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Table I
Dichroism of Infrared Bands for Disklike Molecules and Polymers

BH8-6,6-d_2		PBHA-18	
cm^{-1}	dichroism	cm^{-1}	dichroism
		1780	perpendicular
1778	perpendicular		
1760	parallel		
1483	perpendicular		
1439	parallel		
1433	parallel		
		1416	perpendicular
1415	parallel		
		1379	parallel
1375	parallel		
1321	parallel		
1287	perpendicular		
		1233	parallel
		1220	parallel
1220	parallel		
		1202	parallel
1188	perpendicular		
1173	parallel		

drocarbon chain attached to the oxygen on the benzene ring in the gauche conformation, the six CH_3 deformation modes transform under C_6 symmetry as $A + B + E_1 + E_2$, or as $A_g + E_g + A_u + E_u$ under S_6 symmetry, just as do the carbonyl stretching modes. Again, the A or A_u component has its transition moment along the molecular symmetry axis and is thus parallel to the normal to the external surface when the disklike cores are oriented parallel to it, even though the transition moment of any individual CH_3 symmetric deformation may be inclined at different angles to the plane of the benzene ring and the 6-fold symmetry axis. Thus, no information concerning these angles or the orientation of the zigzag hydrocarbon chain can be secured from the polarization state in the oriented crystal. The E_1 or E_u component is required to have its transition moment in a plane perpendicular to the 6-fold axis, but there is no further directional requirement imposed by symmetry. Possibly this component does not appear in the infrared with appreciable intensity because of an indeterminacy in phase from one molecule to the next, due to small intermolecular interactional forces. Evidently, similar comments apply to the other entries in Table I.

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Registry No. BH8-*6,6-d_2*, 111268-95-2; (hexadecanedioic acid chloride)(hexahydroxybenzene 1,2,4,5-tetraheptanoate) (copolymer), 119243-75-3; (hexadecanedioic acid chloride)(hexahydroxybenzanoate) (SRU), 119365-99-0.

References and Notes

(1) Kreuder, W.; Ringsdorf, H. *Makromol. Chem. Rapid Commun.* **1983**, *4*, 807.
(2) Kreuder, W.; Ringsdorf, H.; Tschirner, P. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 367.
(3) Wenz, G. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 577.
(4) Hermann-Schonherr, O.; Wendorff, J. H.; Ringsdorf, H.; Tschirner, P. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 791.
(5) Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A.; Madhusudana, N. V.; Kumar, S.; Shasshid, R.; Venkatesh, G. *J. Phys. Colloque* **1979**, *C3*, 120.
(6) Goozner, R. E.; Labes, M. M. *Mol. Cryst. Liq. Cryst.* **1979**, *56*, 75.
(7) Sorai, M.; Kazuhiro, T.; Hiroshi, S.; Syuzo, S. *Mol. Cryst. Liq. Cryst.* **1980**, *59*, 33.
(8) Sorai, M.; Hiroshi, S. *Mol. Cryst. Liq. Cryst.* **1981**, *73*, 47.
(9) Sorai, M.; Hideki, Y.; Hiroshi, S. *Mol. Cryst. Liq. Cryst.* **1982**, *84*, 39.
(10) Lifshitz, E.; Goldfarb, D.; Vega, S.; Luz, Z.; Zimmermann, H. *J. Am. Chem. Soc.* **1987**, *109*, 7280.
(11) Yang, X.; Kardan, M.; Hsu, S. L.; Collard, D.; Heath, R. B.; Lillya, C. P. *J. Phys. Chem.* **1988**, *92*, 196.
(12) Kardan, M.; Reinhold, B. B.; Hsu, S. L.; Thakur, R.; Lillya, C. P. *Macromolecules* **1986**, *19*, 616.
(13) Kardan, M.; Kaito, A.; Hsu, S. L.; Thakur, R.; Lillya, C. P. *J. Phys. Chem.* **1987**, *91*, 1809.
(14) Schmidt, P. G. *J. Polym. Sci., A1* **1963**, 1271.
(15) Koenig, J. L.; Itoga, M. *Appl. Spectrosc.* **1971**, *25*, 355.
(16) Frank, F. C.; Chandrasekhar, S. *J. Phys.* **1980**, *41*, 1285.
(17) Yang, X.; Hsu, S. L. *J. Chem. Phys.* **1988**, *89*, 5950.
(18) Levlut, A. M. Proceedings, International Crystals Conference Bangalore, Dec 21, 1979.
(19) Abe, A. *J. Am. Chem. Soc.* **1984**, *106*, 14.
(20) Snyder, R. G.; Hsu, S. L.; Krimm, S. *Spectrochim. Acta* **1978**, *34A*, 395.

