (···) best fit calculated from expression 7 combining segmental motions and independent specific conformational jumps of polydienes ($\tau_1/\tau_i = 150$, $\tau_2/\tau_1 = 40$, $r_{CH} = 1.08$ Å).

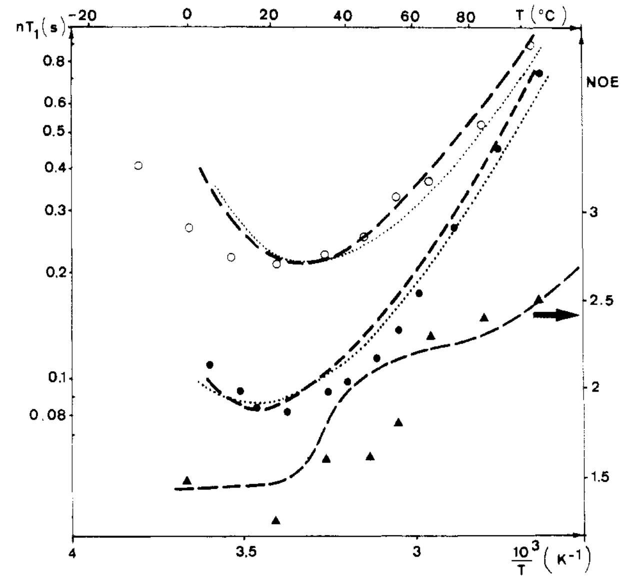


Figure 4. 62.5 (○) and 25.15 (●) MHz ^{13}C spin–lattice relaxation times (nT_1) and nuclear Overhauser enhancements NOE (▲) of the CH_2(c) carbon in bulk *cis*-1,4-polyisoprene: (- - -) best fit calculated from the DLM autocorrelation function ($a = 0.40$, $\tau_1/\tau_0 = 150$, $\tau_2/\tau_1 = 40$, $r_{CH} = 1.09$ Å); (···) best fit calculated from expression 7 combining segmental motions and independent specific conformational jumps of polydienes ($\tau_1/\tau_i = 150$, $\tau_2/\tau_1 = 40$, $r_{CH} = 1.09$ Å).

The second important experimental result is the fact that, for both CH and CH_2 carbons, the values of (nT_1) at the minimum of the curve as a function of temperature are much higher than those which can be calculated from the specific models of chain dynamics. Comparison of experimental (nT_1) and calculated ones by using the Hall–Helfand[3] and Viovy–Monnerie–Brochon[4] autocorrelation functions is shown in Table II. In the case of the CH carbon the discrepancy lies in the range 20–50% according to the experimental frequency and the polymer

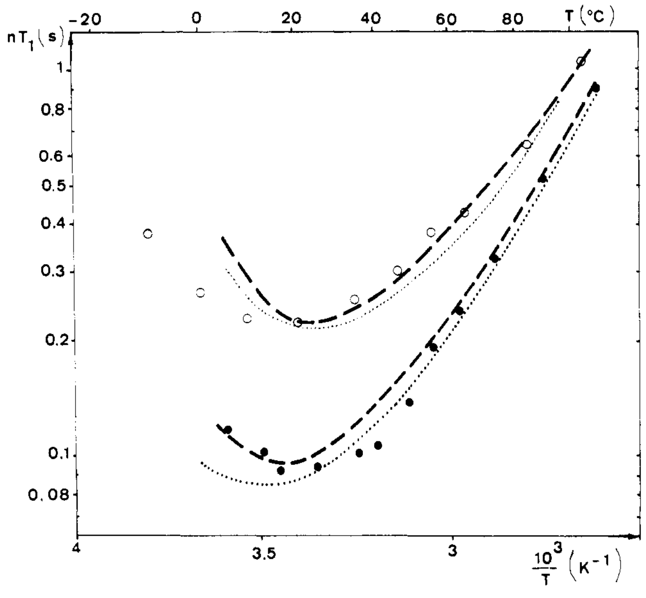


Figure 5. 62.5 (○) and 25.15 (●) MHz ^{13}C spin-lattice relaxation times (nT_1) of the CH_2(d) carbon in bulk *cis*-1,4-polyisoprene: (- - -) best fit calculated from the DLM autocorrelation function (a = 0.48, τ_1/τ_0 = 150, τ_2/τ_1 = 40, r_{CH} = 1.09 Å); (···) best fit calculated from expression 7 combining segmental motions and independent specific conformational jumps of polydienes (τ_1/τ_i = 150, τ_2/τ_1 = 40, r_{CH} = 1.09 Å).

