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# Influence of the Chemical Nature of Cross-Links on the Local Dynamics of Bulk Poly(ethylene oxide) Networks As Studied by Carbon-13 NMR at Temperatures Well above the Glass-Transition Temperature

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ABSTRACT: Carbon-13 spin–lattice relaxation time measurements have been performed on cyclosiloxane cross-linked poly(ethylene oxide)s (PEO) in bulk at temperatures well above the glass-transition temperature. The introduction of cyclosiloxane cross-links does not induce a strong modification of the local dynamics of PEO segments, in contrast to results observed in urethane cross-linked PEOs. Moreover, in these networks, the local chain dynamics are satisfactorily described by considering a damped bond orientation diffusion process and a fast libration of limited extent of the internuclear CH vectors about their rest position. The amplitude of the libration, which is expected to reflect the steric hindrance at the considered site, does not depend on the carbon considered and the chemical nature and density of cross-links.

## Introduction

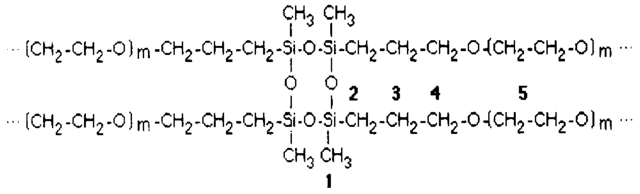
Research on ionically conducting polyether-based networks containing alkali-metal salts has been developed during the last decade, because improved mechanical properties and higher conductivity values due to a lower crystallinity of the materials were expected, compared to the behavior of linear polyethers. Well-defined poly(ethylene oxide) (PEO) networks with urethane or cyclosiloxane cross-links have been prepared, and the conductivity of these products filled with lithium salts has been studied.[1,2] Flexible cyclosiloxane cross-links lead to membranes which have conductivity values higher than those of the more rigid and polar aromatic urethane cross-links. Moreover, the ionization process was shown to depend on the chemical nature of the cross-links.[2] As charge transport is related to the segmental chain motions, a study of the influence of the cross-links on the mobility of PEO segments was undertaken.

Among the techniques that permit investigation of local chain dynamics, analysis of $^{13}C$ spin–lattice relaxation times $T_1$ leads to a detailed description of local motions. Moreover, in bulk polymers at temperatures well above the glass-transition temperature, $T_g$, the carbon–proton dipolar interaction and the chemical shift anisotropy are averaged to a large extent by fast local motions and contribute only to a weak residual line broadening. Therefore, high-resolution $^{13}C$ NMR spectra can be obtained on these materials by using the conventional spectrometers for solution investigations.

This technique has been used to determine carbon-13 spin–lattice relaxation times $T_1$ in cyclosiloxane cross-linked PEO networks at temperatures well above the glass-transition temperature. The results, which are compared with previously reported $T_1$ values in urethane cross-linked PEO's,[3] are described in the present paper.

## Experimental Section

The synthesis of the cyclosiloxane cross-linked PEO's was performed according to a method described previously.[1] Diallyloxy telechelic PEO's of different molecular weights (400, 600, or 1000) were hydrosilylated in toluene with 2,4,6,8-tetramethylcyclotetrasiloxane ($D_4H$) using Pt/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex as catalyst (Petrarch). The tetrafunctional cross-links have the following structure:



$$\begin{array}{c} \cdots(CH_2\text{-}CH_2\text{-}O)_m\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\underset{O}{Si}}\text{-}O\text{-}\overset{CH_3}{\underset{O}{Si}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_m\cdots \\ \cdots(CH_2\text{-}CH_2\text{-}O)_m\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\underset{CH_3}{Si}\text{-}O\text{-}\underset{CH_3}{Si}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_m\cdots \end{array}$$

The average molecular weights, $M_n$, the mean numbers of ethylene oxide units between two cross-links, $m$, the glass-transition temperatures, $T_g$, the melting temperatures of the crystalline part of the membranes, $T_m$, and the abbreviated names of the different samples are listed in Table I.