Carbon-13 NMR Investigation of Local Dynamics in Bulk Polymers at Temperatures Well above the Glass-Transition Temperature. 4. Polyisobutylene

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ABSTRACT: Carbon-13 spin-lattice relaxation time measurements have been performed at two experimental frequencies on the considered polymer in solution and in the bulk state at temperatures well above the glass-transition temperature. 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 must be considered. It can be assigned to librations of limited but significant extent about the rest position. Moreover, the temperature dependence of the segmental motions in bulk polyisobutylene can be understood by considering both glass-transition and secondary relaxation processes.

Detailed analysis of carbon-13 nuclear magnetic relaxation in poly(vinyl methyl ether), poly(propylene oxide), and cross-linked poly(ethylene oxides), polybutadiene, and polyisoprene, either in solution or in bulk at temperatures well above the glass-rubber transition temperature T_g, has been reported in the first papers of this series.[1-3] It has been shown that the well-known autocorrelation functions derived from models of conformational jumps in polymer

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chains,[4-6] which have proven to be relevant in describing fluorescence anisotropy decay data,[7] 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, in addition to 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 the internuclear vectors about their rest position.[1-3] The extent of the libration was shown to be independent of the state (solution or bulk) of the polymer chain and appeared to be related to the steric hindrance at the considered site.

The purpose of this paper is to study the influence of molecular structure on local dynamics and to reach a better understanding of the parameters used in the above orientation autocorrelation function through the example of polyisobutylene. Carbon-13 spin-lattice relaxation times T_1 of polyisobutylene have already been determined by several authors.[8-11] However, the temperature range investigated was not large enough to observe the minimum of T_1. As shown in the previous papers,[1-3] the height of T_1 at its minimum is a crucial parameter for the test of the orientation autocorrelation function. Therefore, we report in this paper the analysis of carbon-13 nuclear magnetic relaxation in polyisobutylene in solution and in bulk at temperatures well above the glass-transition temperature, in a temperature range wide enough to observe the T_1 minimum.

Experimental Section

The polyisobutylene was purchased from Aldrich. Its molecular weight is $M_n = 1\,300\,000$. Its glass-transition temperature, as measured by DSC at the heating rate of 20 deg/min, is -60 °C.

NMR experiments were carried out either on bulk polyisobutylene or on 10% (w/w) deuteriochloroform polymer solutions. Solution and bulk polymer samples were carefully degassed and the tubes were sealed under vacuum. For 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%.

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[12]

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

where ω_H and ω_C are the ^1H and ^{13}C resonance frequencies, r_{CH} is the internuclear distance taken here as 1.09 Å as discussed in ref 1 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.

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	$G(t) = \exp\left(-\frac{t}{\tau_2}\right)\exp\left(-\frac{t}{\tau_1}\right)\left[I_0\left(\frac{t}{\tau_1}\right) + gI_1\left(\frac{t}{\tau_1}\right)\right]$
DLM	$G(t) = (1-a)\exp\left(-\frac{t}{\tau_2}\right)\exp\left(-\frac{t}{\tau_1}\right)I_0\left(\frac{t}{\tau_1}\right) + a\exp\left(-\frac{t}{\tau_0}\right)$

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 discussion, we will use either the Hall-Helfand (HH)[4] or the Viovy-Monnerie-Brochon (VMB)[5] expression for the autocorrelation function $G(t)$ to describe the local polymer chain dynamics. These expressions are given in Table I where I_0 and I_1 are the modified Bessel functions of order 0 and 1, respectively.

Taking into account an additional libration of the internuclear vector about its rest position, described in terms of an anisotropic reorientation occurring with a correlation time τ_0 inside a cone of half-angle θ, and assuming that the segmental motions and libration process are independent, one obtains the complete Dejean-Lauprêtre-Monnerie expression written as[1]

$$G(t) = (1 - a)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) + a\exp(-t/\tau_0)\exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1) \quad (3)$$

where

$$1 - a = [(\cos\theta - \cos^3\theta)/2(1 - \cos\theta)]^2 \quad (4)$$

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 expression for $G(t)$ can be simplified to give the equation later referred as (DLM) and shown in Table I.

