Carbon-13 NMR Investigation of Local Dynamics in Bulk Polymers at Temperatures Well Above the Glass Transition Temperature. 1. Poly(vinyl methyl ether)

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ABSTRACT: Carbon-13 spin-lattice relaxation time determinations have been performed on poly(vinyl methyl ether) in solution and in bulk above the glass transition temperature. The high experimental value of the minimum of T_1 as a function of temperature cannot be accounted for by the specific orientation autocorrelation functions for polymers. We postulate the existence of an additional fast anisotropic motion, which we have assigned to librations of limited extent of the internuclear CH vectors about their rest position. Comparison of solution and bulk data has established that molecular motions of poly(vinyl methyl ether) are of the same nature in solution and in bulk at temperatures above T_g. For bulk poly(vinyl methyl ether), the similarity of the temperature variation of the correlation time τ_1, associated with conformational jumps, to the predictions of the Williams-Landel-Ferry equation for viscoelastic relaxation points to the fact that the local motions observed by NMR belong to the glass transition phenomenon.

The local dynamics of polymers in solution have been studied by a number of spectroscopic techniques. Among these techniques nuclear magnetic resonance has proved to be a very powerful tool since its selectivity allows a detailed analysis of the motions of the different components of the polymer chain. Moreover, according to the type of experiment chosen—measurement of the spin-lattice relaxation time T_1, of the spin-spin relaxation time T_2, of the nuclear Overhauser enhancement, or of the line shape in exchange studies—it provides information on very rapid processes or on much slower modes.

In the domain of bulk polymers, NMR studies of molecular motions are much rarer. However, in this case, two different situations have to be considered: the first one is related to bulk polymers in the solid state at temperatures below the glass transition temperature T_g. In these polymers, molecular processes are very different from those that occur in polymer solutions: they are localized either on side groups or on short sequences of the chain, and they cannot lead to a diffusion process along the chain. From the NMR point of view, the existence of a carbon-proton dipolar coupling and of a chemical shift anisotropy, which are not efficiently averaged by the motions, leads to a strong line broadening. For one to obtain high-resolution ^{13}C NMR spectra in such polymers below T_g, the specific solid-state techniques, proton dipolar decoupling, magic-angle sample spinning, and cross polarization, have to be used.[1]

The other situation, to which are related all the experiments described in this work, corresponds to the case of amorphous bulk polymers at temperatures well above the glass transition temperature. Under these conditions, the carbon-proton dipolar interaction and the chemical shift anisotropy are averaged to a large extent by the fast molecular motions and contribute only to a weak residual line broadening. Therefore, high-resolution ^{13}C NMR spectra can be obtained on bulk polymers at temperatures well above T_g by using the conventional spectrometers for solution investigations.

In the case of *cis*-1,4-polybutadiene, for example, Cohen-Addad et al.[2] and English et al.[3,4] have shown that most, i.e., 99% or more, of the dipolar interaction is averaged by rapid motions. A detailed analysis of the ^1H and ^{13}C NMR line widths of this polymer under different conditions (frequency, temperature, radiofrequency field intensity, spinning speed at the magic angle) has led to the conclusion that, at room temperature, the dipolar residual broadening results from a weak anisotropy of the segmental modes which cannot induce the complete reorientation of the CH internuclear vectors. The segmental motions have correlation times faster than 10^{-10} s, while the complete reorientation is due to much slower modes with correlation times of about 10^{-3} s.[4]

To get a deeper insight of the segmental chain motions, Schaefer[5] has measured the ^{13}C spin-lattice relaxation time T_1, the spin-spin relaxation time T_2, and the nuclear Overhauser enhancement in bulk *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene at 22.6 MHz and 35 °C. Results obtained from these experiments have been interpreted in terms of a distribution of correlation times. The same approach has been used by Dekmezian et al.[6] to account for values of carbon-13 T_1 measured at 67.9 MHz as a function of temperature on a large number of amorphous polymers (such as *cis*-polybutadiene, *cis*-polyisoprene, polyisobutylene, and atactic polypropylene) as well as semicrystalline ones (*trans*-polyisoprene, polyethylene, and polyethylene oxide). These experiments demonstrate that the mean correlation time has a temperature dependence that is very similar to the one predicted by the Williams-Landel-Ferry equation.[7]

In the case of natural rubber, Howarth[8] has observed that the values of the carbon-13 T_1 at its minimum cannot be fitted using a model based on isotropic reorientation, and he has proposed a three-correlation-time autocorrelation function that leads to a good agreement between experimental and calculated values. Similar results have been obtained on polyethylene[9] and a series of polyesters.[10]

Carbon-13 T_1 relaxation times have also been studied by Gronski[11] for 1,4-polybutadienes with different microstructures. At a given temperature, the ratio $T_{1,CH}/T_{1,CH_2}$ of the relaxation time of the methine CH carbon to the relaxation time of the methylene CH_2 carbon was found to be in the range 1.5-1.7, which is quite different from the value of 2 predicted by the number of protons directly bonded to these two carbons. Such a result has been interpreted in terms of very local specific conformational jumps that, in polydienes, affect in a different way the reorientation of the CH vectors in the CH and CH_2 groups.

From this brief literature survey, it appears that experiments with bulk polymers at temperatures well above the glass transition temperature have been interpreted either in terms of a distribution of correlation times, which leads to a satisfactory fit of the data but does not provide any precise description of the involved phenomena, or in terms of the three-correlation-time autocorrelation function

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proposed by Howarth,[8] which does not take into account the specific characteristics of polymer chain motions. Indeed, fluorescence anisotropy decay experiments performed on bulk polybutadiene at temperatures well above the glass transition temperature, which lead directly to the orientation autocorrelation function, have shown[12] that the experimental data can only be accounted for by using the specific orientation autocorrelation functions derived for local chain motions in solution.[13-15] Therefore, it seemed of interest for us to use carbon-13 NMR relaxation to investigate the local chain dynamics of poly(vinyl methyl ether) (PVME) both in bulk at temperatures well above T_g and in solution.