The 22.6-, 25.15-, and 50.3-MHz $^{13}C$ NMR spectra were recorded on a Brüker WH-90, a JEOL PS100, and a Brüker AM200SY spectrometer, respectively, using the technique of proton noise decoupling. Bulk samples were cryoground, put into 8-mm-diameter NMR tubes, carefully dried and degassed under vacuum at 80 °C during at least 3 days, and sealed under high vacuum. Experiments were carried out at temperatures above $T_m$ and $T_g$. The lock signal was obtained from an external coaxial 10-mm-diameter tube filled with DMSO-$d_6$, or with acetone-$d_6$ for measurements carried out at temperatures below 10 °C.

"Quantitative" $^{13}C$ NMR spectra were recorded at 50.3 MHz by using repetition times much longer than 5 times the longest $T_1$ and a gated $^1H$ decoupling pulse sequence. A good agreement between the experimental ratios $C_{4,5}/C_3$ and the theoretical values

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

| abbrev name | $M_n$ | $m$ | $T_g$ (°C) | $T_m$ (°C) |
|---|---|---|---|---|
| PEO 400 | 400 | 9 | −62.5 | |
| PEO 600 | 600 | 13 | −63 | −20 |
| PEO 1000 | 1000 | 22 | −63.5 | 10 |

**Table II**
**Characteristics of the Spectra of the Cross-Linked PEO Samples at 50.3 MHz and 25 °C**

| abbrev name | $\Delta\nu^{1/2}$ of $C_{4,5}$ (Hz) | $C_{4,5}/C_3$ ratio | theor $C_{4,5}/C_3$ ratio |
|---|---|---|---|
| PEO 400 | 135 | 11.0 | 10 |
| PEO 600 | 115 | 12.2 | 14 |
| PEO 1000 | 130 | 24.4 | 23 |

was found for the different samples (Table II). It indicates that dangling chains are not present in noticeable proportion, which is in agreement with the low amounts of extracted products determined in these materials.[1]

Spin-lattice relaxation times $T_1$ were measured by using the standard inversion recovery (180°, t, 90°) technique, with repetition times between pulse sequences longer than 5 times $T_1$ for the spectra recorded on Brüker WH-90 and JEOL PS100. The standard deviation for each $T_1$ measurement is better than 0.01 s (5%) for the $C_{4,5}$ midchain carbons. For the spectra recorded on Brüker AM 200SY, the exponential character of the longitudinal relaxation function was first checked by employing the standard (180°, t, 90°) technique. Then, the FIRFT method (fast inversion recovery Fourier transform)[4] was used with repetition times between sequences greater than the longest $T_1$ of the considered carbon-13 nuclei and with a three-parameter direct exponential fit to extract $T_1$. The standard deviation for each $T_1$ measurement is usually 0.002 s (better than 1%) for the $C_{4,5}$ midchain carbons and 0.02 s (15%) for the $C_2$ and $C_3$ carbons near the cross-links.

## 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 on a C–H carbon under proton noise decoupling conditions is given by the well-known expression:[5]

$$\frac{1}{nT_1} = \frac{\hbar^2\gamma_C^{\,2}\gamma_H^{\,2}}{10}\,\frac{1}{r_{CH}^{\,6}}\,[J(\omega_H-\omega_C) + 3J(\omega_C) + 6J(\omega_H+\omega_C)] \qquad (1)$$

where $\omega_H$ and $\omega_C$ are the $^1H$ and $^{13}C$ resonance frequencies, $r_{CH}$ is the internuclear distance, taken here as 1.09 Å as derived from quantum mechanics calculations,[6] $n$ is the number of protons directly bonded to the carbon of interest, and $J(\omega)$ is the spectral density defined by

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

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 previously.[7a] The motional models for local chain dynamics are based on conformational changes, characterized by a correlation time $\tau_1$, which propagate along the chain according to a damped diffusional process. The damping is described by the correlation time $\tau_2$. It accounts for nonpropagative specific motions and distortions of the chain with respect to its most stable local conformations.[7] In the following, the expression of $G(t)$ that we will use for the description of the local chain dynamics will be the Hall–Helfand (HH) expression for the autocorrelation function:[8]

$$G(t) = \exp(-t/\tau_2)\exp(-t/\tau_1)I_0(t/\tau_1)$$

where $I_0$ is the modified Bessel function of order 0.

