nificant 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.

Acknowledgment. We express our gratitude to Dr. J. L. Viovy for helpful discussions.

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]

Table I
Abbreviated Names and Characteristics of the Linear and Cross-Linked PEO Samples

abbr name	M_n	n_s	T_g, °C
PEO 400	400	9	0
PEO 600	600	14	-26
PEO 1000	1000	23	-42
PEO 1500	1500	34	-43
PEO	9200	0	-43

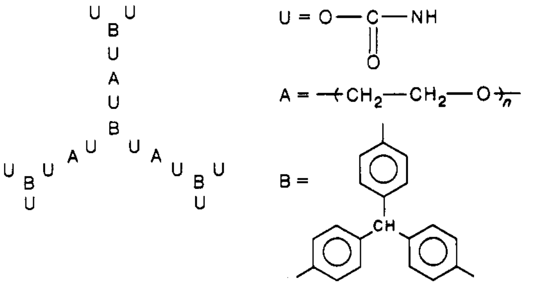
cannot account for the particularly high value of the minimum of T_1 observed as a function of temperature. Such a behavior indicates that besides the conformational jumps, which induce a damped orientation diffusion along the chain, there exists an additional fast process that is not observed in the fluorescence depolarization experiments. In the previous paper, this fast process was assigned to a libration of limited extent about the rest position of the internuclear vectors. Such librations, which are very local modes at the site of each carbon-proton bond, do not affect the reorientation of the bulky labeling fluorescent group whose motion is probed in the fluorescence depolarization technique.

The purpose of this study is to examine whether this particular behavior is specific to poly(vinyl methyl ether) or if it is a general feature of local polymer dynamics. This work deals with carbon-13 spin-lattice relaxation time determinations in bulk poly(propylene oxide) and linear and cross-linked poly(ethylene oxides) at temperatures above the glass transition phenomenon. Comparison of the results obtained on poly(vinyl methyl ether)[1] and on this series of polymers will also allow the influence of the chemical structure on the local dynamics to be studied. It should lead to a better understanding of the different parameters that are involved in the autocorrelation function and to a deeper knowledge of the motional processes occurring above the glass transition temperature T_g.

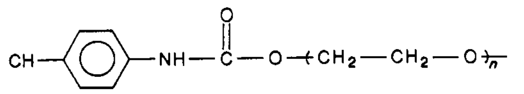
Experimental Section

Poly(propylene oxide), of molecular weight M_n = 4000, was purchased from Ega Chemie. Its glass transition temperature, as measured by differential scanning calorimetry (DSC), is -75 °C.

Cross-linked poly(ethylene oxides), obtained from reaction of low molecular weight poly(ethylene oxides) with triphenylmethane-*p,p′,p″*-triisocyanate,[6] were kindly supplied by H. Cheradame. Their chemical formula can be summarized in the following way:



Thus the poly(ethylene oxide) chains are interrupted by urethane cross-links:



The molecular weight, M_n, the mean number of ethylene oxide units between two cross-links, n_s, the glass transition temperature, and the abbreviated names of the different samples are listed in Table I.

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

The 25.15- and 62.5-MHz ^{13}C NMR spectra were recorded on a JEOL PS100 spectrometer and a Bruker WP250 spectrometer, respectively, by using the technique of proton noise decoupling. Experiments were carried out on bulk samples that were carefully degassed, and the tubes were sealed under vacuum. The lock signal was obtained from an external DMSO-d_6 tube.

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 carbon-13 nuclei. T_1 values were determined from exponential regression of the carbon-13 magnetization as a function of time *t*. The relative accuracy for each T_1 measurement has been estimated to be better than 7%.

^{13}C cross-polarization, proton dipolar decoupling, and magic-angle spinning NMR experiments were performed at 25.15 MHz on a Bruker CXP100 spectrometer, employing quadrature detection and a single radio frequency coil, which is double-tuned for both ^{13}C and ^1H. The matched spin-lock cross-polarization transfers employed ^{13}C and ^1H magnetic field strengths of 50 kHz. Spin-temperature inversion techniques were used to minimize base-line noise and roll.[7] Flip-back[8] was systematically employed to reduce the delay time between two successive pulse sequences. The spinning speed was 3.5, kHz and the spinners were made from boron nitride.