Experimental Section

Poly(vinyl methyl ether) was purchased from Polysciences Inc. Its molecular weight characteristics are $M_n = 45\,000$ and $M_p = 90\,000$. Its glass transition temperature, as measured by differential scanning calorimetry, is −26 °C.

NMR experiments were carried out either on bulk PVME or on 15% (w/w) deuteriochloroform PVME solution. Solution and bulk PVME 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 5 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%.

Theoretical Background

With the assumption of a purely ^{13}C–^{1}H dipolar relaxation mechanism, the spin–lattice relaxation time T_1 obtained from a ^{13}C experiment is given by the well-known expression[16]

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

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

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

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

For rapid isotropic rotation of the internuclear vector, $J(\omega)$ can be written as

$$J(\omega) = \frac{\tau}{1 + \omega^2 \tau^2} \quad (3)$$

where τ is the rotational correlation time.

In the case of polymers, due to the constraint resulting from the connectivity of the chain, the motions that are responsible for the NMR spin-lattice relaxation are usually too complicated to be described by such a simple picture.

First of all, in the case of polymers in solution, it has been established that ^{13}C spin–lattice relaxation times T_1 are independent of the degree of polymerization (DP) when DP is higher than 100:[17,18] this is evidence for the segmental or local character of the phenomena that are responsible for the T_1 relaxation. Another piece of evidence for complicated polymer relaxation comes from fluorescence depolarization experiments that allow the observation of the decrease of the orientation autocorrelation function as a function of time. Such experiments have unambiguously shown that the experimental data obtained on anthracene-labeled polymers in solution cannot be described by an isotropic rotational model.[14,19] Indeed, the connectivity of the chain induces a correlation between local conformational jumps that leads to a description of the time evolution of a bond orientation in terms of a damped diffusional process along the chemical sequence.[13,14] It must be noted that this correlation effect has been observed in a Brownian dynamics simulation of an alkane chain of 200 bonds carried out by Helfand et al.[20] Moreover, the very local nature of the fastest modes contributing to the segmental relaxation is supported by electron spin resonance experiments on spin-labeled polymers.[21,22] All these results indicate that from a fundamental point of view, the molecular motions that are involved in the NMR relaxation of a polymer chain in solution must be described in terms of segmental or local modes rather than in terms of overall isotropic motion combined with anisotropic local modes.

However, although conformational jumps have been shown to be responsible for the local chain dynamics in solution, the precise nature of these jumps and their relation with the chemical structure of the polymer remain questionable. These motions may be either localized processes such as three-bond jumps or crankshafts,[23] which do not induce any displacement of the ends of the sequence undergoing the motion, or bond rotation inside a specific conformational sequence such as gtt–ttg conformational change. In the first case, the viscous friction is limited to the group of moving atoms and is therefore very weak. However, due to the simultaneous orientational change of the moving bonds, two energy barriers have to be crossed. In the latter case, the motion does not alter the relative orientation of the chain moieties on each side of the moving bond but leads to a translation of a part of the chain. However, such bond motion is very often associated with an opposite motion of the second neighboring bond, which accommodates the motion of the first bond and avoids the translation of a chain moiety.[20] It must also be noted that only one energy barrier has to be crossed in this type of process.

In the case of bulk polymers at temperatures well above the glass transition temperature, fluorescence anisotropy decay experiments have shown that high-frequency motions (>10^7 Hz) in bulk poly(propylene oxide) with molecular weights 425 and 4000 present correlation times whose difference is less than 20%.[24] In the same way, the correlation times in bulk polybutadiene obtained from similar measurements differ by less than a factor of 2 when the number of bonds of the polymer chain increases from 50 to 10000.[25] These results indicate the segmental or local character of the high-frequency modes observed by these fluorescence techniques. The ^{13}C NMR spin–lattice relaxation times that are determined only by high-frequency motions should also be governed by such segmental modes.

Fluorescence anisotropy decay studies carried out on polybutadiene[12] and polyisoprene[26] have shown that the local dynamics in bulk at temperatures well above the glass transition temperature are described by the same orientation autocorrelation function, which suggests that the segmental motions far above T_g consist of conformational jumps. However, is must be noted that besides the intramolecular contribution to the damping of the orientation diffusion, there may exist intermolecular effects resulting from the density of the medium.

Among the various expressions that are based on a conformational jump model and have been proposed for the orientation autocorrelation function of a polymer chain, the formula derived by Hall and Helfand[13] leads to a very good agreement with experimental data. It is written as

$$G(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) \tag{4}$$

the Fourier transform of which is

$$J(\omega) = \mathrm{Re}\,[1/(\alpha + i\beta)^{1/2}] \tag{5}$$

where $\alpha = \tau_2^{-2} + 2\tau_1^{-1}\tau_2^{-1} - \omega^2$ and $\beta = -2\omega(\tau_1^{-1} + \tau_2^{-1})$. I_0 is the modified Bessel function of order zero, τ_1 is the correlation time associated with correlated jumps responsible for orientation diffusion along the chain, and τ_2 corresponds to damping which consists either of nonpropagative specific motions or of distortions of the chain with respect to its most stable local conformations.

The expression for the autocorrelation function derived by Hall and Helfand[13] can be identified, in a generalized diffusion and loss equation, with the cross-correlation function of two neighboring bonds inside the polymer chain. To account for motional coupling of nonneighboring bonds, resulting for example from the presence of side chains, Viovy et al.[14] have introduced cross-correlation functions of a pair of bonds separated by j bonds into the orientation autocorrelation function. These functions are written

$$C_j(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)I_{|j|}(t/\tau_1) \tag{6}$$

where I_j is a modified Bessel function of order j. The expression for $G(t)$ is then

$$G(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)[I_0(t/\tau_1) + \sum_{i=1}^{n} g_i I_i(t/\tau_1)] \tag{7}$$

where g_i is a rapidly decreasing function of i. It should be noted that the Hall–Helfand autocorrelation function is a particular case of eq 7, corresponding to $g_i = 0$, whatever the value of i.