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

$$\frac{1}{T_1} = (1 - a)\frac{\hbar^2\gamma_C^2\gamma_H^2}{10}\frac{1}{r_{CH}^6}[J_{HH}(\omega_H - \omega_C) + 3J_{HH}(\omega_C) + 6J_{HH}(\omega_H + \omega_C)] + a\frac{\hbar^2\gamma_C^2\gamma_H^2}{10}\frac{1}{r_{CH}^6}[J_0(\omega_H - \omega_C) + 3J_0(\omega_C) + 6J_0(\omega_H + \omega_C)] \quad (5)$$

where

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

and

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

With the assumption of fast segmental motions, $\tau_0 \ll \tau_1$, τ_2 and $(\omega_H + \omega_C)\tau_1 \ll 1$, the second term can be neglected in expression 5. Under this condition, the minimum value of T_1 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. But, as shown by calculations reported in ref 1, the correlation

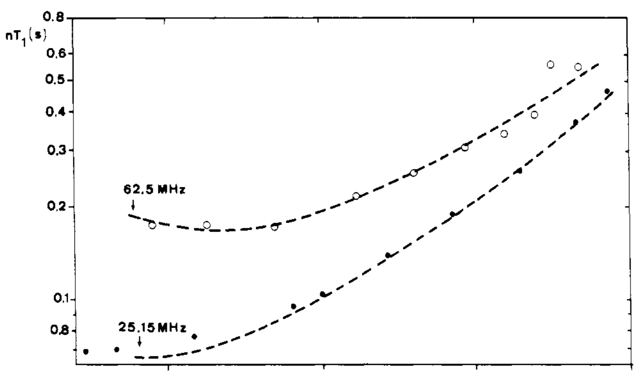

Figure 1. 62.5- and 25.15-MHz ^{13}C spin-lattice relaxation times (nT_1) for polyisobutylene in $CDCl_3$ solution: (--) best fit calculated from the DLM autocorrelation function; $a = 0.21$, $\tau_1/\tau_0 = 150$, $\tau_2/\tau_1 = 40$, $r_{CH} = 1.09$ Å.

Table II
Comparison of Experimental and Calculated (nT_1) (s) Values in Polyisobutylene

ω_C	62.5 MHz	25.15 MHz
exptl (in soln)	0.170	0.066
exptl (in bulk)	0.180	0.060
isotropic model	0.100	0.040
HH	0.128	0.050
VMB	0.135	0.054

time of the libration only influences the T_1 values in the "long time" part of the curves.

Results and Discussion

Polyisobutylene Nuclear Magnetic Relaxation in Solution. ^{13}C spin-lattice relaxation times have been determined for a 10% (w/w) $CDCl_3$ solution of polyisobutylene at 25.15 and 62.5 MHz in the temperature range -64 to 55 °C. The temperature dependence of (nT_1) for the methylene carbon of polyisobutylene is shown in Figure 1. n is the number of protons directly bonded to the carbon of interest.

Results presented in Figure 1 show that T_1 is minimized in the low-temperature region under investigation. Thus extreme narrowing conditions are not fulfilled, which indicates that in this temperature range molecular motions in polyisobutylene solution are slow enough to allow a very precise analysis of molecular dynamics in solution.

The (nT_1) minima are 0.066 and 0.170 s at 25.15 and 62.5 MHz, respectively. These values are much higher than those which can be calculated from the specific models of chain dynamics. A comparison of experimental and calculated (nT_1) values using the Hall–Helfand[4] and Viovy–Monnerie–Brochon[5] autocorrelation functions is shown in Table II. These results, which are very similar to those observed in poly(vinyl methyl ether),[1] poly(propylene oxide),[2] polybutadiene, and polyisoprene[3] show that, independent of the chain structure, at the temperature of its minimum, the carbon-13 spin-lattice relaxation time is too high to be accounted for by the above specific models for chain dynamics. Such a high value of T_1 is evidence that a rapid motion is 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,[3] as well as in polypropylene 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. For the polymers previously investigated this anisotropic process has been interpreted in terms of a libration, the amplitude of which depends on the steric hindrance at the considered site. According to the treatment of Howarth,[13] this libration is described by an anisotropic reorientation inside a cone of half-angle θ and with an axis which is the rest position of the carbon–proton bond. Using expression 5 to represent the T_1 values of the minimum in polyisobutylene in solution leads to $a = 0.21$ and $\theta = 23°$. It must be noticed that among all the polymers which we have studied by this technique,[1-3] polyisobutylene presents the largest steric hindrance at a methylene site and the smallest amplitude of libration. Therefore, for this polymer too, the correlation between θ and the steric hindrance appears to hold true.