Theoretical Background

With the assumption of a purely $^{13}C-^1H$ dipolar relaxation mechanism, the spin-lattice relaxation time T_1 obtained from a ^{13}C experiment is given by the well-known expression[9]

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

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 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.

The autocorrelation functions that 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[2] or the Viovy-Monnerie-Brochon (VMB)[3] expression. These expressions are given in Table II, 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, 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.[1] Results obtained from this study demonstrate that the internuclear vectors are involved in an additional fast anisotropic process, which has been assigned to a libration of limited extent about the rest position and is described by an anisotropic reorientation occurring inside a cone of half-angle θ. The axis of the cone is the equilibrium position of the carbon–proton bond. The characteristic correlation time of the libration is τ_0. This leads to 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 checked 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 II.

$(T_1)^{-1}$ 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

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

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

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

Under the assumption of fast segmental motions $\tau_0 \ll \tau_1,\tau_2$ and $(\omega_H + \omega_C)\tau_1 < 1$, the second term can be neglected in expression 5. 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 influences the T_1 values only in the "long time" part of the curves.

Results and Discussion

Poly(propylene oxide). The ^{13}C NMR spectrum of bulk poly(propylene oxide) recorded at 25 °C at the experimental frequency of 25.15 MHz presents three peaks at 76.0, 74.3, and 18.5 ppm, assigned to the CH, CH_2, and CH_3 carbons, respectively. There is partial overlap of the peaks corresponding to the CH and CH_2 carbons, which increases at lower temperatures, making the spin–lattice relaxation time T_1 determinations less accurate.

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, respectively. In these sets of data, two points must be noticed: the first point concerns the value of the $T_{1,CH}/T_{1,CH_2}$ ratio in the temperature range of study. This ratio is 1.36 for measurements at 25.15 MHz and 1.43 for the 62.5-MHz experiments. These experimental values are very different from the approximate value of 2, which is expected from the number of protons directly bonded to each of the considered carbons and which is observed in the case of solution and bulk poly(vinyl methyl ether).[1] They indicate that the local motions in poly(propylene oxide), as observed by NMR, are not identical for the internuclear vectors associated with the CH and CH_2 carbons.

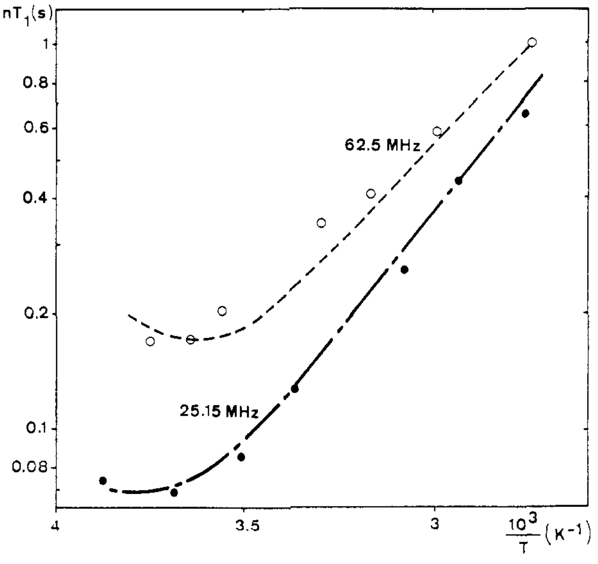


Figure 1. 62.5- and 25.15-MHz ^{13}C spin-lattice relaxation times nT_1 for the CH carbon in bulk poly(propylene oxide). Experimental points: (○) 62.5 MHz; (●) 25.15 MHz. Best fit calculated from the DLM autocorrelation function with $a = 0.24$, $\tau_1/\tau_0 = 200$, $\tau_2/\tau_1 = 80$: (- - -) 62.5 MHz; (– –) 25.15 MHz.