As previously shown for a number of polymers,[9] either in bulk or in solution, autocorrelation functions based on damped conformational changes only, cannot account for the high value of the spin-lattice relaxation time $T_1$ at the minimum observed as a function of temperature. Results obtained have demonstrated 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 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 $\tau_0$. This leads to the complete Dejean-Lauprêtre-Monnerie (DLM) expression written as[7a]

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

where

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

$a$ is the amplitude of the libration mode.

Assuming that $\tau_0$ is much shorter than $\tau_1$ and $\tau_2$, the second term in the $G(t)$ expression can be simplified, yielding the expression later referred to as DLM:

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

$1/nT_1$ can then be written as

$$\frac{1}{nT_1} = (1-a)\frac{\hbar^2\gamma_C^{\,2}\gamma_H^{\,2}}{10}\,\frac{1}{r_{CH}^{\,6}}[J_{HH}(\omega_H-\omega_C) + 3J_{HH}(\omega_C) + 6J_{HH}(\omega_H+\omega_C)] + a\frac{\hbar^2\gamma_C^{\,2}\gamma_H^{\,2}}{10}\,\frac{1}{r_{CH}^{\,6}}[J_0(\omega_H-\omega_C) + 3J_0(\omega_C) + 6J_0(\omega_H+\omega_C)] \qquad (5)$$

where $J_{HH}(\omega) = (\alpha + i\beta)^{-1/2}$ and $J_0(\omega) = \tau_0/(1+\omega^2\tau_0^{\,2})$ with $\alpha = \tau_2^{-2} + 2\tau_1^{-1}\tau_2^{-1} - \omega^2$ and $\beta = -2\omega(\tau_1^{-1} + \tau_2^{-1})$.

Under the assumption of fast segmental motions $\tau_0 << \tau_1, \tau_2$, 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.

## Results and Discussion

**$^{13}C$ NMR Spectra.** The $^{13}C$ NMR spectrum of PEO 600 recorded at 25 °C at the experimental frequency of 50.3 MHz is shown in Figure 1. It exhibits four peaks which have been assigned by using the numbering scheme defined in the Experimental Section. Carbons 4 and 5 have quite similar chemical shifts and yield only one wide peak at 72 ppm. Resonances of carbons 1–3 are observed at 0, 14, and 24 ppm, respectively. It is noteworthy that the resonances of carbons 1–3 can be detected even for high $C_{4,5}/C_2$ (or $C_{4,5}/C_3$) ratios ($C_{4,5}/C_3$ = 23 for PEO 1000) or in rather highly cross-linked materials (PEO 400). This last observation implies that the local motions of the carbons near the cross-links are fast enough to allow the observation of these carbons under the conventional solution-type NMR conditions used here. An opposite result was reported by Dejean et al.[3] for urethane cross-linked PEO networks in the same temperature range, for