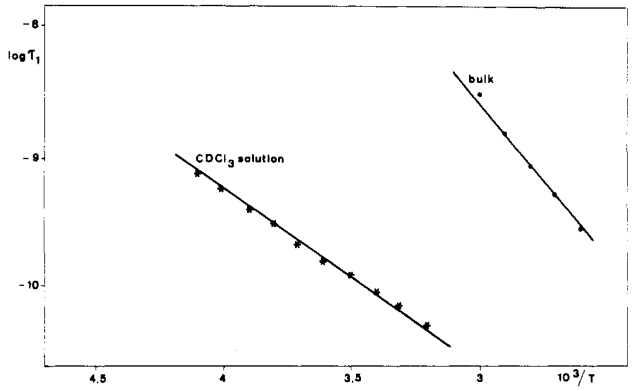

Figure 2. Plot of log τ_1 versus $1/T$ in polyisobutylene in $CDCl_3$ solution and in bulk.

In order to fit 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. In the case of poly(vinyl methyl ether), the experimental (nT_1) values in solution and in bulk are identical at the T_1 minimum, which implies that the libration amplitude is the same in both states[1] and supports the above assumption. Under those 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. The best fit is shown in Figure 1 for the spin–lattice relaxation times at the two Larmor frequencies. It corresponds to $\tau_1/\tau_0 = 150$. In the domain of temperature under study, τ_2 (and therefore the τ_2/τ_1 ratio) cannot be accurately determined. However a good agreement between theory and experiment is obtained for τ_2/τ_1 equal to 40. This last result indicates that, in polyisobutylene in solution, the diffusion motion of bond orientations along the chain is slightly damped.

τ_1 values obtained from fitting experimental data of polyisobutylene in $CDCl_3$ solution to the motional model based on independent segmental motions and librations of the internuclear vectors are plotted as a function of $1/T$ in Figure 2. 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 leads to an apparent activation energy: $E_{sol} = 6.4 \pm 0.5$ kcal/mol. Using the same DLM orientation autocorrelation function and values of a, τ_1/τ_0, and τ_2/τ_1 determined for polyisobutylene in $CDCl_3$ solution, we have obtained $E_{sol} = 6.7$ and 6.0 kcal/mol from data reported by Jones et al.[11] and Inoue et al.[10] for polyisobutylene in CCl_4 and o-dichlorobenzene solutions, respectively. In terms of the Kramers theory for the diffusion of a particle over a potential barrier,[14] the activation energy E_{sol} is the sum of an activation energy for the

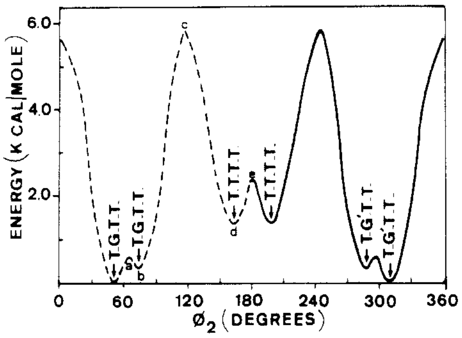

Figure 3. Rotational energy diagram of 2,2,4,4,6,6-hexamethylheptane (PIB "dimer") along the least energy path (see ref 17).

solvent viscosity, E_η (E_η = 1.4 kcal/mol in the case of chloroform and E_η = 2.4 kcal/mol for CCl_4 and *o*-dichlorobenzene), and an energy barrier originating from conformational jumps, E^*, which is 5.0 kcal/mol from our experiments. The same calculation yields E^* = 4.3 and 3.6 kcal/mol from the data of Jones et al.[11] and Inoue et al.,[10] respectively. These rather large values, which are in the range of 4–5 kcal/mol within experimental precision, are in reasonable agreement with the value U_0 of the height of the rotational barrier about the CH_3–$C(CH_3)_3$ bond in 2,2-dimethylpentane, as determined from infrared spectroscopy: U_0 = 4.4 kcal/mol.[15] They can also be compared with results of conformational energy calculations carried out by Allegra et al.[16] and Boyd and Breitling.[17] In both papers, the chain conformation in the unperturbed state is satisfactorily described in terms of a statistical sequence of "staggered" (T, G, and G′) rotational states: pairs of bonds are distorted (about 20°) in the same sense (+ or −), leading to T^+T^+, T^-T^-, T^+G^+, $T^+G'^+$, T^-G^-, and $T^-G'^-$ conformations. Results reported in ref 16 indicate that the energy barriers between T, G, and G′ rotational states are in the range 5–10 kcal/mol. More precise values of the energy barriers have been calculated by Boyd and Breitling.[17] They are shown in Figure 3. Large-amplitude conformational jumps require the crossing of energy barriers of 4.5, 5.5, and 5.85 kcal/mol, in quite reasonable agreement with out experimental determination of E^*. The small-amplitude conformational jumps between staggered states correspond to rotational angle changes of about 30° and energy barriers of 0.4–0.6 kcal/mol.