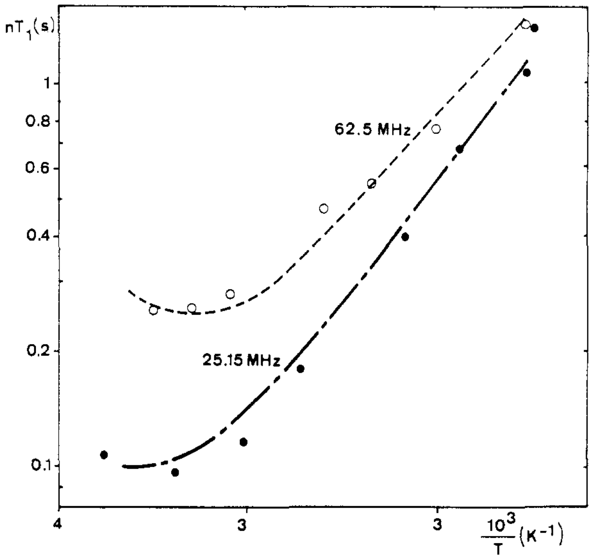


Figure 2. 25.15- and 62.5-MHz nT_1 values for the CH_2 carbon in bulk poly(propylene oxide): experimental points and best fit calculated from the DLM autocorrelation function with $a = 0.49$, $\tau_1/\tau_0 = 200$, $\tau_2/\tau_1 = 80$; same symbols as in Figure 1.

The second result is the fact that, for both CH and CH_2 carbons, the value of nT_1 at the minimum of the curve as a function of temperature is much higher than those that can be calculated from the specific models of polymer chain dynamics. Comparison of the experimental nT_1 at the minimum and calculated values from Hall–Helfand and Viovy–Monnerie–Brochon autocorrelation functions is given in Table III. Such a discrepancy might come from the fact that the isotropic overall reorientation of the chain has been neglected in the above motional description. However, the poly(propylene oxide) used in this work contains an average of 70 monomer units per polymer chain. For such a chain length, the contribution of the overall motion to the ^{13}C spin–lattice relaxation time is

Table III
Comparison of Experimental and Calculated nT_1 (Second) Values at the T_1 Minimum in Bulk Poly(propylene oxide)

	ω_C	
	62.5 MHz	25.15 MHz
CH carbon	0.168	0.068
CH_2 carbon	0.250	0.096
isotropic model	0.100	0.040
HH	0.128	0.050
VMB	0.135	0.054

generally considered to be very weak, if not insignificant. Moreover, an isotropic overall motion should affect the height of the nT_1 minimum in a similar way for both CH and CH_2 carbons. This point is not verified experimentally: as shown in Table III, the experimental nT_1 minimum at 62.5 MHz for the CH carbon is 0.168 s, quite different from the value of 0.25 s measured for the CH_2 carbon. Similar results are obtained at 25.15 MHz. It must be noted that the same type of discrepancies between experimental values and calculated ones by using Hall–Helfand or Viovy–Monnerie–Brochon autocorrelation functions has been observed in the case of poly(vinyl methyl ether) both in solution and in bulk.[1] For this high molecular weight polymer, the height of the nT_1 minimum is much larger than the values expected from the above motional models. This result has been shown to indicate the existence of an additional fast motion, which has been assigned, in the case of poly(vinyl methyl ether), to a libration of limited but significant extent of the internuclear vectors about their equilibrium position.[1] With a model of combined segmental motions of the polymer chain and librations of the internuclear vectors, the height of the nT_1 minimum is highly dependent on the amplitude of the libration mode. Under these conditions the differences in the nT_1 values at the T_1 minimum observed for the CH and CH_2 carbons of poly(propylene oxide) reflect differences in the mean amplitude of the librations associated with the carbon–proton bonds at the various sites.

Use of expression 5 to represent the T_1 values at the minimum leads to $a = 0.24$ and $a = 0.49$ corresponding to $\theta = 25°$ and $\theta = 37°$ for the CH and CH_2 carbons, respectively. These different values of θ account for the fact that the $T_{1,CH}/T_{1,CH_2}$ ratio is not approximately equal to 2, and they underline the above observation that the internuclear vectors at the two carbon sites do not share exactly the same local dynamics. It should also be noted that the size of θ can be related to the steric hindrance at the carbon site: θ and therefore the amplitude of the libration mode are larger for the internuclear vector associated with the CH_2 than for the internuclear CH vector for which the presence of the adjacent methyl group restricts the amplitude of the local libration. This correlation between the steric hindrance at the carbon site and the mean amplitude of the libration mode has been observed in a large series of polymers, and the results will be published later.

The best fit of the T_1 data obtained from formula 5 is plotted in Figures 1 and 2 for the CH and CH_2 carbons, respectively. The fitting has been performed as described in ref 1 and corresponds to $\tau_2/\tau_1 = 80$ and $\tau_1/\tau_0 = 200$. Agreement between experimental and calculated values is very satisfactory.