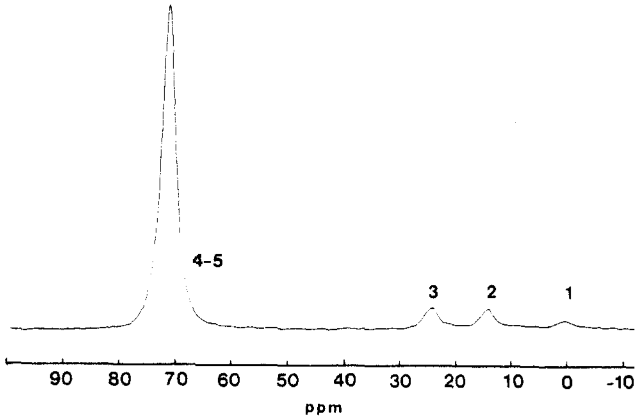

**Figure 1.** 50.3-MHz $^{13}C$ NMR spectrum of PEO 600 in bulk at 25 °C.

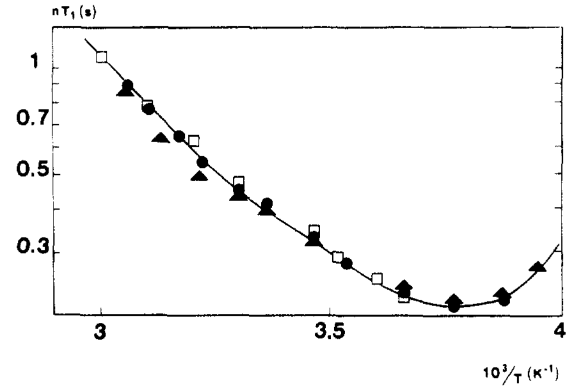

**Figure 2.** 50.3-MHz $^{13}C$ $nT_1$ values versus $1/T$ for $C_{4,5}$ in PEO samples: (□) PEO 1000; (●) PEO 600; (▲) PEO 400.

which there exist, on each side of a cross-link, about two $CH_2$–$CH_2$–O segments with low mobility that are not observed under solution NMR conditions. In the urethane cross-linked PEO networks, the slowing down of the cross-link motions was due to the rigid bulky nature of the aromatic urethane cross-links and/or to a microdomain segregation of the urethane units. PEO-*b*-poly(dimethylsiloxane) are known to undergo microphase separation above a certain degree of polymerization of the segments, due to their pronounced incompatibility.[10] In the networks under study, the siloxane sequences are very short and the microphase separation does not occur. More information on the relative rates of motions of the midchain carbons and carbons next to the siloxane cross-links can be derived from the detailed analysis of their $T_1$ relaxation times.

Line widths of the $C_{4,5}$ carbons, measured at 50.3 MHz and 25 °C, are reported in Table II. At 25 °C, the line width is practically independent of the length of the PEO segments. For PEO 400, the line width remains unchanged between 15 °C (135 Hz) and 55 °C (130 Hz). On decreasing the temperature, the line width increases and reaches 300 Hz at −20 °C. Even in the low-temperature region, the quality of the signal to noise ratio allows the determination of accurate $T_1$ values.

**Nuclear Magnetic Relaxation of the Midchain PEO Carbons.** Figure 2 shows the variations 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 $T$ for carbons 4 and 5 of PEO 400, 600, and 1000 at the experimental frequency of 50.3 MHz. The midchain PEO carbons of the different networks exhibit very similar $nT_1$ values at a given temperature, whatever the length of the PEO segments. These observations indicate that the segmental mobility is identical in long flexible PEO 1000 subchains and in shorter PEO 400 and PEO 600 ones. Moreover, the $nT_1$ values of the midchain carbons in PEO 400, 600, and 1000 are very close to those determined for linear PEO under the same conditions.[3] It is also of interest to recall that the glass-transition temperatures (determined by DSC) of the three siloxane cross-linked networks which lie between −62.5 and −63.5 °C are nearly equal to the $T_g$ of linear PEO ($T_g$ = −66 °C). The motional modes observed by $^{13}C$ NMR $T_1$ relaxation in the temperature range investigated are known to belong to processes involved in the glass-transition phenomena.[11] The similarity of the $T_g$ values, as well as that of the $T_1$ relaxation times, in the considered networks and in linear PEO, clearly indicates that, even in the most cross-linked network, the presence of the cyclosiloxane cross-links does not significantly modify the local motions of the PEO segments with respect to those of linear PEO. Identical conclusions have been reached for poly(siloxane)-*g*-poly(ethylene oxide) randomly cross-linked by difunctional PEO chains, which exhibits $^{13}C$ $T_1$ values comparable to those measured on the un-cross-linked graft material.[12]

### Table III
**Comparison of Experimental and Calculated $nT_1$ Values at the $T_1$ Minimum in Bulk Cyclosiloxane Cross-Linked Poly(ethylene oxide) at 50.3 MHz**

| | $T_1$ (s) | | $T_1$ (s) |
|---|---|---|---|
| isotropic model | 0.080 | PEO 600 | 0.220 |
| HH[a] | 0.105 | PEO 400 | 0.218 |

[a] Hall–Helfand autocorrelation function.