Table II
Comparison of Experimental nT_1 at the Minimum and Calculated Values Using the HH and VMB Orientation Autocorrelation Functions

	exptl nT_1, s		calcd nT_1, s	
	polybutadiene	polyisoprene	HH model	VMB model
62.5 MHz				
CH	0.166	0.154	0.121	0.128
CH_2	0.24	0.21 (c), 0.22 (d)	0.128	0.135
25.15 MHz				
CH	0.072	0.064	0.047	0.051
CH_2	0.095	0.080 (c), 0.095 (d)	0.050	0.054

under interest. The difference between experimental and calculated values is still larger for the CH_2 carbon and is of the order of 50–100%. These results are very similar to those observed in poly(vinyl methyl ether)[1] and poly(propylene oxide).[2] Hence, independently of the structure of the chain, the carbon-13 spin-lattice relaxation time presents a particularly high value at the temperature of its minimum that cannot be accounted for by the above specific models for chain dynamics. Such a high value of T_1 is evidence for a rapid motion inducing a partial reorientation of the CH internuclear vectors. In the case of poly(vinyl methyl ether), this motion has been shown to affect the internuclear vectors in the CH and CH_2 groups in a similar way.[1] In contrast, differences in (nT_1) observed for the CH and CH_2 carbons in polybutadiene and polyisoprene, as well as in poly(propylene oxide),[2] show that this anisotropic fast process induces a reorientation of the internuclear CH vector which depends on the group to which it is attached.

As for poly(vinyl methyl ether) and poly(propylene oxide), this anisotropic process can be interpreted in terms of a libration. According to the treatment of Howarth,[18] this libration is described by an anisotropic reorientation inside a cone whose half-angle is θ and whose axis equals the rest position of the carbon–proton bond. Use of expressions 5 and 6 to represent the T_1 values of the minimum leads to the a and θ values listed in Table III. θ is larger for the CH_2 carbons than for the CH ones, which shows that the libration has a larger amplitude in the CH_2 groups. As observed in the previous studies,[1,2] the relative size of θ can be anticipated from the steric hindrance at the considered sites; the larger the steric hindrance, the smaller θ. In order to achieve the fit of the DLM function over the whole temperature range under study, the parameter a has been assumed to be independent of temperature and equal to the value determined from the T_1 minimum. Such an assumption means that the amplitude of the libration remains constant as a function of temperature. It is partly supported by the fact that for a given carbon the nT_{1CH}/nT_{1CH_2} ratio, which is equal to the $(1 - a)_{CH_2}/(1 - a)_{CH}$ ratio in the case of $\tau_0 \ll \tau_1$, is practically independent of temperature for the bulk polymers under study. This shows that the ratio of the a parameters for the different carbons of the chain is also independent of temperature for each polymer. Moreover, in the case of poly(vinyl methyl ether), the experimental (nT_1) values in solution and in bulk have been found to be identical at the T_1 minimum. This implies that the libration amplitude is the same in both states.[1] Under these conditions, the fit can be obtained at a given temperature by looking for τ_0, τ_1, and τ_2 values which lead to calculated (nT_1) values at 25.15 and 62.5 MHz as close as possible to the experimental ones. In the case of polybutadiene, the best fits obtained by using the DLM function and the a values reported in Table III are shown in Figures 1 and 2 for the spin–lattice relaxation times at the two Larmor frequencies for the CH and CH_2 carbons, respectively. Calculated values of nuclear Overhauser enhancement are also in good agreement with experimental determinations. It has to be noticed that the τ_1/τ_0 ratio cannot be accurately determined and that good agreement between theory and experiment is obtained in so far as τ_1/τ_0 is greater than 150. In the temperature range (T > 30 °C) for which the calculated values of the spin–lattice relaxation time are sensitive to variations of the τ_2/τ_1 ratio, one observes that this τ_2/τ_1 ratio is higher than 500. This last result shows that, in *cis*-1,4-polybutadiene, the diffusion motion of bond orientations along the chain is only slightly damped.