Variations of log τ_1 as a function of $1/T$ are plotted in Figure 3. In the temperature range under study, these variations are linear and yield an apparent activation energy of 11.7 kcal/mol. This value is compatible with those reported for bulk poly(propylene oxide) above T_g by Baur and Stockmayer,[10] Yano et al.,[11] and Fofana et al.[12] It is much higher than the activation energy for the β relaxation ($E \simeq 4$ kcal/mol) determined by Pathmanathan et al.[13] Therefore, it suggests that the observed motions, characterized by the correlation time τ_1, belong to the glass transition phenomena and not to secondary transition processes. Correlation times τ_1 calculated in this work are very close to those determined by Yano et al. using dielectric relaxation,[11] noting that under the assumption of an isotropic model where $\tau_{diel}/\tau_{NMR} = 3$, the dielectric and magnetic resonance correlation times are concerned with the first- and second-order spherical harmonics of the position coordinates, respectively. They are about 2.5 times shorter than those obtained by Patterson et al.[14] using ^1H NMR and about 10–20 times shorter than those measured by Fofana et al.,[12] Huang and Wang,[15] and Jones and Wang.[16]

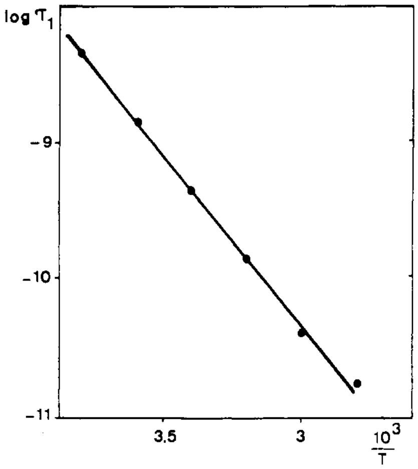


Figure 3. Plot of log τ_1 versus $1/T$ in bulk poly(propylene oxide).

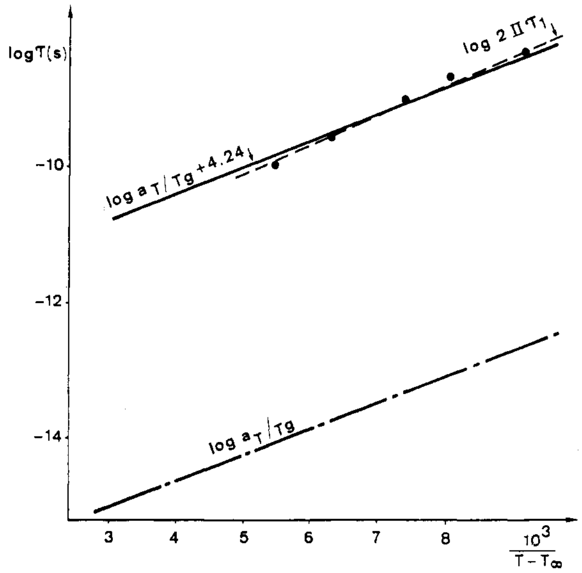


Figure 4. Comparison of log τ_1 and log a_{T/T_g} dependences on $10^3/(T - T_\infty)$ in bulk poly(propylene oxide).

In Figure 4, the temperature dependence of τ_1 is compared with the predictions of the Williams–Landel–Ferry (WLF) equation for viscoelastic relaxations:[17]

$$\log a_{T/T_g} = -C_1{}^g + \frac{C_1{}^gC_2{}^g}{T - T_\infty} \qquad (6)$$

In the case of poly(propylene oxide), WLF coefficients have been determined by Ferry:[18] $T_\infty = 174$ K, $C_1{}^g = 16.2$, and $C_1{}^gC_2{}^g = 388.8$ K. As already observed for poly(vinyl methyl ether)[1] and indeed for a large series of polymers,[19] the agreement between the viscoelastic and nuclear re-