Nuclear Magnetic Relaxation in Bulk Polyisobutylene. Spin–lattice relaxation times T_1 determined for the CH_2 carbon of bulk polyisobutylene at 25.15 and 62.5 MHz are plotted on Figure 4. The values of (nT_1) at the T_1 minimum are 0.060 and 0.18 s at 25.15 and 62.5 MHz, respectively. They are very close to those determined for polyisobutylene in solution. This result implies that in bulk polyisobutylene there also exists, besides the segmental modes described by τ_1 and τ_2, a fast anisotropic motion whose amplitude is close to the amplitude of the additional fast process observed in solution. Assuming a libration of the internuclear vector, the parameter a in expression 5 is a = 0.21. The best fit of the experimental values using the DLM autocorrelation function is shown in Figure 4. It corresponds to τ_1/τ_0 = 150 and τ_2/τ_1 greater than 40. Within the accuracy of the data analysis, the ratios τ_2/τ_1 and τ_1/τ_0 are almost identical in bulk and in solution.

The temperature dependence of the correlation time τ_1 associated with the correlated conformational jumps in bulk polyisobutylene can be compared to the temperature dependence of the motional processes associated with the glass-transition phenomena, which can be anticipated from the Williams, Landel, and Ferry (WLF) equation for viscoelastic relaxations:[18]

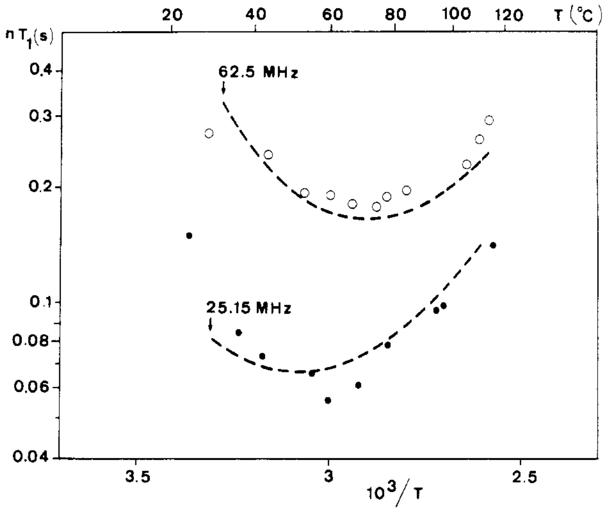

Figure 4. 62.5- and 25.15-MHz ^{13}C spin–lattice relaxation times (nT_1) of the CH_2 carbon in bulk polyisobutylene: (- -) best fit calculated from the DLM autocorrelation function; a = 0.21, τ_1/τ_0 = 150, τ_2/τ_1 > 40, r_{CH} = 1.09 Å.

$$\log a_{T/T_g} = -\frac{C_1^g(T - T_g)}{C_2^g + T - T_g} \qquad (6)$$

where $a_{T/T_g} = \tau_C(T)/\tau_C(T_g)$, $\tau_C(T)$ is the viscoelastic relaxation time at temperature T, $\tau_C(T_g)$ 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. Using the temperature $T_\infty = T_g - C_2^g$ for which a_{T/T_g} tends to infinity, the WLF equation is written:

$$\log a_{T/T_g} = -C_1^g + \frac{C_1^g C_2^g}{T - T_\infty} \qquad (7)$$

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 polyisobutylene are[19] T_∞ = 101 K, C_1^g = 16.6 for T_g = 205 K, and $C_1^g C_2^g$ = 1733 K. 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 5. The slope derived from the alignment of the NMR correlation times τ_1 is smaller than that predicted by the WLF law in the temperature range under study. This behavior indicates that in polyisobutylene NMR does not probe exactly the same type of motions as those which are responsible for the glass-transition phenomena. This result is in contrast to the behavior of poly(vinyl methyl ether),[1] poly(propylene oxide),[2] and polyisoprene,[3] whose correlation times τ_1 as determined by NMR have been shown to follow the WLF law. It can be understood by using the complete relaxation map (Figure 6) established by Tormala[20] from a large series of relaxation data obtained from a number of different techniques including dielectric, mechanical, ^1H NMR, and ESR experiments. We have added the motional frequencies, $f = 1/2\pi\tau_1$, derived from our ^{13}C NMR experiments on bulk polyisobutylene, to this relaxation map. All of the data plotted on the map, including ours, are distributed on a set of curves which have been interpreted in terms of glass-transition and secondary δ, γ, and γ' relaxation processes. The δ relaxation process has been assigned to

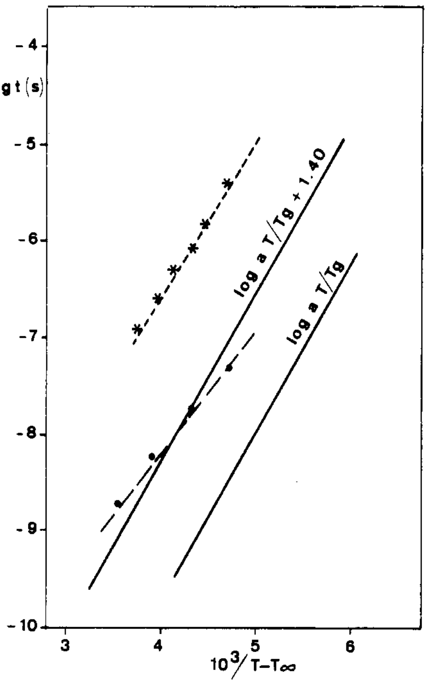

Figure 5. Comparison of log $2\pi\tau_1$ and log a_{T/T_g} dependences on $10^3/(T - T_\infty)$: (●) NMR data; (*) reciprocal of excimer formation frequencies from ref 25.

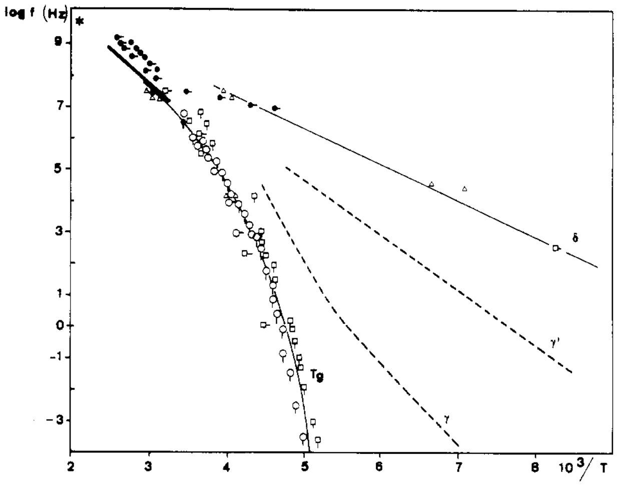

Figure 6. Relaxation map of polyisobutylene. ^{13}C NMR: (—) (this work). Brillouin scattering data: (*).[24] Dielectric data: (○);[27] (○-);[21] (♀).[22] Mechanical data: (□);[27] (□-);[21] (□̩).[22] ^{1}H NMR data: (△).[21] ESR data: (●);[28] (●-);[29] (♦);[23] (-●).[30] (See ref 20).

the rotation of the methyl groups of polyisobutylene.[21] The γ and γ' relaxations are due to isolated large-amplitude conformational jumps of the main chain.[22] Correlation times τ_1 derived from NMR spin–lattice relaxation experiments are in the high-frequency domain of the relaxation map. Since they describe the main-chain methylene carbon dynamics, they are not expected to be influenced by the δ relaxation of the methyl groups of polyisobutylene. On the other hand, they lie in the region where the glass-transition and γ and γ' relaxations merge. In this region, the temperature dependence is no longer ruled by the WLF law. The variation of log τ_1 as a function of $10^3/T$ is plotted in Figure 2. It appears to be linear in the temperature range under study and the measured apparent activation energy, 10.7 kcal/mol, reflects the temperature evolution of the different motional processes as a whole. It must be noticed that the agreement between ^{13}C NMR and ESR data using large probes[23] in these frequency and temperature ranges is very good. Additionally, the maximum loss at gigahertz frequencies measured by Brillouin scattering[24] correlates reasonably well with the extrapolation of the ^{13}C NMR data. ESR experiments using large probes, ^{13}C NMR, and Brillouin scattering thus appear to reflect similar local motional processes. They differ somewhat from the excimer fluorescence technique which probes slower motions and whose results shown in Figure 5 are in better agreement with the predictions of the WLF equation for viscoelastic relaxation.[25]