Table III
Values of the a and θ Parameters Characterizing the Libration Motion and Determined from Experimental Results Reported in Figures 1–5

	polybutadiene		polyisoprene		
	CH	CH_2	CH	CH_2(c)	CH_2(d)
a	0.27	0.46	0.17	0.40	0.48
θ, deg	26	36	20	33	37

In the case of bulk polyisoprene, the fit has to be achieved simultaneously for the three carbons belonging to the CH and CH_2 groups. The fits obtained from the DLM autocorrelation function and values of a reported in Table III are shown in Figures 3–5. The agreement is excellent for all temperatures except the lower ones where the T_1 determinations are less accurate. As for polybutadiene, the correlation time τ_0 has to be 150 times shorter than τ_1. The τ_2/τ_1 ratio is smaller than in polybutadiene and is of the order of 40.

Another way to account for the high value of the T_1 minimum is to consider the specific ability of polydienes to reorient through rapid conformational jumps. Indeed, the presence of double bonds in polybutadiene and polyisoprene chains leads to a decrease in the height of the rotation barriers about the single bonds linking the CH and CH_2 groups,[19] which thus favors the existence of very fast motional jumps between the different rotational isomers of the chain. For *cis*-1,4-polybutadiene, Gronski[14]

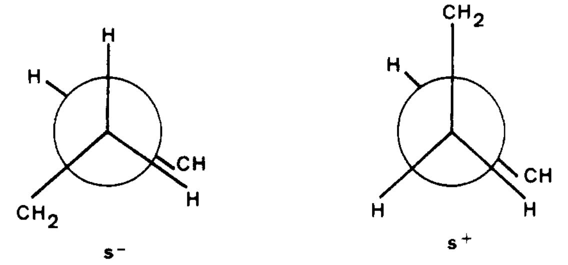


Figure 6. Definition of the s$^+$ and s$^-$ conformations of the C–C bonds adjacent to a double bond.

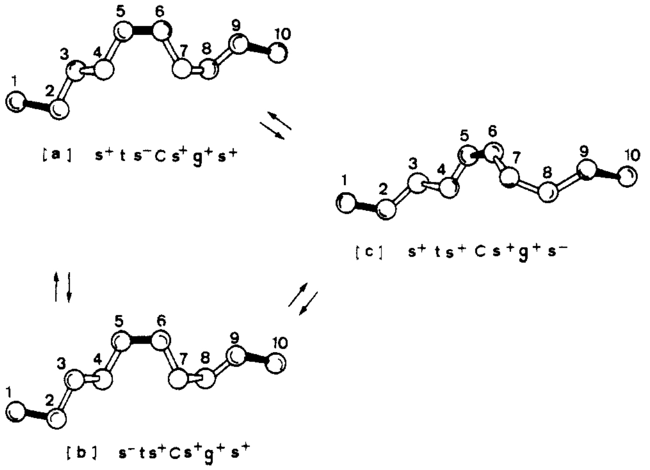


Figure 7. Specific counterrotations in *cis*-1,4-polybutadiene (from ref 14). Double bonds are represented by a thick line. The central unit considered for the calculation of the autocorrelation function is composed of C(4)H$_2$—C(5)H═C(6)H—C(7)H$_2$ groups.

has proposed a model based on anisotropic motions arising from two 120° counterrotations between the more stable s$^+$ and s$^-$ conformations. The definition of these conformations is recalled in Figure 6. Specific motions are sketched in Figure 7 showing the reorientation of the CH and CH$_2$ groups of a central unit CH$_2$(4)CH(5)═CH(6)CH$_2$(7) having CH$_2$CH═CH groups on each side. In the *a*–*b* type of motion, for example, two counterrotations occur about the C(2)–C(3) and C(4)–C(5) bonds, which are parallel to each other. Therefore, the CH(5)═CH(6)CH$_2$(7)CH$_2$(8)CH(9)═CH(10) part of the chain remains immobile, the CH$_2$(4) group is involved in a 120° rotation about the C(4)–C(5) axis, and the CH(1)═CH(2)CH$_2$(3) groups are translated from position *a* to position *b*. In the case of the *a*–*c* motion, the counterrotations occur in a similar way about the C(4)–C(5) and C(8)–C(9) bonds. In the case of the *b*–*c* motion, rotation is about the C(2)–C(3) and C(8)–C(9) bonds. In such motional processes, one can observe that the rotational angle of the CH vectors belonging to the CH or the CH$_2$ groups of the central unit depends on the group to which the vectors belong. In the *a*–*b* process, for example, the CH vectors of the CH(5)═CH(6)CH$_2$(7) central unit are not reoriented whereas those belonging to the CH$_2$(4) group are involved in a 120° rotation about the C(4)–C(5) axis.