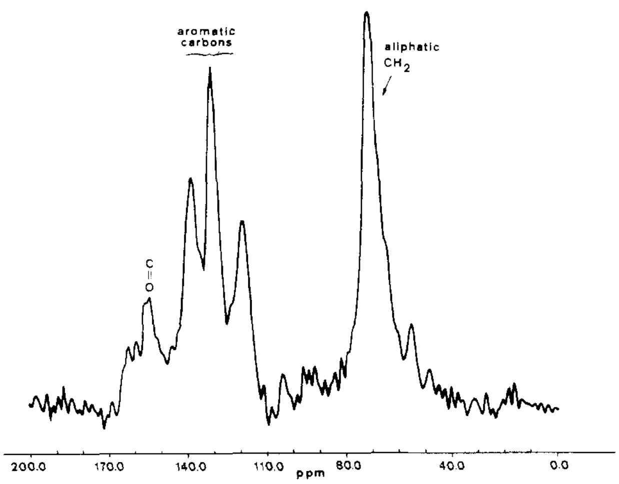
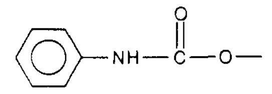


Figure 5. Cross-polarization, magic-angle spinning, dipolar decoupled 25.15-MHz ^{13}C NMR spectrum of bulk PEO 200.

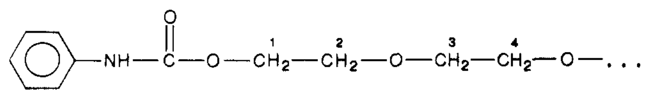
laxation behaviors is quite good, indicating that the motional modes described by the correlation time τ_1 and observed by ^{13}C NMR relaxation belong to processes that are involved in the glass transition phenomenon.

Cross-Linked Poly(ethylene oxides) (PEO). By use of the high-resolution solution ^{13}C NMR conditions of scalar proton noise decoupling, the carbons that are involved only in fast molecular motions can be observed (i.e., $\tau_1 \ll 10^{-9}$ s). The ^{13}C NMR spectra of PEO samples recorded under such conditions at 25.15 and 62.5 MHz exhibit only one peak. Located at 70.5 ppm relative to TMS, this peak can be assigned to the mobile methylene carbons of the poly(ethylene oxide) strands. On the other hand, no lines are observed in the range 100–180 ppm, corresponding to the aromatic and carbonyl carbons of the urethane groups



which act as cross-linking junctions. As may be expected, the mobility of these carbons is too low for them to be observed under solution NMR conditions.

To demonstrate the existence of these regions of low mobility in cross-linked PEOs, we recorded high-resolution solid-state ^{13}C NMR spectra of bulk cross-linked samples at 25.15 MHz and room temperature under proton dipolar decoupling, magic-angle sample spinning, and cross-polarization conditions. Only carbons possessing a carbon-13–proton dipolar interaction that is not averaged to zero by fast molecular motions can acquire magnetization through the cross-polarization mechanism.[20] The spectrum of PEO 200, which has the highest amount of cross-links and therefore is expected to present the largest percent of rigid units, is shown in Figure 5. It has been obtained by using a 1-ms contact time and exhibits several lines that are assigned to aromatic and carbonyl carbons of the cross-linking unit according to data reported in ref 21. The detailed peak assignment is given in Figure 5. An intense composite line also appears in the 60–80 ppm range, which corresponds to methylene groups of low mobility, i.e., methylene groups close to the cross-linking junctions:



Carbons 1–4 have chemical shifts that do not differ much from one another, yielding a nonresolved peak in the 60–80 ppm range. Comparison of the relative peak intensities corresponding to the carbonyl and methylene carbons leads to a very rough estimate of four methylene carbons per urethane unit which exhibit a "solid-state" behavior in the PEO 200 sample. Therefore, on each side of a cross-link there are on average about two CH$_2$–CH$_2$–O segments with very low mobility that cannot be observed in the spin–lattice relaxation time experiments carried out under scalar proton decoupling conditions. The same type of solidlike behavior for the cross-links has been observed by Patterson et al.[22] and Curran and Pawda[23] on cross-linked polybutadiene. However, in the case of the PEOs under study, this effect may also arise from a microdomain segregation of the urethane units. Experiments reported in this paper cannot distinguish between a simple slowing down of the dynamics at the cross-link sites and such a microphase separation.