Independently of this work, Jones and Stockmayer[27] have developed a motional model for chains undergoing three-bond jumps on a tetrahedral lattice. A recent analysis[28] of the derived autocorrelation function has shown that this function can be written as

$$G(t) = \exp(-2\omega t)\exp(-\omega_0 t)[I_0(2\omega t) + 2\sum_{j\geq 1}\exp(-j\gamma)I_j(2\omega t)] \tag{8}$$

where γ is equal to 2 ln 3 in the case of the tetrahedral lattice. This expression is equivalent to the Viovy–Monnerie–Brochon autocorrelation function in the case of

$$2\omega = 1/\tau_1 \qquad \omega_0 = 1/\tau_2$$

and $g_j = 2\exp(-j\gamma)$ whatever the value of j.

From a practical point of view, expression 7 is not easy to use because of the large number of parameters it involves. Therefore, use of its first-order development has been suggested:

$$G(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)[I_0(t/\tau_1) + gI_1(t/\tau_1)] \tag{9}$$

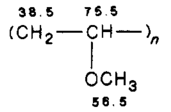
the Fourier transform of which is

$$J(\omega) = \mathrm{Re}\,\frac{1}{(\alpha + i\beta)^{1/2}}\left|1 + \frac{g\tau_1^{-1}}{\tau_1^{-1} + \tau_2^{-1} - i\omega + (\alpha + i\beta)^{1/2}}\right| \tag{10}$$

It should be pointed out that the molecular origin of the damping of the diffusion process characterized by the correlation time τ_2 is still not well identified. Molecular processes such as specific isolated jumps, fluctuations of internal rotation angles, and chemical defects (head-to-head linking, stereochemical sequences) can affect the propagation of conformational changes along the chain sequence leading to a damping effect. Results presented in this series,[29] as well as studies recently performed by fluorescence anisotropy decay,[26] clearly show that the damping strongly depends on the chemical structure of the polymer chain.

Results

Figure 1 shows the proton-decoupled ^{13}C NMR spectrum of PVME in 15% (w/w) $CDCl_3$ solution recorded at 30 °C at an experimental frequency of 25.15 MHz, together with a series of spectra of bulk PVME, obtained under the same conditions of scalar proton decoupling in the temperature range 40–115 °C. Chemical shifts (expressed in ppm with reference to TMS) and peak assignments in the bulk PVME sample are summarized in the following formula:



$$\overset{38.5}{(\mathrm{CH_2}}-\underset{\underset{56.5}{\mathrm{OCH_3}}}{\overset{75.5}{\mathrm{CH}}}-)_n$$

With the exception of tacticity effects that can be observed more clearly on the CH_2 carbon in the solution spectrum, the bulk PVME NMR spectra obtained at high temperature ($T > 60$ °C) appear to be very similar to the solution spectrum: at these temperatures, molecular motions are fast enough to effectively average the line broadenings resulting from carbon-13–proton dipolar interaction and from chemical shift anisotropy. In the bulk PVME spectra, lines get broader as temperature is decreased, which is evidence for an increase in the natural line width $(\pi T_2)^{-1}$ of the carbon-13 nuclei. For example, in the 25.15-MHz spectra, at 63 and 80 °C, the line widths at midheight of the methine carbon line are 70 ± 5 and 60 ± 5 Hz, respectively. At an experimental frequency of 62.5 MHz, these line widths are 105 ± 5 and 90 ± 5 Hz, respectively. These data show that for a given temperature, the line width, as expressed in hertz, is not independent of the observation frequency. This result is due partly to the fact that the extreme narrowing conditions are not fulfilled and partly to mechanisms inducing a line-width variation with the Larmor frequency. These mechanisms can result from the static field inhomogeneity which varies from one NMR apparatus to another, from variation of the magnetic susceptibility inside the sample (H_0 dependence), from a chemical shift distribution (H_0 dependence), or from a residual chemical shift anisotropy (H_0^2 dependence). Therefore, estimation of the carbon-13 spin–spin relaxation time, T_2, from line widths is difficult, and motional contributions to T_2 cannot be determined with sufficient accuracy. Thus, in the following, we will limit our discussion to T_1 results.

Carbon-13 spin-lattice relaxation times T_1 measured in bulk PVME at 63 °C and 25.15 MHz are 0.072 ± 0.005, 0.037 ± 0.004, and 0.25 ± 0.04 s for the methine, methylene, and methyl carbons, respectively. The spin–lattice relaxation time of the methyl carbon is much longer than those of the methine and methylene ones, indicating the existence of a fast rotation of the methyl group about its symmetry axis. Moreover, the spin–lattice relaxation time of the methylene carbon is about half that of the methine carbon, which is in agreement with the number of directly bonded protons, assuming that cross-relaxation inside the methylene group can be neglected,[30] which generally holds true. This set of T_1 values supports the whole assignment of the spectrum.