As regards the height of the conformational barrier to be crossed during these specific motions, Gronski[14] refers to unpublished calculations for the s$^+$ts$^-$–s$^-$ts$^+$ motion (or *a*–*b* type of motion in Figure 7) which lead to a 3.6 kcal/mol barrier for *cis*-1,4-polybutadiene. This value is noticeably higher than the barrier between the s$^+$ and s$^-$ conformations which was obtained by Abe and Flory[19] from conformational energy calculations as slightly less than 1 kcal/mol. It must be noted that Cook and Helfand[20] have shown that the height of the energy barrier has an influence on the nature, diffusive or localized, of the motion. From both a theoretical point of view and computer simulations, Cook and Helfand have studied the reorientation of vectors attached to a unidimensional chain and the interactions between immediate neighbors. They have shown that, in the case of a low energy barrier of less than 5 kT between two stable positions, the corresponding motion is mainly of a localized type.

Table IV
Calculated Values of a_0, a_1, and a_2 (Expression 7)

	a_0	a_1	a_2
CH	0.492	0.297	0.277
CH$_2$	0.667	0.358	0.420

In the absence of detailed conformational energy calculations relative to the processes described in Figure 7, the motional law in *cis*-1,4-polybutadiene will be established assuming that the s$^+$ts$^-$–s$^-$ts$^+$ processes are of a localized type. It will also be assumed that these processes ensure a partial reorientation of the C–H vectors characterized by a monoexponential autocorrelation function and a correlation time τ_i. As for the libration considered above, the segmental reorientation will result from slower processes, either diffusive modes with a correlation time τ_1 or damping characterized by a correlation time τ_2 and occurring independently of the localized conformational jumps. Under these assumptions, the calculation of the autocorrelation functions associated with the different spherical harmonics leads to the following expression for the ^{13}C spin–lattice relaxation time T_1:

$$\frac{1}{T_1} = \frac{\hbar\gamma_C^2\gamma_H^2}{10}\frac{1}{r_{CH}^6}[(1-a_0)J_{HH}(\omega_H-\omega_C) + 3(1-a_1)J_{HH}(\omega_C) + 6(1-a_2)J_{HH}(\omega_H+\omega_C)] + \frac{\hbar\gamma_C^2\gamma_H^2}{10} \times \frac{1}{r_{CH}^6}[a_0J_i(\omega_H-\omega_C) + 3a_1J_i(\omega_C) + 6a_2J_i(\omega_H+\omega_C)] \quad (7)$$

with

$$J_{HH}(\omega) = 1/(\alpha + i\beta)^{1/2} \qquad \alpha = \tau_2^{-2} + 2\tau^{-1}\tau_2^{-1} - \omega^2$$

$$\beta = -2\omega(\tau_1^{-1} + \tau_2^{-1}) \qquad J_i(\omega) = \frac{\tau_i}{1+\omega^2\tau_i^2}$$

Numerical values of coefficients a_0, a_1, and a_2 are listed in Table IV. One can observe that the analytical expression of T_1 is quite similar to formula 6 obtained by assuming a random reorientation of the C–H vector inside a cone, with the restriction that the parameters a_0, a_1, and a_2 are entirely determined by the specific jump model. The dominant terms in expression 7 are those corresponding to frequencies ω_C and $\omega_H + \omega_C$, i.e., a_1 and a_2, whereas those involving the $\omega_H - \omega_C$ term and thus a_0 are of minor importance. Therefore, values of the spin–lattice relaxation times calculated for the CH groups from expression 6 using $a = 0.29$ and those calculated from expression 7 should be quite similar since $a_1 = 0.297$ and $a_2 = 0.277$. In the same way, results obtained from expressions 6 and 7 in the case of the CH$_2$ groups should not be significantly different, taking $a = 0.39$ in expression 6.

The fit of the experimental data using the specific conformational jump model is shown in Figures 1 and 2 for the CH and CH$_2$ groups of bulk polybutadiene. It requires $\tau_1/\tau_i \gg 150$, which means that the local conformational jumps are at least 150 times more rapid than the diffusive processes, and $\tau_2/\tau_1 = 100$, which indicates a weak damping of the orientation bond diffusion process in polybutadiene.