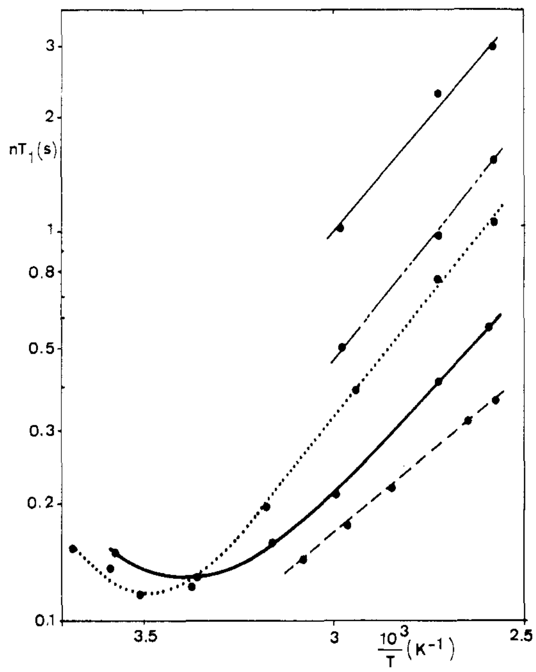


Figure 6. 25.15-MHz carbon-13 nT_1 values in bulk PEO samples: (light unbroken line) linear PEO; (- - -) PEO 1500; (···) PEO 1000; (heavy unbroken line) PEO 600; (— — —) PEO 400.

In the following, we will focus our attention on the "mobile" methylene units of cross-linked poly(ethylene oxide) samples observed by solution-type NMR experiments. The variation of the spin–lattice relaxation times T_1 determined at 25.15 and 62.5 MHz for the different compounds as a function of $1/T$ is shown on Figures 6 and 7. It can be seen that at a given temperature, these polymers present very different T_1 values. This result is particularly noticeable in the case of linear PEO (T_g = −43 °C), PEO 1500 (T_g = −43 °C), and PEO 1000 (T_g = −42 °C), which have identical glass transition temperatures as determined by DSC experiments.

From data reported in Figures 6 and 7, it appears that the T_1 value at the minimum of the curve does not depend on the length of the ethylene oxide strand: at 25.15 MHz, PEO 600 and PEO 1000 present the same value of T_1 at the minimum. Similar results are obtained at 62.5 MHz for PEO 400 and PEO 600. Due to crystallization phenomena, it was not possible to reach the T_1 minimum in the case of linear PEO and PEO 1500. In our calculations, we will assume that the T_1 minima of these two polymers have the same value as in the other poly(ethylene oxides). As observed in poly(propylene oxide), the experimental T_1 at the minimum are much too high to be represented

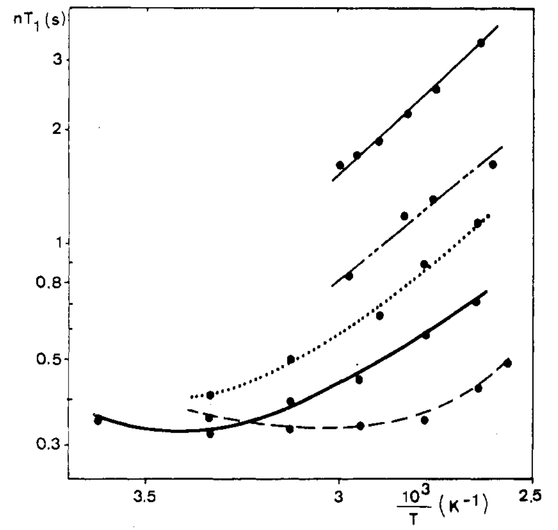


Figure 7. 62.5-MHz carbon-13 nT_1 values in bulk PEO samples: (light unbroken line) linear PEO; (- - -) PEO 1500; (···) PEO 1000; (heavy unbroken line) PEO 600; (— — —) PEO 400.

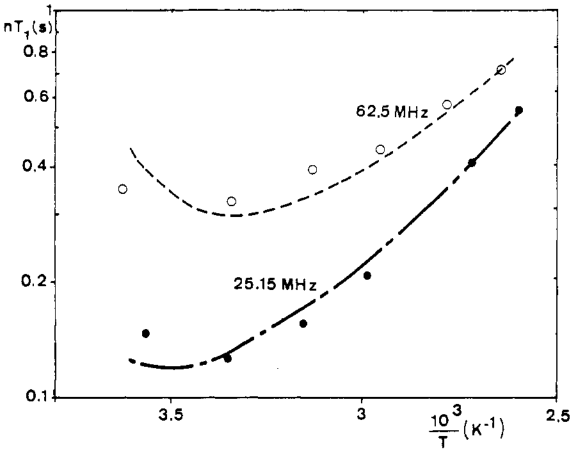


Figure 8. Comparison of experimental 25.15- and 62.5-MHz nT_1 values for bulk PEO 600 with the fit from DLM autocorrelation function with $a = 0.56$, $\tau_2/\tau_1 = 30$, $\tau_1/\tau_0 = 20$; same symbols as in Figure 1.