Figure 2 shows the behavior of nT_1, where n is the number of directly bonded protons, as a function of the

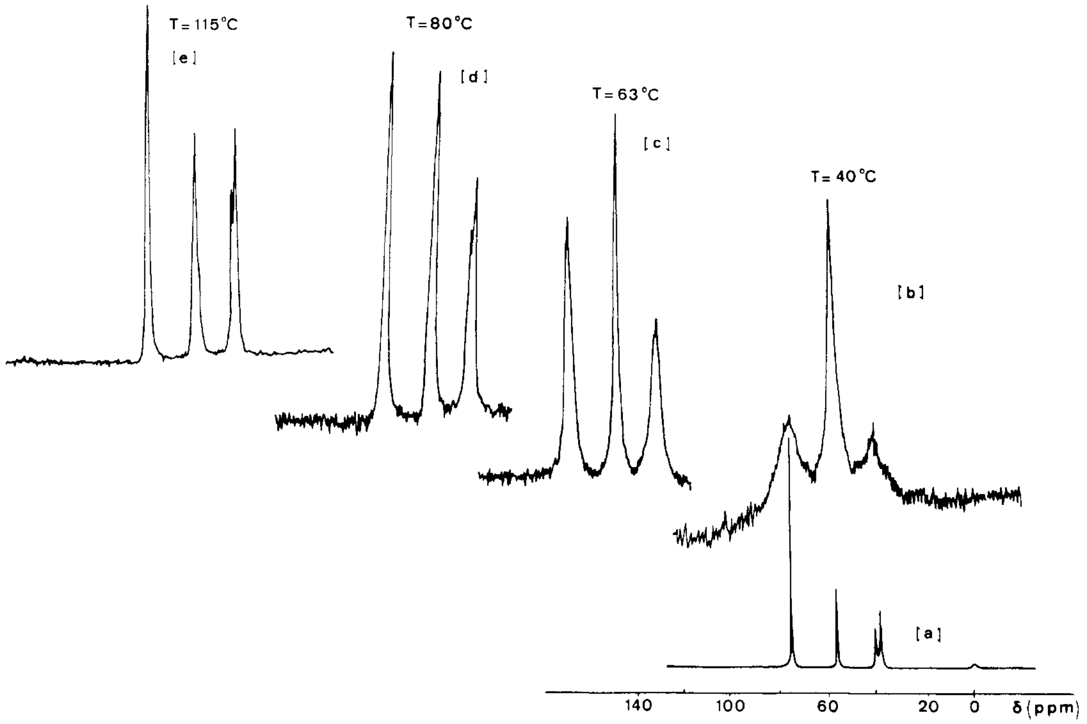


Figure 1. 25.15-MHz ^{13}C NMR spectra of PVME in $CDCl_3$ solution (a) and in bulk at several temperatures (b–e).

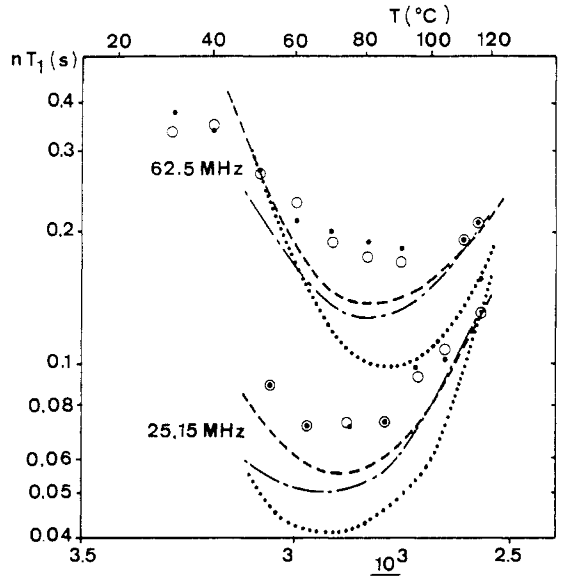


Figure 2. 62.5- and 25.15-MHz ^{13}C spin–lattice relaxation times nT_1 in bulk PVME: (○) CH carbon; (●) CH_2 carbon; (···) best fit calculated from the isotropic motional model; (– – –) best fit calculated from Hall–Helfand autocorrelation function; (-·-) best fit calculated from Viovy–Monnerie–Brochon autocorrelation function.

reciprocal of temperature T for the CH and CH_2 carbons. The nT_1 minimum is observed at 90 °C at 62.5 MHz and 70 °C at 25.15 MHz. nT_1 values at the minimum are 0.177 and 0.070 s at 62.5 and 25.15 MHz, respectively. Throughout the range of temperatures under study and at both observation frequencies the ratio of the spin–lattice relaxation times associated to the CH and CH_2 carbons is given by

$$T_{1,CH}/T_{1,CH_2} = 1.95 \pm 0.12$$

Discussion

Internuclear Distances r_{CH}. As shown in formula 1, the 6th power of the interatomic distance r_{CH} intervenes in the expression for the carbon-13 spin–lattice relaxation time, and therefore r_{CH} has to be known to a high accuracy. Unfortunately, crystallographic data are not very precise because of the low intensity of radiation scattered by the hydrogen atoms, and there are no experimental data from neutron scattering relevant to these distances in macromolecules. For these reasons we have used mean distance values derived from quantum mechanics calculations:[31] r_{CH} = 1.09 Å for CH and CH_2 carbons.

For molecules that have been studied by neutron scattering, interatomic distances thus obtained do not differ by more than 0.005 Å from those calculated from quantum mechanics.[32] Therefore, in the case of the polymers under study, we will assume that the absolute error on the internuclear distance is also less than 0.005 Å, leading to a better than 3% accuracy in the evaluation of T_1 from the different motional models.

Spin–Lattice Relaxation Time Minima. The values of the experimental T_1 minima are compared with those calculated from the different motional models in Table I. It can be seen that the experimental values are always higher than the calculated ones, in proportions ranging from about 35% in the case of the Hall–Helfand[13] and Viovy–Monnerie–Brochon[14] models to 75% in the case of isotropic reorientation. This large discrepancy cannot be accounted for by internuclear distance imprecision and is in fact the major problem encountered in this study. It will be carefully discussed and interpreted below.

It should be noted that experimental data comparable to ours have been obtained by Howarth[8] on bulk natural

Table I
Comparison of Experimental and Calculated nT_1 (Second) Values at the Minimum in Bulk PVME

	ω_C	
	62.5 MHz	25.15 MHz
exptl	0.177	0.070
isotropic model	0.100	0.040
H-H[a]	0.128	0.050
V-M-B[b]	0.135	0.054

[a] H-H: Hall–Helfand autocorrelation function. [b] V-M-B: Viovy–Monnerie–Brochon autocorrelation function.

rubber and by Horii et al.[9] on bulk polyethylene. The inadequacy of the isotropic model in these two examples has been underlined by these authors.