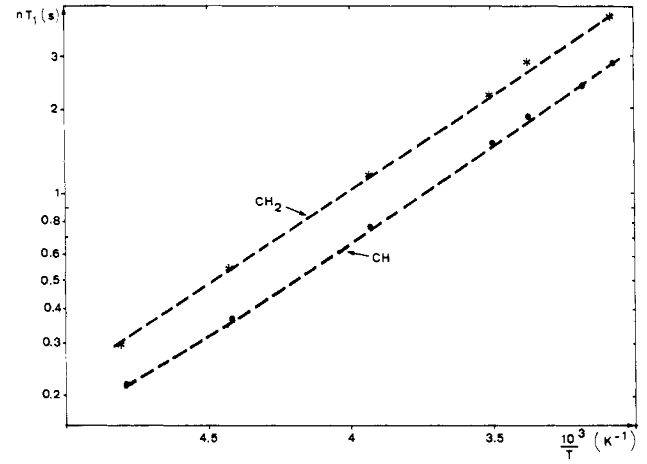


Figure 8. 25.15-MHz ^{13}C spin–lattice relaxation times (nT_1) for *cis*-1,4-polybutadiene in $CDCl_3$ solution: (- - -) best fit calculated from the DLM autocorrelation function.

As anticipated from the compared numerical values of a, a_1, and a_2, the calculated values of T_1 at its minimum are very close to the experimental ones in the case of the CH carbon. This occurs since a_1 and a_2 differ only slightly from the value of $a = 0.27$ which leads to the best adjustment of the minimum of T_1 with the model of reorientation inside a cone. For the CH_2 carbons, the calculated T_1 at the minimum is 10% less than the experimental value, which reflects the fact that a_1 and a_2 are somewhat different from the best fit value of $a = 0.46$. In spite of this slight discrepancy which solely concerns the T_1 minimum of the CH_2 carbons, one observes in Figures 1 and 2 that the parameters a_0, a_1, and a_2 evaluated from the specific conformational jump model proposed by Gronski[14] lead to a very good fit of the whole set of experimental data.

As the main-chain structure of *cis*-1,4-polyisoprene is quite similar to that of *cis*-1,4-polybutadiene, results obtained on bulk polyisoprene can also be analyzed in terms of the above specific conformational jump model with the values of a_0, a_1, and a_2 calculated for polybutadiene. Fits plotted in Figures 3–5 show that both models lead to a very satisfying agreement. They correspond to $\tau_1/\tau_i \gg 150$ and $\tau_2/\tau_1 = 40$. As for polybutadiene, the agreement with experimental data could have been anticipated from the comparison of a_1 and a_2 with a.

The above analysis shows that the anisotropic motion of the internuclear vector evidenced by the high value of the T_1 minimum can be interpreted, in the cases of *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene, either in terms of a libration or in terms of specific conformational jumps in polydienes. Considering only the results obtained from these polymers, it cannot be straightforwardly decided between these two models. However, it must be noticed that the same type of fast anisotropic motion has been observed in all the polymers which we have previously investigated using NMR relaxation. Those polymers have no double bonds. The case of poly(propylene oxide) is of particular interest since no specific conformational jump exists for this polymer chain, which affects the CH and CH_2 internuclear vectors differently. Besides, the high frequency of the fast anisotropic process is in favor of a libration rather than a conformational jump, which corresponds to a much larger rearrangment. Therefore both the generality of the phenomenon and its high frequency lead us to identify it as a libration.

***cis*-1,4-Polybutadiene and Polyisoprene Nuclear Magnetic Relaxation in Solution.** ^{13}C spin–lattice relaxation times determined in $CDCl_3$ solutions of polybutadiene and polyisoprene at 25.15 MHz are plotted in Figures 8 and 9. Extreme narrowing conditions are approximately fulfilled between −50 and 55 °C: in this temperature range, for a given carbon, T_1 is nearly independent of the experimental frequency and nuclear Overhauser enhancement at 62.5 MHz is close to the limiting value of 3.

