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Two-Step Swelling of Poly(ethylene oxide) Gels. NMR Characterization

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ABSTRACT: The states of intermediate and maximum swelling of trifunctional poly(ethylene oxide) (PEO) gels are analyzed from the relaxation of the transverse magnetization of protons attached to end-linked chains. Cross-links were formed either from tris(4-isocyanatophenyl) groups or from tris(4-isocyanatophenyl) thiophosphate groups. The solvent volume fraction of synthesis was kept at a constant value of $\nu_s = 0.56$. The maximum swelling ratio Q_m was found to be proportional to $\overline{M}_n^{4/5}$ within the range of chain molecular weight $0.42 \times 10^3 \leq \overline{M}_n \leq 3 \times 10^3$ g mol^{-1}; this shows that the statistical structure of short-chain solutions at concentration C^* is trapped during the gelation process. The swelling ratio is found to be proportional to $\overline{M}_n^{1/2}$ within the range $3 \times 10^3 \leq \overline{M}_n \leq 10^4$ g mol^{-1}; this result shows that a branched structure is trapped. It is clearly shown from the chemical shift of ^{31}P or dipole–dipole interactions of protons that a residual tensorial interaction of spins characterizes all states of swelling even for very long chains. The transverse relaxation function of protons is given a quantitative description. The progressive swelling of PEO is found to occur according to two steps. Spin–spin relaxation rates are first found to decrease, because of the progressive disinterpersion of elementary chains. Then, the excluded volume effect becomes more and more efficient; this smooth transition is perceived as an increase of relaxation rates. In the state of maximum swelling, the relaxation rate Σ_m is nearly proportional to Q_m^{-1} for short-chain precursors ($\overline{M}_n < 3 \times 10^3$ g mol^{-1}). This result indicates that correlation domains observed from NMR participate also in the determination of the state of swelling.

I. Introduction

This work deals with investigations into properties of the statistical structure of end-linked chain systems; it is based upont the analysis of the mechanism of progressive swelling induced by adding small amounts of solvent to the gel. The transverse magnetic relaxation of protons linked to poly(ethylene oxide) network structures is used to observe transformations of chain segments resulting from the effect of osmotic pressure.[1] The state of stretching of segments is disclosed from the strength of the residual dipole–dipole interaction of nuclear spins, which is associated with nonisotropic motions of monomeric units; this is even observed in fully swollen gels. The purpose of this study is manyfold.

(i) It first illustrates the possibility of giving a quantitative description of NMR properties observed in polymeric gels. In no cases were the dynamics of rotational diffusion of monomeric units involved in the observed magnetic relaxation function; this was governed by a pure property of asymmetry of motions, only. The basic expression of the residual interaction of spins used to describe NMR properties is the ratio

$$\epsilon_{ij} \propto \Delta_G r_{ij}^2 / L_{ij}^2 \qquad (1)$$

L_{ij} is the contour length of the chain segment joining two coupling junctions i and j while $\vec{r}_{ij}$ is the corresponding end-to-end vector (Figure 1); Δ_G is the dipole–dipole interaction that would correspond to a fully stretched segment.[2] The average of magnetic properties applies over all end-to-end vectors; it is carried out by using a gel function $\mathcal{G}(\vec{r}_{ij})$, which will be discussed in this study.

(ii) Then, the quantitative NMR approach is used to disclose the behavior of elementary network chains when small amounts of solvent are added to the gel system to increase the internal osmotic pressure. It has already been shown that the progressive swelling of end-linked poly(dimethylsiloxane) (PDMS) segments or vulcanized poly(ethylene) chains occurs according to two steps (Figure 2).[3,4]

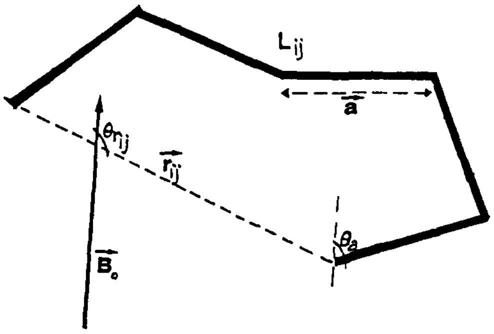

Figure 1. Elementary chain segment.

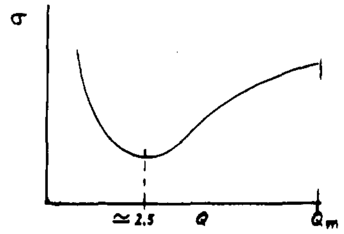

Figure 2. Schematic progressive swelling of a gel observed from NMR.