Table IV
Parameters Used for the DLM Fit of PEO Samples

sample	a	τ_2/τ_1	τ_1/τ_0
PEO 400	0.56	30	200
PEO 600	0.56	30	200
PEO 1000	0.56	30	200
PEO 1500	0.56	100	200
PEO	0.56	200	200

by a simple Hall–Helfand[2] or Viovy–Monnerie–Brochon[3] autocorrelation function. Use of formula 5 indicates that the internuclear vectors are also involved in an additional partial reorientation inside a cone of angle $\theta = 40°$. This value is slightly higher than the one determined for the methylene carbon of poly(propylene oxide) and supports the idea that θ is mainly determined by steric hindrance. An example of the best fit obtained from formula 5 is shown in Figure 8. The agreement between the experimental and calculated T_1 at the two observation frequencies is very satisfactory. The parameters used in these fits are given in Table IV. For all the polymers under study, the τ_1/τ_0 ratio is of the order of 200. The τ_2/τ_1 ratio is accurately estimated. It is practically independent of temperature, but it decreases when the degree of cross-linking increases. This result reflects the fact that the orientation diffusion process along the chain, characterized by the τ_1 correlation time, is interrupted when it reaches the cross-linking points.

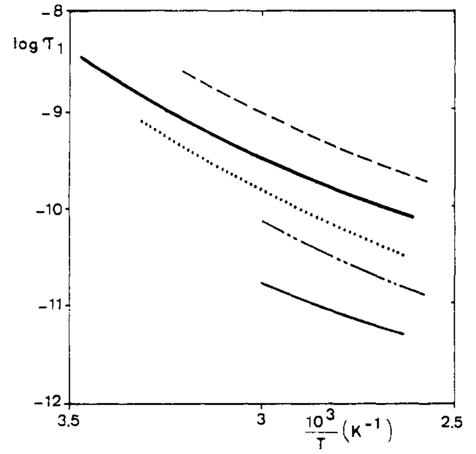


Figure 9. Plot of log τ_1 versus $1/T$ in bulk PEO samples: (light unbroken line) linear PEO; (- - -) PEO 1500; (···) PEO 1000; (heavy unbroken line) PEO 600; (— — —) PEO 400.

Table V
Experimental T_1 and T_{1c} and τ_{1c} Values Calculated at $10^3/T = 3$ and 25.15 MHz for $t = 1$ s in PEO Samples

sample	no. of bonds	central bonds	T_1, s	T_{1c}, s	$10^{11}\tau_{1c}$, s
PEO 400	27	0	0.164		
PEO 600	41	14	0.21	0.26	25
PEO 1000	68	27	0.33	0.45	9
PEO 1500	102	34	0.46	0.71	5
PEO			0.977		3

Variations of log τ_1 as a function of $1/T$ are plotted in Figure 9 for the different samples under study: The curves representing the log τ_1 versus $1/T$ variation are practically parallel for cross-linked poly(ethylene oxides), with an apparent activation energy of 11.7 kcal/mol. On the other hand, the line corresponding to linear poly(ethylene oxide) presents a smaller slope. Besides, at a given temperature, the τ_1 mobility increases from PEO 400 to PEO 600 and then to PEO 1000 and PEO 1500, in agreement with the fact that the segmental mobility is higher in long flexible subchains than in shorter ones.