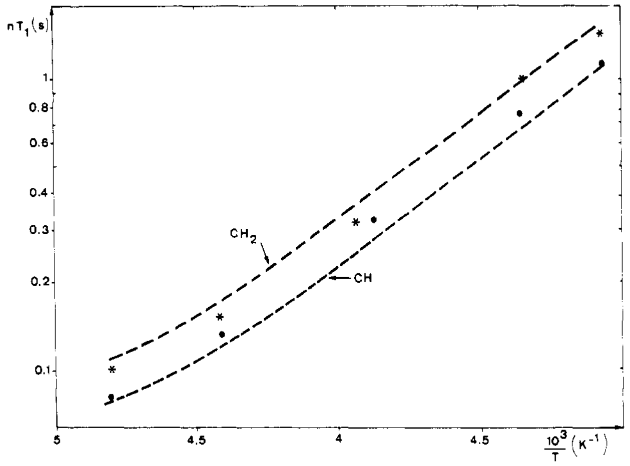


Figure 9. 25.15-MHz ^{13}C spin–lattice relaxation times (nT_1) for *cis*-1,4-polyisoprene in $CDCl_3$ solution: (- - -) best fit calculated from the DLM autocorrelation function.

The T_{1CH}/T_{1CH_2} ratio is 1.41 for polybutadiene in solution. For polyisoprene in solution, the corresponding values are 1.61 and 1.54 for the CH_2 group vicinal to the methyl one and the other CH_2 group, respectively. These values are clearly different from 2. Moreover they are close to the results observed in the bulk polymers, which shows that molecular motions do not ensure the same reorientation for the CH vector of the CH and CH_2 groups in these polydienes in either bulk or solution.

It would also be of interest to measure the T_1 minima in these polymers in $CDCl_3$ solution. However, due to the high mobility of the polydiene chains, T_1 minima occur at experimentally inaccessible temperatures since they are below the melting temperature of deuteriochloroform (−64 °C). To solve this problem, we have used deuteriated 1,1,2,2-tetrachloroethane as a solvent. Its viscosity at 15 °C is about three times higher than that of chloroform and we have limited our investigation to polyisoprene which is less mobile than polybutadiene. Results of T_1 determinations at 25.15 MHz obtained on polyisoprene in 1,1,2,2-tetrachloroethane are shown in Figure 10. The T_1 minimum is reached at −40 °C. It is 0.058 and 0.070 s for the CH and CH_2 carbons, respectively. The comparison of these values with those reported in Table II shows that, although the T_1 minima are slightly lower in solution than in bulk, they are still higher than those predicted from the Hall–Helfand and Viovy–Monnerie–Brochon models. It can therefore be concluded that for polyisoprene in solution there exists a fast anisotropic motion whose amplitude is close to the amplitude of the bulk process. This motion is in addition to the segmental modes described by τ_1 and τ_2. Assuming a libration of the internuclear vector, the parameter a in expression 6 is $a = 0.15$ and $a = 0.26$ for the CH and CH_2 carbons, respectively. The best fit of the experimental values using the DLM autocorrelation function is shown in Figure 10.

Assuming that the a parameter has the same values in deuteriochloroform and in deuteriated 1,1,2,2-tetrachloroethane, the best fit of the polyisoprene data in $CDCl_3$ with the DLM function is shown in Figure 9. As regards polybutadiene in $CDCl_3$ solution, we will assume that variations in a are small from bulk to solution as was

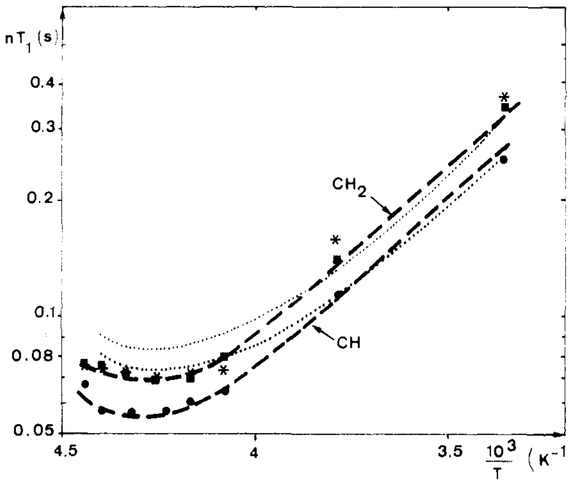


Figure 10. 25.15-MHz ^{13}C spin-lattice relaxation times (nT_1) for *cis*-1,4-polyisoprene in deuteriated 1,1,2,2-tetrachloroethane solution: (■) CH_2(c); (*) CH_2(d); (●) CH; (- - -) best fit calculated from the DLM autocorrelation function; (···) best fit calculated from expression 7 combining segmental motions and independent specific conformational jumps of polydienes.

observed in polyisoprene. Therefore the best fit obtained from the DLM autocorrelation function is derived with the value of a determined in bulk polybutadiene and plotted in Figure 8. For both polymers, these fits correspond to τ_1/τ_0 higher than 150. The τ_2/τ_1 ratio has nearly no influence on the quality of the fit in the temperature range under study. Therefore this ratio was arbitrarily taken as equal to the value determined in the bulk state. Under these conditions, as shown in Figures 8 and 9, agreement with experimental data is very good.