On the contrary, $^{13}C$ NMR analysis[3] of aromatic urethane-based PEO networks have shown that the relaxation times of the midchain carbons are strongly dependent upon the chain length between two rigid urethane cross-links. At 25.15 MHz and 60 °C, $nT_1$ increases from 0.18 to 0.34 s with increasing molecular weight of the PEO subchain from 400 to 1000. For these networks, $nT_1$ is significantly smaller than the 1.0-s value determined for linear PEO under the same experimental conditions. In the case of well-defined poly(propylene oxide) (PPO) networks prepared with tris(4-isocyanatophenyl) thiophosphate, $^{13}C$ and $^{31}P$ solid-state NMR[13,14] investigations of the local motions of both the PPO segments and the cross-links have also pointed out the strong influence of the PPO length on the mobility of the PPO segments.

**$T_1$ Minima.** As shown in Figure 2 for the 50.3-MHz experiments, the $nT_1$ value determined for the $C_{4,5}$ carbons at the minimum is 0.220 s for both PEO 400 and PEO 600. It does not depend on the length of the PEO subchain. Moreover, the $nT_1$ minimum is observed at −10 °C for both networks. Due to crystallization, it was not possible to reach the $T_1$ minimum for PEO 1000. In the case of urethane cross-linked PEO's, the $nT_1$ value measured for the midchain PEO carbons at the minimum was also shown to be independent of the length of the PEO segment.[3] However, the temperature for which the $nT_1$ minimum is observed is significantly lower for the cyclosiloxane than for the urethane cross-linked networks. The latter result is in agreement with the lower glass-transition temperature and higher mobility at a given temperature of the cyclosiloxane cross-linked networks as compared to the urethane ones.

The comparison of experimental and calculated $nT_1$ values at the $T_1$ minimum is shown in Table III. As observed in previous studies on PEO networks and other polymer systems,[7a–c] the experimental $nT_1$ at the minimum is much too high to be represented by a simple Hall–

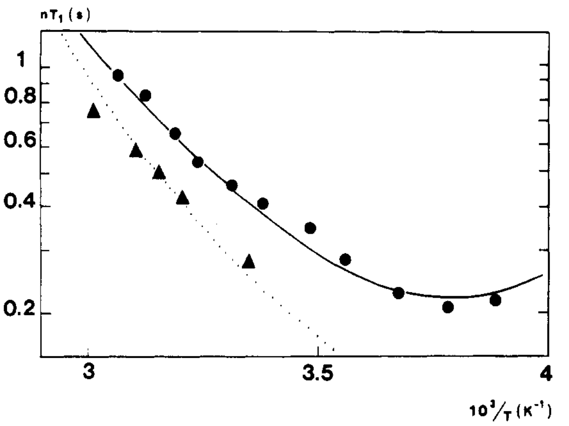

**Figure 3.** Comparison of experimental and calculated 50.3- and 22.6-MHz $nT_1$ values versus $1/T$ for $C_{4,5}$ of PEO 600. Experimental points: (●) 50.3 MHz; (▲) 22.6 MHz. Best fit calculated from the DLM autocorrelation function with $a = 0.54$, $\tau_2/\tau_1 = 50$, $\tau_1/\tau_0 = 200$: (—) 50.3 MHz; (···) 22.6 MHz.

Helfand autocorrelation function. Therefore, the $nT_1$ data have been analyzed by using the DLM autocorrelation function which takes into account both conformational jumps and C–H librations. According to the treatment described in ref 7a, the use of expression 5 to represent the $nT_1$ values at the minimum leads to $a = 0.54$ for both PEO 600 and PEO 1000, corresponding to a conic half-angle Θ of 40 °. The same value was determined for the urethane cross-linked PEO's.[3] This result indicates that the extent of the libration for the PEO subchain carbons is the same whatever the chemical nature of the cross-link and the length of the PEO subchain, in agreement with the fact that the extent of the libration is related to the steric hindrance of the considered site, i.e. the central PEO chain carbons.