Conclusion

The carbon-13 spin–lattice relaxation time determinations performed on polyisobutylene in solution and in the bulk state at temperatures well above the glass-transition temperature have shown that the local dynamics of these polymers can be satisfactorily represented by considering a fast anisotropic process, interpreted as a libration, in addition to the segmental motions characterized by the two correlation times of the Hall–Helfand model. The same motional model has been successfully used to describe the NMR relaxation of a number of polymers.[1-3] Moreover, the fact that libration-type motions have been also observed by neutron scattering[26] leads us to conclude that the existence of fast bond librations 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 of this study is the fact that the correlation times τ_1, associated with correlated conformational jumps in bulk polyisobutylene, do not depend as strongly on temperature as anticipated from the Williams, Landel, and Ferry equation for viscoelastic relaxation. In the frequency domain under investigation, the spin–lattice relaxation of the main-chain methylene carbon probes the ensemble of processes which result from the merging of both glass-transition and secondary relaxations of polyisobutylene.

Registry No. Polyisobutylene, 9003-27-4.

References and Notes

(1) Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1988**, *21*, 2045.
(2) Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1988**, *21*, 2052.
(3) Dejean de la Batie, R.; Laupretre, F.; Monnerie, L. *Macromolecules* **1989**, *22*, 122.
(4) Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.
(5) Viovy, J. L.; Monnerie, L.; Brochon, J. C. *Macromolecules* **1983**, *16*, 1845.
(6) Jones, A. A.; Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *15*, 847.
(7) Viovy, J. L.; Monnerie, L.; Merola, F. *Macromolecules* **1985**, *18*, 1130.
(8) Komoroski, R. A.; Mandelkern, L. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 54*, 201.
(9) Heatley, F. *Polymer* **1975**, *16*, 493.
(10) Inoue, Y.; Nishioka, A.; Chûjô, R. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 2237.
(11) Jones, A. A.; Lubianez, R. P.; Hanson, M. A.; Shostak, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1685.
(12) Allerhand, A.; Doddrell, D.; Komoroski, R. J. *J. Chem. Phys.* **1971**, *55*, 189.
(13) Howarth, O. W. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 863.
(14) Kramers, H. A. *Physica (Amsterdam)* **1950**, *7*, 248.
(15) Volkenstein, M. V. *Configurational Statistics of Polymeric Chains*; Interscience: New York, 1963.
(16) Allegra, G.; Benedetti, E.; Pedone, C. *Macromolecules* **1970**, *3*, 727.
(17) Boyd, R. H.; Breitling, S. M. *Macromolecules* **1972**, *5*, 1.
(18) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(19) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(20) Tormala, P. *J. Macromol. Sci., Rev. Macromol. Chem.* **1979**, *17*, 297.

(21) Slichter, W. P. *J. Polym. Sci., Part C* **1966**, *14*, 33.
(22) Stoll, B.; Pechhold, W.; Blasenbrey, S. *Kolloid Z. Z. Polym.* **1972**, *250*, 1111.
(23) Alexandrovna, A. T.; Vasserman, A. M.; Kovarskii, A. L.; Tager, A. A. *Vysokomol. Soedin., Ser. B* **1976**, *18*, 322.
(24) Patterson, G. D. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 455.
(25) Jing, D. P. Thèse de l'Université Pierre et Marie Curie, Paris, 1988.
(26) Buchenau, U.; Monkenbusch, M.; Stamm, M.; Majkrzak, C. F.; Nucker, N. Workshop on Polymer Motion in Dense Systems, Grenoble, Sept 23–25, 1987.
(27) McCrum, M. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: London, 1967.
(28) Stryukov, V. B.; Korolev, G. V. *Vysokomol. Soedin., Ser. A* **1969**, *11*, 419.
(29) Stryukov, V. B.; Sosnina, T. V.; Kraitsberg, A. M. *Vysokomol. Soedin., Ser. A* **1973**, *15*, 1397.
(30) Tormala, P.; Weber, G. *Polymer* **1978**, *19*, 1026.