Spin-lattice relaxation in polyisoprene solution can also be analyzed in terms of specific conformational jumps in polydienes. The best fit obtained from expression 7 is shown on Figure 10. It is not as good as the one derived from the DLM autocorrelation function since the experimental T_1 minima are shorter than the calculated ones.

From the analysis of polybutadiene and polyisoprene NMR relaxation in solution only, it is not possible to decide between the two motional models based either on libration or on specific conformational jumps. In the case of polyisoprene however, the adjustment of the model to the experimental data is better with the assumption of a libration. As for bulk polymers, the high frequency of the process and the fact that it has been observed in polymers without double bonds are also in favor of a libration. Finally, the behavior of the two methylene carbons of polyisoprene is not exactly the same in solution and in bulk: the T_1 minima are equal in solution while they slightly differ in bulk. Such a difference can only be accounted for by the motional model based on libration. The equality of the methylene T_1 minima in solution should result from the quasi-suppression of intramolecular constraints which thus allows the two CH_2 to undergo motions of identical amplitude.

All these considerations on NMR relaxation in polymers both in the bulk state and in solution have led us to assign the fast anisotropic process to a libration of the internuclear vector about its rest position. In the following we will restrict our analysis to this interpretation.

Motional Temperature Dependence. I. Segmental Motions in Polymer Solutions. τ_1 values obtained from fitting our experimental data on polybutadiene and polyisoprene in $CDCl_3$ solution with the motional model based on independent segmental motions and librations of the internuclear vectors are plotted as a function of $1/T$ in Figure 11. For both polymers, log τ_1 appears to be a linear function of $1/T$ in the frequency and temperature domains under study. In the case of polybutadiene, the slope of the line leads to an apparent activation energy E_{sol} = 4.9 + 0.5 kcal/mol. This value is in good agreement with that obtained by Gronski and Murayama for *cis*-1,4-polybutadiene in $CDCl_3$ solution.[21] In terms of the Kramers theory for the diffusion of a particle over a potential barrier[22] this activation energy can be considered as the sum of an activation energy for the solvent viscosity, E_η = 1.4 kcal/mol, and of an energy barrier originating from conformational jumps, E^* = 3.5 kcal/mol. In the case of polyisoprene, the apparent activation energy for τ_1 processes is 4.6 + 0.5 kcal/mol, which leads to a conformational barrier height of E^* = 3.2 kcal/mol. This is very close to that determined for polybutadiene in solution. These results seem to indicate that the differences in mobility that exist between polyisoprene and polybutadiene in bulk are mainly of intermolecular origin. The methyl substituent on the polyisoprene chain would have only a weak influence on the height of the intramolecular barriers, but the intermolecular ones might be modified by steric hindrance.

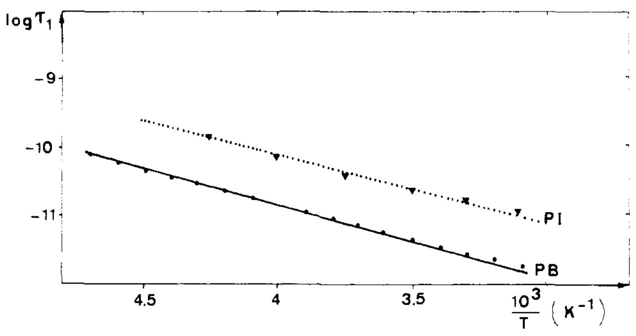


Figure 11. Plot of log τ_1 versus $1/T$: *cis*-1,4-polybutadiene in $CDCl_3$ solution (PB); *cis*-1,4-polyisoprene in $CDCl_3$ solution (PI).