The first one reflects a disengagement of elementary chains from one another. The second one is a smooth transition from a state where excluded volume effects are screened to a state where they are fully observed. In the state of maximum swelling, elementary network chains

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obey the C^* theorem proposed by de Gennes.[5] The maximum swelling ratio Q_m is expressed as

$$Q_m \propto L_{ij}^{4/5} \tag{2}$$

Correspondingly, the relaxation rate Σ_m of the proton-transverse magnetization is expressed, from (1) and (2), as

$$\Sigma_m \propto L_{ij}^{-4/5} \propto Q_m^{-1} \tag{3}$$

This work is focused on the extension of these properties to trifunctional poly(ethylene oxide) (PEO) gels.

(iii) Finally, the concentration of the end-linking reaction was kept at a nearly constant value, whereas the molecular weight of the PEO precursor was varied over a broad range of values to observe possible trapped topological constraints. Earlier measurements concerning the possible presence of such constraints have been performed in PDMS by varying the polymer concentration of the end-linking reaction but keeping the length of the chain precursor at a constant value.[3]

The main question which is raised about end-linked chain systems concerns the size of correlation domains that originate macroscopic properties of the corresponding polymeric gel. We attempted to determine the real nature of coupling junctions or active nodes that govern gel properties when the end-linking reaction is completed; they are not necessarily identical with covalent cross-links.

II. Experimental Section

Poly(ethylene oxide) network structures were formed by cross-linking α,ω-diol PEO chains with a trifunctional group. The molecular weight of the chain precursor was varied from 420 to 10^4 g mol^{-1}. The polydispersity index was 1.05. Two species of networks were prepared. The first one was obtained from the reaction of PEO chains with tris(4-isocyanatophenyl) groups; the molecular weights of the precursor polymers were $\overline{M}_n$ = 420, 1050, 2100, 3200, 6000, and 10^4 g mol^{-1}. The second species was prepared by using a tris(4-isocyanatophenyl) thiophosphate group and precursor polymers characterized by $\overline{M}_n$ = 420, 1050, and 2100 g mol^{-1}. As a result of this preparation, all nodes are labeled with a ^{31}P nucleus. All network structures were prepared in similar solutions defined by the solvent volume fraction ν_s = 0.56. The solvent was methylene chloride. In all cases, 1 mol of polymer chains was added to 0.66 mol of isocyanatophenyl groups. The network was first dried in a nitrogen flux at room temperature and then under vacuum (10^{-2} Torr) for 48 h, at 80 °C. Such networks are characterized by a low amount of free chains (less than 1%), extracted by washing the polymer system. Swelling properties were investigated by using methylene chloride or deuterated methylene chloride in the case of NMR observations.

Partly swollen samples were obtained by adding small amounts of solvent to the network structure. NMR tubes were sealed under vacuum. NMR spectra (^{1}H or ^{31}P) were recorded after calculating a Fourier transform of the free induction decay. Experiments were performed by using a variable-temperature CP-MAS probe in a 2.3-T magnetic field (MSL 100 Bruker spectrometer). No proton–phosphorus cross-polarization has been observed at temperatures above the glass transition.[6] In this study, the attention was focused upon sample spinning effects, induced at a low spinning rate Ω_R ($100 < \Omega_R < 10^3$ Hz).

Relaxation functions (^{1}H) of partly swollen network structures were measured through a multiple spin–echo sequence: $(\pi/2)/y-\tau(-\pi/x-2\tau-\pi/x-2\tau-\pi/-x-2\tau-\pi/-x-2\tau-)_n$; π/x denotes a rotation of the magnetization around axis x in the rotating frame (π is the rotation angle). In this case, measurements were performed on a low-Q probe associated with a 1.5-T steady magnetic field (CXP Bruker spectrometer). Pseudosolid echoes were formed to characterize the presence of residual tensorial interactions. The corresponding experimental procedure has been already described in a previous paper; it is based on the pulse sequence $(\pi/2)/y-\tau-\pi/y-\tau-(\pi/2)/x-\tau_1(-\pi/x-2\tau_1-\pi/-x-)_n$.

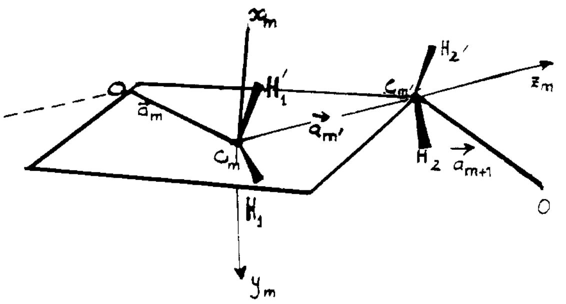

Figure 3. Local reference frame attached to one bond.