Comparison of Experimental Data with Predictions of Motional Models. The best fit of the experimental nT_1 values over the temperature range of interest and for the two observation frequencies with the isotropic model is shown in Figure 2. It is obvious that the agreement is not satisfactory: although the minima of the experimental and calculated curves appear at the same temperature, as noted above, the absolute values of the calculated nT_1 minima are quite different. Moreover, in the temperature range under study, the isotropic model cannot account for the T_1(62.5 MHz)/T_1(25.15 MHz) ratio of the spin-lattice relaxation times measured at the two observation frequencies for the same carbon, which means that at a given temperature, it is not possible to account simultaneously for the 25.15- and 62.5-MHz data.

Let us now consider the fit of our data with the Hall-Helfand model for polymer main-chain motions.[13] At high temperature, when the correlation time τ_1 is short, the ratio T_1(62.5 MHz)/T_1(25.15 MHz) depends on the value of the τ_2/τ_1 ratio. It is therefore possible to account simultaneously for the experimental data at the two observation frequencies at the highest temperature studied (T = 115 °C). At this temperature we get $\tau_2/\tau_1 = 20$.

For lower temperatures, calculated values are practically insensitive to the variations in the τ_2/τ_1 ratio. We have thus assumed that τ_2/τ_1 remains constant and equal to 20. Taking care that the experimental and calculated minima be observed at the same temperature, we have obtained the best fit from the Hall-Helfand model, as represented in Figure 2. The agreement between experimental and calculated values is better than with the isotropic model. However, the calculated T_1 values at the minima are still too low, and the fit cannot be further improved with variations of the τ_2/τ_1 ratio since the T_1 minimum is practically insensitive to the value of this parameter.

Very similar results are obtained with the Viovy-Monnerie-Brochon model for polymer chain motion,[14] assuming a value of 1 for the g parameter, which leads to the highest value of the T_1 minimum and a τ_2/τ_1 ratio of 40, which gives a good fit between experimental and calculated values at 115 °C. The best fit calculated from these parameters is plotted in Figure 2. It presents only very slight differences with the Hall-Helfand fit. T_1 values at the minimum are somewhat higher, but they are still very far from the experimental data.

The above analysis shows that the isotropic model as well as the motional models for polymer chain motions fails to account for the high value of T_1 at the minimum. Such a high experimental value, measured in bulk PVME as well as in a series of other polymers,[29] indicates that there exists, inside the polymer chain, an additional motion that is not considered in the previous models and that contributes to a partial reorientation of the CH vectors with a characteristic time that differs from the correlation time for orientation diffusion along the chain. Assignment of this additional motion to a process slower than the orientation diffusion along the chain associated with τ_1 must be precluded since results derived from fluorescence anisotropy decay[12] and NMR[2,4] on polybutadiene have shown that such slow modes contribute only to a very small extent (1% or less) to the decay of the orientation autocorrelation function in this temperature range.

Therefore, this additional motion has to be a faster mode and thus more local than the orientation diffusion process along the chain. A similar fast process has recently been observed by neutron scattering experiments.[33] It can be assigned to molecular librations of limited extent of the CH vectors about their equilibrium conformation and corresponds to oscillations inside a potential well. Such librations have already been shown to be of importance in the quantitative explanation of NMR relaxation parameters.[8,34,35] For this reason, we adopt the description of libration proposed by Howarth[35] in terms of a random anisotropic fast reorientation of the CH vector inside a cone of half-angle θ, the axis of which is the rest position of the CH bond. The local chain motions would then consist in conformational jumps and bond librations. Assuming that these two kinds of motions occur independently and using the Hall-Helfand orientation autocorrelation function to describe the effect of conformational jumps and the Howarth description of bond libration, we can write the whole orientation autocorrelation function as

$$G(t) = (1 - a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) + a\exp(-t/\tau_0)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) \quad (11)$$

where τ_0 is the correlation time associated with the local anisotropic reorientation, i.e., the libration, and

$$1 - a = [(\cos\theta - \cos^3\theta)/2(1 - \cos\theta)]^2 \quad (12)$$

Assuming that τ_0 is much shorter than τ_1 and τ_2, the second term in the expression for $G(t)$ can be simplified and written as

$$G(t) = (1 - a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) + a\exp(-t/\tau_0) \quad (13)$$

the Fourier transform of which is the reduced spectral density:

$$J(\omega) = \frac{1 - a}{(\alpha + i\beta)^{1/2}} + \frac{a\tau_0}{1 + \omega^2\tau_0^2} \quad (14)$$

with

$$\alpha = \tau_2^{-2} + 2\tau_1^{-1}\tau_2^{-1} - \omega^2$$

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

If we designate

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

$(T_1)^{-1}$ can be written as the sum of two terms:

$$\frac{1}{T_1} = (1 - a)\frac{\hbar^2\gamma_{\mathrm{C}}^2\gamma_{\mathrm{H}}^2}{10}\frac{1}{r_{\mathrm{CH}}^6}[J_{\mathrm{HH}}(\omega_{\mathrm{H}} - \omega_{\mathrm{C}}) + 3J_{\mathrm{HH}}(\omega_{\mathrm{C}}) + 6J_{\mathrm{HH}}(\omega_{\mathrm{H}} + \omega_{\mathrm{C}})] + a\frac{\hbar^2\gamma_{\mathrm{C}}^2\gamma_{\mathrm{H}}^2}{10}\frac{1}{r_{\mathrm{CH}}^6}[J_0(\omega_{\mathrm{H}} - \omega_{\mathrm{C}}) + 3J_0(\omega_{\mathrm{C}}) + 6J_0(\omega_{\mathrm{H}} + \omega_{\mathrm{C}})] \quad (15)$$