In order to perform the $nT_1$ fit by 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. This restrictive assumption implies that the amplitude of the libration does not depend on temperature in this temperature range. Under these conditions, the fit can be obtained at a given temperature by looking for the $\tau_0$, $\tau_1$, and $\tau_2$ values which lead to calculated $nT_1$ values at the two frequencies as close as possible to the experimental ones. The best $nT_1$ fit is shown in Figures 3 and 4 for the $C_{4,5}$ carbons of PEO 600 and PEO 1000, at two observation frequencies. Agreement between experimental and calculated values is excellent. Data obtained for the $C_{4,5}$ carbons of PEO 600 and PEO 1000 are represented by exactly the same set of parameters. In the particular case of the cyclosiloxane cross-linked PEO networks, there is not noticeable dependence of the damping parameter on the number of cross-links.

Variations of log $\tau_1$ as a function of $1/T$ are plotted in Figure 5 for linear PEO and for cyclosiloxane and urethane cross-linked PEO's. For the cyclosiloxane cross-linked PEO, these variations are identical whatever the length of the PEO subchains. They are close to that of linear PEO. As already noted, the segmental mobility is higher in these networks than in the urethane-based systems. However, the different curves drawn in Figure 5 mainly differ by a translational factor along the log $\tau_1$ axis, which means that the networks and the linear polymer share the same temperature law for their segmental dynamics at temperatures above the glass-transition temperature.

**Carbons near the Cross-Links.** Figure 6 shows the variations of $nT_1$ as a function of the reciprocal of

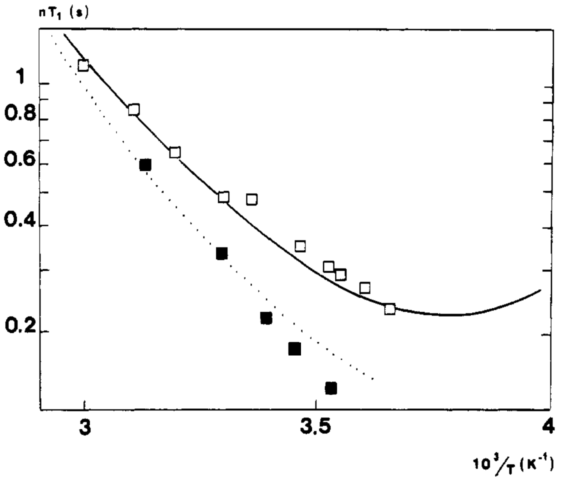

**Figure 4.** Comparison of experimental and calculated 50.3- and 25.15-MHz $nT_1$ values for $C_{4,5}$ of PEO 1000. Experimental points: (□) 50.3 MHz; (■) 25.15 MHz. Best fit calculated from the DLM autocorrelation function with $a = 0.54$, $\tau_2/\tau_1 = 50$, $\tau_1/\tau_0 = 200$: (—) 50.3 MHz; (···) 25.15 MHz.

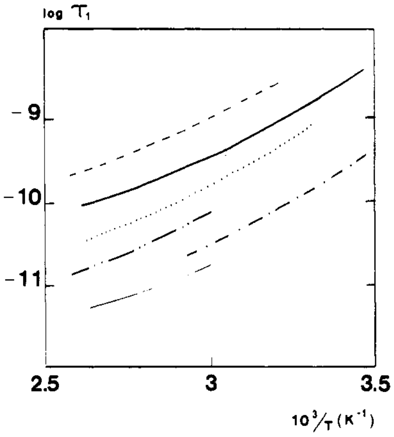

**Figure 5.** Plot of log $\tau_1$ versus $1/T$ in PEO samples: (– · –) this work, PEO 600 and PEO 1000. The other curves were determined for urethane cross-linked PEO (reproduced from ref 3): (light unbroken line) linear PEO; (– ·· –) PEO 1500; (···) PEO 1000; (heavy unbroken line) PEO 600; (- - -) PEO 400.