II. Segmental Motions in Bulk Polymers at $T > T_g$. The frequency dependence of the motional processes associated with the glass-transition phenomena can be anticipated from the Williams, Landel, and Ferry (WLF) equation for viscoelastic relaxations:[23]

$$\log a_{T/T_g} = -\frac{C_1^g(T - T_g)}{C_2^g + T - T_g} \qquad (8)$$

where $a_{T/T_g} = \tau_C(T)/\tau_C(T_g)$, $\tau_C(T)$ is the viscoelastic relaxation time at temperature T, and $\tau_C(T_g)$ is the viscoelastic relaxation time at T_g which serves here as a reference. C_1^g and C_2^g are two parameters which depend on the reference temperature. With the temperature $T_\infty = T_g - C_2^g$ for which a_{T/T_g} tends to infinity, the WLF equation is written

$$\log a_{T/T_g} = -C_1^g + \frac{C_1^g C_2^g}{T - T_\infty} \qquad (9)$$

T_∞ and the product $C_1^g C_2^g$ are constants characteristic of a given polymer. They do not depend on the reference temperature. Variation of log a_{T/T_g} as a function of $1/(T - T_\infty)$ is linear and a change in the reference temperature only induces a translation of the line without any modification of its slope.

WLF coefficients for a bulk polybutadiene presenting a microstructure very close to that of our sample (96% cis-1,4; 2% trans-1,4; 2% 1,2) have been determined by Ferry[24] as T_∞ = 101 K, C_1^g = 11.35 for T_g = 161 K and $C_1^g C_2^g$ = 676.3 K. In the case of polyisoprene, WLF coefficients are[24] T_∞ = 146 K, $C_1^g C_2^g$ = 900.2 K, and C_1^g = 16.79 for T_g = 200 K.

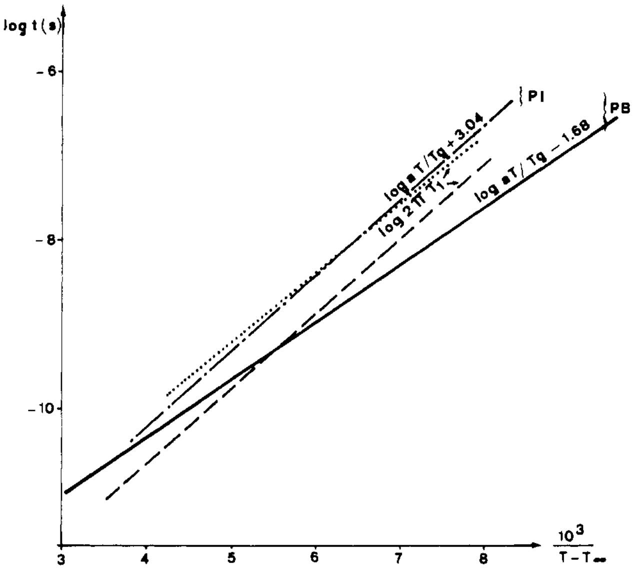


Figure 12. Comparison of log $2\pi\tau_1$ and log a_{T/T_g} dependences on $10^3/(T - T_\infty)$ in bulk *cis*-1,4-polybutadiene (PB) and in bulk *cis*-1,4-polyisoprene (PI).

Plots of log $(2\pi\tau_1)$ and log a_{T/T_g} as a function of $1/(T - T_\infty)$ are shown in Figure 12. It can be observed that the agreement between the two sets of data is very good in the case of bulk polyisoprene. For polybutadiene, the slope derived from the alignment of the NMR correlation times τ_1 is slightly higher than that predicted by the WLF law in the temperature range under study.

Conclusion

The carbon-13 spin-lattice relaxation time determinations performed on *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene in the bulk state at temperatures well above the glass-transition temperature and in solution have shown that the local dynamics of these polymers can be satisfactorily described by considering a fast anisotropic process in addition to the segmental motions characterized by the two correlation times of the Hall-Helfand model. In spite of the main-chain chemical structure of the polymers which presents both single and double bonds and allows specific conformational jumps to be performed, the high frequency of this anisotropic motion and the fact that it has been also observed on vinyl polymers by NMR[1,2] and by neutron scattering[25] lead us to assign it to a libration of limited but significant extent of the internuclear vector about its rest position. It must also be concluded that the existence of fast librations of carbon-proton bonds is a general phenomenon encountered in the carbon-13 spin-lattice relaxation of all polymers in solution or in bulk at temperatures above T_g.

Another important result in this study is the close similarity of the temperature variation of the correlation time τ_1, associated with correlated conformational jumps, to the predictions of the Williams, Landel, and Ferry equation for viscoelastic relaxation. This similarity indicates that the segmental motions observed by NMR belong to the glass-transition phenomena.

Registry No. Polybutadiene, 9003-17-2; polyisoprene, 9003-31-0.

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