The first term, which is proportional to $1 - a$, contains only factors originating from the Hall-Helfand function and thus depends only on τ_1 and τ_2. The second term, which is proportional to a, corresponds to the local libration of limited angular extent and depends on τ_0. Under the assumption of fast librations and segmental motions, $\tau_0 \ll \tau_1$, $\tau_0 \ll \tau_2$, $(\omega_{\mathrm{H}} + \omega_{\mathrm{C}})\tau_1 < 1$, the second term in eq 15 can be neglected, giving

$$\frac{1}{T_1} \simeq (1 - a)\frac{\hbar^2\gamma_{\mathrm{C}}^2\gamma_{\mathrm{H}}^2}{10}\frac{1}{r_{\mathrm{CH}}^6}[J_{\mathrm{HH}}(\omega_{\mathrm{H}} - \omega_{\mathrm{C}}) + 3J_{\mathrm{HH}}(\omega_{\mathrm{C}}) + 6J_{\mathrm{HH}}(\omega_{\mathrm{H}} + \omega_{\mathrm{C}})] \quad (16)$$

T_1 values derived from expression 15 as a function of τ_1 are shown in Figure 3 for several values of a and for τ_2/τ_1

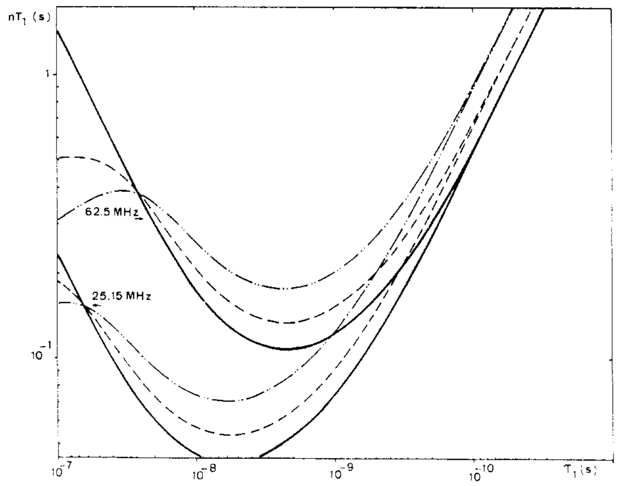


Figure 3. Plots of calculated nT_1 values from expression 15 versus τ_1 assuming $\tau_2/\tau_1 = 2$, $\tau_1/\tau_0 = 400$: (—) $a = 0$; (– –) $a = 0.20$; (–··) $a = 0.40$.

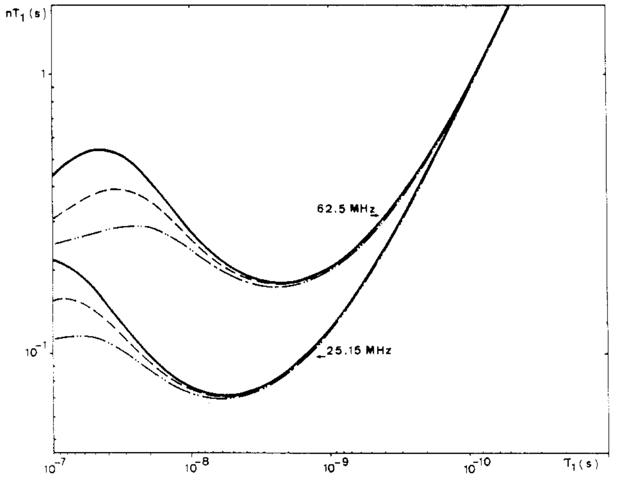


Figure 4. Plots of calculated nT_1 values from expression 15 versus τ_1 assuming $\tau_2/\tau_1 = 2$, $a = 0.40$: (—) $\tau_1/\tau_0 = 400$; (– –) $\tau_1/\tau_0 = 200$; (–··) $\tau_1/\tau_0 = 100$.

= 2 and $\tau_1/\tau_0 = 400$. Calculations performed by using relations 15 and 16 lead to the same values at the minimum of T_1, which indicates that the T_1 value at the minimum is directly proportional to $1/(1 - a)$. Therefore the height of the T_1 minimum is highly dependent on the amplitude of the libration mode.

Figure 4 shows the behavior of T_1 as a function of τ_1 for different τ_1/τ_0 ratios. It can be seen that τ_0 influences only the T_1 values in the "long time" part of the curves.

In the case of bulk PVME, nT_1 values at the minimum are 0.177 and 0.070 s at 62.5 and 25.15 MHz, respectively. They correspond to $a = 0.40$. With this parameter fixed, the best fit obtained from relation 16 at high temperature leads to $\tau_2/\tau_1 = 2$. Results given in Figure 5 show that this fit is very satisfactory in the temperature range 60–115 °C, while in the range 50–60 °C, where the experimental data are less precise due to the broadening of the lines, the differences between calculated and measured T_1 values are small.

Figure 4 indicates that τ_1/τ_0 has to be higher than 200 to achieve a good fit of the low-temperature data, which means that the libration of the CH vectors is at least 200 times faster than the diffusive chain motions. This result supports the above assumption, $\tau_1 \gg \tau_0$, used to derive the expression of the autocorrelation function (eq 13). Moreover, the calculated value of a ($a = 0.40$) corresponds to a conic half-angle θ of 33°.