Electron Spin Resonance Study of Radicals in Photopolymerized Di(meth)acrylate Network

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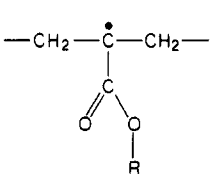
ABSTRACT: ESR spectra of free radicals trapped in photopolymerized HDDA (1,6-hexanediol diacrylate) and HDDMA (1,6-hexanediol dimethacrylate) were (re)examined. Careful analyses of the spectral patterns, the hyperfine structures due to β-protons, revealed that the radicals in the polymethacrylate are the propagation radicals of the conformation with the least strain energy (trans form) and those in the polyacrylate are the midchain radicals resulting from the C_α–H_α cleavage at diad sectors of the conformation with the highest strain energy (gauche–gauche form). When both polymers were formed on an inert high-surface-area substrate and exposed to oxygen at low temperature (−18 °C), instant conversion of the radicals to the peroxy radicals ROO• was observed. The resulting peroxy radicals decayed rapidly at room temperature ($t_{1/2}$ = ~3 min).

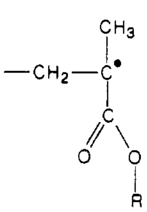
Introduction

A densely cross-linked poly(meth)acrylate network produced by polymerization of multi(meth)acrylate (e.g., 1,6-hexanediol diacrylate) is used in many commercial applications.[1] The monomer formulation typically contains several weight percent of radical photoinitiator such as α,α-dimethoxy-α-phenylacetophenone and is *photopolymerized* by exposure to UV light. It is not surprising that the dense polymer network thus created hosts either the propagation radical or the secondary radical product of the polymerization processes trapped as the monomer ingredients are consumed, and the rigidity and size of the polymer network increase rapidly during the photocuring process.

Kloosterboer et al. indeed reported on the ESR spectra of stable radicals trapped in photopolymerized 1,6-hexanediol diacrylate (HDDA)[2] and bis(2-hydroxyethyl)bisphenol A dimethacrylate (HEBDMA).[3] The stable radical in the former network was identified unequivocally, through the use of HDDA deuterated in the α position of the acrylate sector, as the midchain radical I resulting from the C–H cleavage at the α position of the acrylate chain.[2] The stable radical in the latter network exhibited the well-known, well-characterized "5 + 4" line ESR pattern ascribed to the propagation radical II of the methacrylate chain.[4]



I



II

The ESR spectrum of the midchain radical observed from polymerized HDDA (I) has an appearance of being a 1:2:1 triplet of ~25-G spacings. The pattern was hence attributed to the hyperfine (hf) interaction of ~25 G with one proton each of the two β-methylene groups and negligibly small hf interaction with the remaining β-protons.[2] The reported spectrum of the midchain radical, however, does not possess a simple 1:2:1 triplet pattern. A further scrutiny of the spectrum appeared warranted; a successful scrutiny should shed light on the conformation of radical sites. The "5 + 4" line pattern of the propagation radical II of the polymethacrylate system had long eluded a definitive assignment but was elegantly elucidated by Iwasaki and Sakai as that arising from the hf interactions of the protons of a freely rotating methyl group and those of the β-methylene group in a certain conformation with some statistical scatter.[5]

Kloosterboer et al. also reported that the radicals I and II trapped in the network of polymerized HDDA and HEBDMA were extremely stable under vacuum at room temperature but decayed rapidly at room temperature under oxygen. No ESR signal due to peroxy radical was detected, however.[2]

The present paper reports on the results of detailed analysis of the ESR spectra of the midchain and propagation radicals I and II detected in photopolymerized HDDA and HDDMA (1,6-hexanediol dimethacrylate). The analysis revealed that the midchain radical I was generated at sites where the diad segment of the acrylate chain had the conformation of the highest strain energy (gauche–gauche form), while the conformation of the propagation radical II was consistent with the methacrylate chain end having the conformation of the least strain energy (trans form). We also succeeded in observing (by ESR) instant conversion of radicals I and II to peroxy radicals on exposure to oxygen. It was achieved by dispersing the monomer formulations on an inert, high-surface-area substrate (porous Vycor quartz). The resulting peroxy radicals decayed rapidly at room temperature.

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