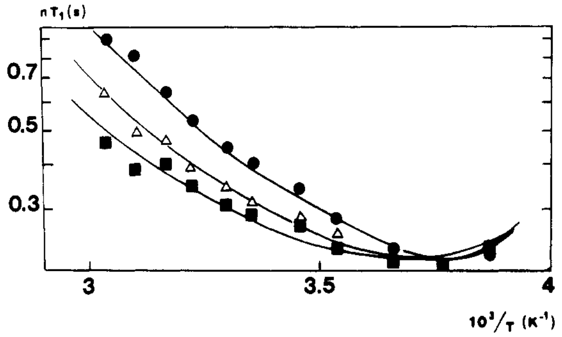

**Figure 6.** 50.3-MHz $^{13}C$ spin–lattice relaxation time $nT_1$ values versus $1/T$ in PEO 600: (●) $C_{4-5}$; (△) $C_3$; (■) $C_2$.

temperature $T$ for the carbons 2, 3, and 4,5 of PEO 600 at the experimental frequency of 50.3 MHz. Identical results have been obtained for PEO 400 and PEO 1000. All carbons exhibit the same $nT_1$ value at the minimum, which implies that the libration amplitude does not depend on the considered PEO carbon. However, this minimum is reached at higher temperatures for $C_2$ and $C_3$. Moreover, at a given temperature, the carbons near the cross-links have spin–lattice relaxation times slightly shorter than those of the midchain carbons. These results indicate that the cross-links induce a slight slowing down of the motions of the carbons near the cross-links. Long relaxation times

($nT_1 > 1$ s) have been determined for the methyl carbon of the cross-links. Although the segmental motion is expected to be still more slowed down at the cross-link site, the internal rotation of the methyl group is responsible for the long $T_1$ and rather narrow line width of this nucleus.

These results are in agreement with data reported by Oeser for spatial fluctuations of cross-link points in poly(dimethylsiloxane) (PDMS). As shown by neutron spin-echo studies, the time scale of motion for the cross-links is comparable to the time scale of segmental diffusion within the chains attached to the junctions.[15] On the opposite, the local motions of the carbons near the cross-links in urethane cross-linked PEO networks were too slow to be observed under solution NMR conditions.[3] Quantitative information about the relative rates of motion of the mid-chain and cross-link nuclei has been obtained in the case of urethane cross-linked poly(propylene oxide) (PPO) networks. For these systems, the analysis of the spin-lattice relaxation times, $T_{1\rho}$, of both the $^{13}$C (PPO) and $^{31}$P (cross-links) nuclei has shown that the correlation times describing the segmental motion of these two nuclei have parallel variations as a function of temperature,[14] which indicates that the motions of each species may be coupled so that the segmental motion and cross-link motion differ by what may be called an entropy factor. At a given temperature, the $\tau$ values of the two nuclei differ by a factor of 3 for PPO 1000 and by a factor 5 for PPO 3000. Therefore, for these urethane cross-linked networks, the coupling is weaker in longer chain networks, which results in a larger lag in frequency between the cross-link motion and the chain motion.

## Conclusion

In contrast to the results obtained for urethane cross-linked PEO's, carbon-13 spin-lattice relaxation time determinations performed on cyclosiloxane cross-linked poly(ethylene oxide)s have shown that the introduction of siloxane cross-links does not induce a strong modification of the local dynamics of PEO segments. Motion of the cross-links is only slightly slower than that of the subchains. Moreover, in these networks, the local chain dynamics are satisfactorily described by considering a damped bond orientation diffusion process and a fast libration of limited extent of the internuclear CH vectors about their rest position. The amplitude of the libration, which is expected to reflect the steric hindrance at the considered site, does not depend on the carbon considered (midchain carbons or carbons near the cross-links) and the chemical nature and density of cross-links. All these observations lead to the conclusion that siloxane-based PEO networks have a very interesting behavior: they exhibit the high segmental mobility of the linear PEO chain with the advantage of being membranes. Further work is in progress on the NMR characterization of these networks filled with lithium salts in order to gain a better insight on the influence of the cross-links on salt complexation by the PEO segments.

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**Registry No.** $(H_2C{=}CHCH_2(OCH_2CH_2)_nOCH_2CH{=}CH_2)$-$(D_4H)$ (copolymer), 121248-15-5.