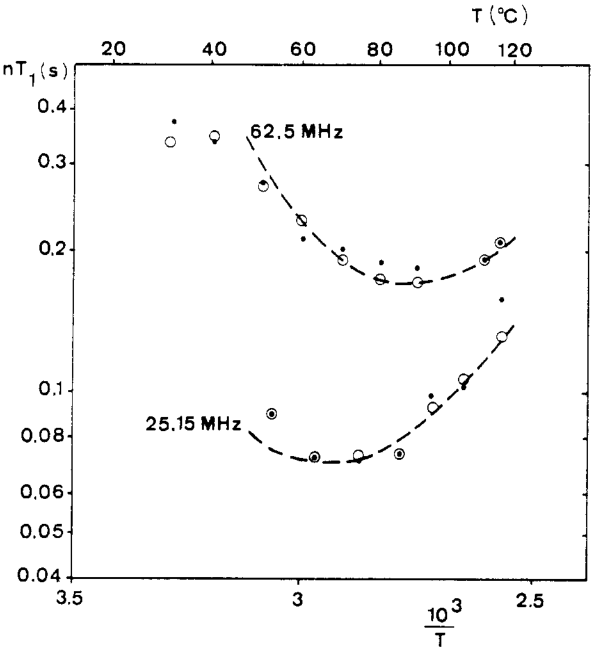


Figure 5. Comparison of experimental 25.15- and 62.5-MHz nT_1 values for bulk PVME with fit from expression 15: $a = 0.40$, $\tau_1/\tau_0 = 200$, $\tau_2/\tau_1 = 2$; (○) CH carbon, (●) CH_2 carbon.

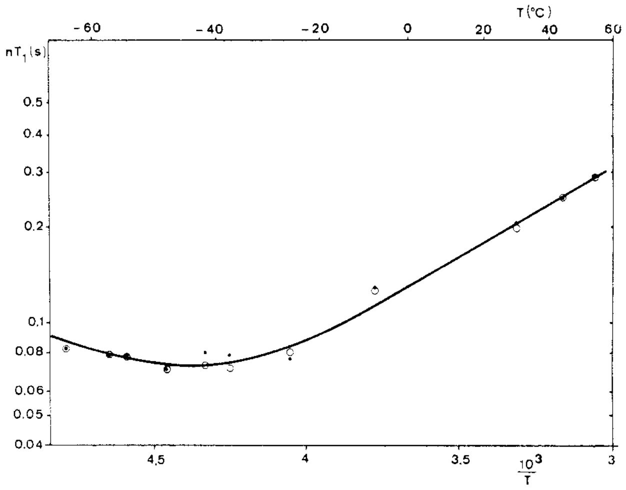


Figure 6. Comparison of 25.15-MHz nT_1 values for PVME in $CDCl_3$ solution with fit from expression 15: $a = 0.40$, $\tau_2/\tau_1 = 2$, $\tau_1/\tau_0 = 400$; (●) CH carbon; (○) CH_2 carbon.

Concerning main-chain motion, the best fit of the experimental data leads to a value of 2 for the τ_2/τ_1 ratio, which remains constant over the temperature range in which it can affect the T_1 data. This result indicates that in bulk PVME, at temperatures well above T_g, the orientation diffusion process is strongly damped.

PVME Nuclear Magnetic Relaxation in Solution. T_1 measurements have been carried out at 25.15 MHz in 15% $CDCl_3$ solution to compare the dynamic behavior of PVME in bulk and in solution. Variations of nT_1 as a function of temperature are shown in Figure 6.

It can first be seen that, throughout the temperature range under study, the $T_{1,CH}/T_{1,CH_2}$ ratio is 1.96, which is the same as the value measured for bulk PVME. The minimum of T_1 is observed at a temperature about 110 °C lower than that of the bulk PVME T_1 minimum. At the minimum, nT_1 is 0.070 s, much higher than the values that can be derived from specific motional polymer chain models. Such a T_1 minimum value points to the fact that in a polymer solution as well as in bulk PVME, a partial reorientation of the CH internuclear vectors occurs that

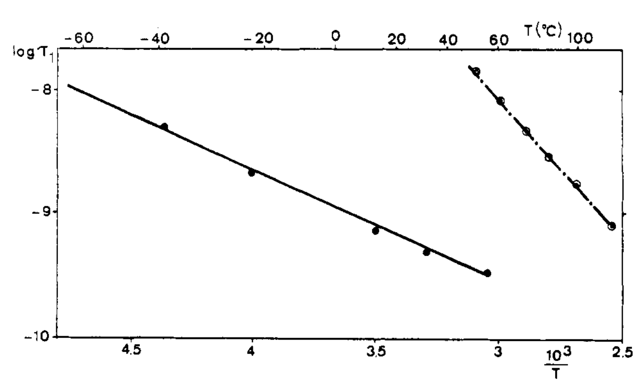


Figure 7. Plot of log τ_1 versus $1/T$: (—) PVME in $CDCl_3$ solution; (-•-) bulk PVME.

is added to the segmental modes of the chain. As far as we know, the inadequacy of the polymer chain motional models in accounting for the experimental value of T_1 at the minimum in polymer solutions has never been evidenced before. Moreover, the experimental nT_1 values in solution and bulk PVME are identical, which indicates that the anisotropic reorientation motion has the same amplitude in both states. Therefore, a fit to the experimental results can be achieved with the same a parameter value used for bulk PVME. Results presented in Figure 6 show that the agreement between experimental T_1 and calculated ones, assuming $\tau_2/\tau_1 = 2$ and $\tau_1/\tau_0 = 200$, is excellent and indicate the fact that local motions, as studied by NMR, are of the same nature, i.e., conformational jumps and librations, in bulk at temperatures well above T_g and in solution.

Motional Temperature Dependence. log τ_1 values obtained from fitting our experimental data with the motional model we have proposed above are plotted as a function of $1/T$ in Figure 7. For the bulk polymer as well as for the polymer solution, log τ_1 appears to be a linear function of $1/T$ in the frequency and temperature ranges under study. The slope of the line is much higher in the bulk polymer than in the polymer solution. These slopes lead to apparent activation energies $E_{\text{bulk}} = 9.2 \pm 0.5$ kcal/mol for bulk PVME and $E_{\text{sol}} = 3.6 \pm 0.3$ kcal/mol for PVME solution.