For an estimation of the extent to which the cross-linking junctions oppose these motions, the relaxation times T_1 of the central units of PEO 600 have been estimated. This is done by assuming that the total T_1 evolution of the carbon-13 magnetization of PEO 600, in a (180°, t, 90°) sequence, is the sum of the evolution of the 27 bonds of PEO 400 characterized by T_1(PEO 400) and of the evolution of the central bonds of PEO 600 with T_{1c}(PEO 600). T_{1c}(PEO 1500) and T_{1c}(PEO 1000) have been calculated in the same way by using T_1(PEO 1000) and T_1(PEO 600) respectively for describing the motional constraints of the urethane functions. Results obtained at $10^3/T = 3$ and 25.15 MHz for a value of the interval $t = 1$ s are listed in Table V, together with the τ_{1c} values derived by using the τ_2/τ_1 and τ_1/τ_0 ratios determined above. It can be seen that even in PEO 1500 the motion of the central units is slower than in linear PEO. This means that even at a distance of about 50 bonds from a cross-link, the local dynamics remains affected by the constraint. However, at a given temperature, the damping of this effect as a function of the number of bonds between two urethane units is quite rapid. For example, the correlation time τ_{1c} of the central units is about 8 times slower than in linear PEO when the central units are separated by 20 bonds (PEO 600) from the cross-links, it is 3 times slower in the case of 34 bonds (PEO 1000), and only 1.7 times slower in the case of 51 bonds (PEO 1500).

Conclusion

The carbon-13 spin–lattice relaxation time determinations performed on bulk poly(propylene oxide) and linear and cross-linked poly(ethylene oxides) have confirmed the results obtained on poly(vinyl methyl ether) and reported in the preceding paper in this issue. Indeed, the segmental dynamics of these polymers are satisfactorily described by considering a fast libration of limited extent of the internuclear CH vectors about their rest position and a damped bond orientation diffusion process. In addition, the data on poly(propylene oxide) show that the amplitude of the rapid CH libration mode depends on the steric hindrance at the site of the considered carbon. On the other hand, the results obtained on cross-linked poly(ethylene oxides) clearly demonstrate that the cross-links interrupt the orientation diffusion process along the chain and that the segmental motions of the central flexible units are quite significantly slowed down by the constraints arising from the cross-links. It is worthwhile to note that when the central PEO units are located at a distance of about 50 bonds from the urethane junction, their dynamics are about twice as slow as in linear PEO.

Acknowledgment. We express our gratitude to Dr. H. Cheradame for supplying the cross-linked poly(ethylene oxides) samples.

Registry No. PEO, 25322-68-3; (PEO)(triphenylmethane-*p*,*p*′,*p*″-triisocyanate) (copolymer), 114379-12-3; poly(propylene oxide), 25322-69-4.

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^{2}H NMR Analysis of the Molecular Origin of the Thermal Relaxations in Polycarbonates

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ABSTRACT: ^{2}H NMR spectroscopy has been utilized to characterize the molecular dynamics associated with the thermal relaxations in amorphous polycarbonate materials. The methyl and phenyl groups of bisphenol A polycarbonate (BPA PC) and poly(ester carbonates) derived from BPA and tere- or isophthalic acid were independently deuterium labeled so as to characterize the molecular dynamics of each group as a function of temperature. The phenyl motions of both the BPA and terephthalate units were characteristic of 180° ring flips and large angle rocking motions. These motions ceased (relative to 100 KHz) between 40 and −30 °C. The terephthalate phenyls were more motionally restricted at temperatures between −30 and 120 °C than the BPA phenyls. The backbone motions of these systems were also shown to be quite restricted until very near T_g. Physical aging was observed to have much more of an effect on the dynamics of the terephthalate phenyl than those of the BPA phenyl. PEC systems, however, have been shown to be much more aging resistant and to possess ductility at lower temperatures than the BPA homopolymer, thus indicating that simple free volume arguments are not sufficient to explain these observations.

Introduction

The relationship between the molecular dynamics of a glassy polymer and its deformation properties remains a controversial subject. The spectroscopic investigation of the molecular motions of solid polymers in general has attracted much attention for the purpose of defining such a relationship. Polycarbonate polymers have been the focus of much of this attention for many reasons, not the least of which is the unusual toughness that this engineering plastic exhibits at room temperature.[8]

The molecular dynamics of bisphenol A polycarbonate (BPA PC) have been extensively characterized in the solid state by NMR techniques. The phenyl motions (at ambient temperature) were defined as 180° ring flips about the C_2 symmetry axis, superimposed upon approximately 30° ring oscillations.[1–3,11] Schaefer et al.[3] also observed

0024-9297/88/2221-2058$01.50/0