The activation energy determined for τ_1 processes can be interpreted in terms of the Kramers theory for the diffusion of a particle over a potential barrier.[36] This theory has been applied to the case of conformational transitions in polymer chains by Helfand.[37] According to this theory, the correlation time associated with a motional mode involving the crossing of an energy barrier E^* in a hydrodynamic regime governed by viscous friction can be written as

$$\tau \simeq \eta C \exp(E^*/RT) \tag{17}$$

where η is the viscosity and C is a molecular constant.

The activation energy of the conformational jumps associated with the τ_1 correlation time can then be estimated from

$$E^* = E_{\text{sol}} - E_\eta \tag{18}$$

where E_η is the activation energy for the solvent viscosity.

In the case of chloroform at 25 °C, $E_\eta = 1.4$ kcal/mol, and therefore $E^* = 2.2$ kcal/mol.

Inasmuch as the segmental motions in the bulk state have been shown to be of the same nature as the solution ones, the height of the conformational barrier for type τ_1 motions in bulk PVME should not differ significantly from the solution conformational barrier. Therefore, the large difference observed between E_{bulk} and E^* indicates that intermolecular interactions have a major importance in bulk polymers.

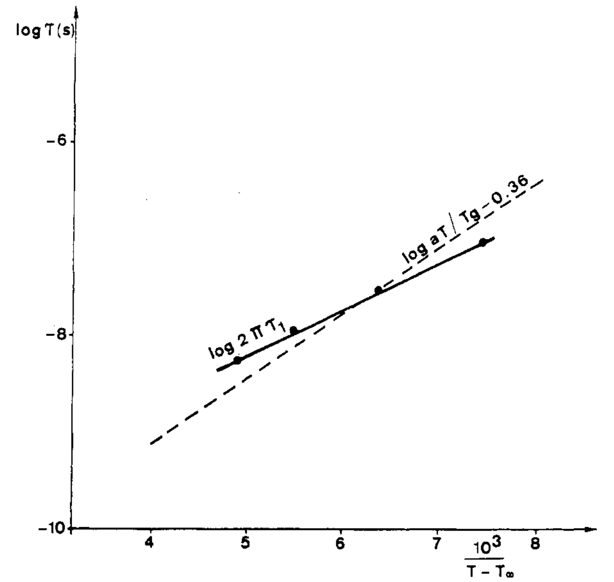


Figure 8. Comparison of log τ_1 and log a_{T/T_g} dependences on $10^3/(T - T_\infty)$.

It is also of interest to compare the variations of τ_1 as a function of temperature with the predictions of the Williams–Landel–Ferry (WLF) equation,[7] which describes the frequency dependence of the motional processes associated with the glass transition phenomena. It can be written as[38]

$$\log a_{T/T_g} = -\frac{C_1^g(T - T_g)}{C_2^g + T - T_g} \tag{19}$$

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 that 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

$$\log a_{T/T_g} = -C_1^g + \frac{C_1^g C_2^g}{T - T_\infty} \tag{20}$$

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 bulk PVME are $T_\infty = 188$ K, $C_1^g = 11.46$, and $C_1^g C_2^g = 671.64$ K.[39] In Figure 8 are plotted the variations of log a_{T/T_g} and of log τ_1 as a function of $10^3/(T - T_\infty)$. The slopes of the two lines are quite similar, which shows that the segmental motions associated with the τ_1 process belong to the processes that are involved in the glass transition phenomenon. Identical results have been reported in ref 6.

Conclusion

The most striking results reported in this paper relate to the high value of the carbon-13 T_1 relaxation time minimum observed as a function of temperature, which can be accounted for only by considering, in addition to the conformational jumps of a polymer chain described by the Hall–Helfand[13] or Viovy–Monnerie–Brochon[14] autocorrelation functions, fast librations of limited but significant angular extent of the internuclear CH vectors. The amplitude of these librations is identical in bulk at temperatures well above T_g and in solution, pointing to their entirely intramolecular origin. It must be noticed that the presence of this high-frequency motion as detected by NMR relaxation is not in contradiction with results obtained from fluorescence anisotropy decay experiments:[12] molecular librations of limited angular extent are very local processes, which cannot be probed by a bulky fluorescent label and its fluorescence depolarization.

Another important result in this study of bulk poly(vinyl methyl ether) is the similarity of the temperature variation of the correlation time τ_1, associated with conformational jumps, to the predictions of the Williams–Landel–Ferry equation for viscoelastic relaxation, which indicates that the segmental motions observed by NMR belong to the glass transition phenomena.

These conclusions that have been derived for the case of poly(vinyl methyl ether) are supported by similar experiments that we have carried out on a large series of bulk polymers. Results obtained on poly(ethylene oxide) and poly(propylene oxide) are reported in the following paper in this issue.[29] Other investigations of local dynamics of bulk polybutadiene, polyisoprene, and polyisobutylene, which allow the influence of the chemical structure of the polymer chain to be studied and generalize the results of the PVME study, will be published later.

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Registry No. PVME, 9003-09-2.

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Carbon-13 NMR Investigation of Local Dynamics in Bulk Polymers at Temperatures Well Above the Glass Transition Temperature. 2. Poly(propylene oxide) and Linear and Cross-Linked Poly(ethylene oxides)

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ABSTRACT: Carbon-13 spin–lattice relaxation time measurements have been performed at two experimental frequencies on the considered polymers, and 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 the preceding paper. As observed in the latter compound, a fast motion of the internuclear vector has to be considered and has been assigned to a libration of limited extent about the rest position. The temperature dependence of the segmental motions proves that these modes are involved in the glass–rubber transition process. Furthermore, the effect of cross-linking on the dynamics of poly(ethylene oxide) segments has been studied.

Detailed analysis of carbon-13 spin–lattice relaxation times T_1 of poly(vinyl methyl ether) both in solution and in the bulk state at temperatures above the glass transition phenomenon have been reported in the first paper of this series.[1] It has been shown that the well-known autocorrelation functions derived from models of conformational jumps in polymer chains,[2-4] which have proved to be very powerful in describing fluorescence depolarization data,[5]

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