A simple least-squares fit was used to simulate three-parameter relaxation functions that describe NMR properties of network structures, observed in any state of swelling, throughout this work:

$$M_x(t) = p_s\mathcal{R}(\Delta_1 t) + (1 - p_s)\mathcal{R}(\Delta_2 t)$$

p_s is a weight factor; $\mathcal{R}(\Delta t)$ is the relaxation function of one proton pair linked to a slightly stretched chain segment.[2] A computer was used to fit experimental data within an accuracy of 1%.

III. Residual Tensorial Spin–Spin Interactions

NMR investigations into properties of polymeric gels are based on a simple feature: the end-to-end vector $\vec{\mathbf{r}}_{ij}$ joining any two consecutive coupling junctions i and j is not equal to zero whether it undergoes time fluctuations or not. Consequently, random motions of monomeric units are necessarily nonisotropic, and the time average of tensorial spin–spin interactions of nuclei attached to elementary network chains is not equal to zero. It is now well established that residual tensorial interactions that arise from this time average fully govern the transverse magnetic relaxation of nuclei in polymeric gels.

One elementary network chain joining two coupling junctions i and j and one monomeric unit m pertaining to this chain segment are considered; a local reference frame $\{l\}$ is associated with the monomeric unit m. The z axis of $\{l\}$ is parallel to one skeletal bond $\vec{\mathbf{a}}_m$ (Figure 3). The vector $\vec{\mathbf{r}}_{ij}$ is supposed to have fixed ends. Then, the monomeric unit m undergoes fluctuations in space that have an axial symmetry with respect to the vector $\vec{\mathbf{r}}_{ij}$. Let $\mathcal{H}_T$(m) denote the adiabatic part of dipole–dipole interactions between nuclei located on the monomeric unit m; $\mathcal{H}_T$(m) is expressed as

$$\mathcal{H}_T(\mathrm{m}) = \sum_{kk'} A_{kk'}[3\cos^2(\Theta_{kk'}) - 1] \tag{4}$$

$\Theta_{kk'}$ is the angle between the steady magnetic field direction and the vector joining nuclear spins k and k'; $A_{kk'}$ is the dipole–dipole spin operator:[7]

$$A_{kk'} = \gamma^2 h(3I_z^k I_z^{k'} - \vec{\mathbf{I}}^k \cdot \vec{\mathbf{I}}^{k'})/b_{kk'}^{\,3}$$

Then, the time average of $\mathcal{H}_T$(m), calculated within an axial symmetry, is written as

$$\langle \mathcal{H}_T(\mathrm{m}) \rangle_{ij} = \frac{1}{2}\langle 3\cos^2(\theta(\vec{\mathbf{a}}_m)) - 1\rangle_{ij} \times \sum_{kk'} A_{kk'}[3\cos^2(\theta_{kk'}) - 1] \tag{5}$$

Whatever the complex structure of the monomeric unit m, the angular coordinate $\theta_{kk'}$ is now defined in the local frame $\{l\}$ and $\theta(\vec{\mathbf{a}}_m)$ is the angle between the magnetic field and the skeletal bond $\vec{\mathbf{a}}_m$. The average $\langle 3\cos^2(\theta(\vec{\mathbf{a}}_m)) -$

$1\rangle_{ij}$ has already been calculated;[8] $\langle \mathcal{H}_T(m)\rangle_{ij}$ reads

$$\langle \mathcal{H}_T(\mathrm{m})\rangle_{ij} = \frac{3}{5}(3\cos^2\theta_{ij} - 1)\langle \vec{\mathbf{r}}_{ij}\rangle^2 \Lambda a^2 / \langle \vec{\mathbf{r}}_{ij}{}^2\rangle_0{}^2 \sum_{kk'} A_{kk'}[3\cos^2(\theta_{kk'}) - 1] \quad (6)$$

in which θ_{ij} is the angle that the vector $\langle \vec{\mathbf{r}}_{ij}\rangle$ makes with the magnetic field; Λ depends upon the chain stiffness:

$$\Lambda = \frac{15}{4}\sum_{pn} \langle \{3[a_z{}^m]^2 - a^2\} a_z{}^p a_z{}^p \rangle_0 / a^4 \quad (7)$$

The strength of residual tensorial interactions of spins located on the monomeric unit m is closely related to the state of elongation of the elementary network chain i,j; it is also a function of the number of monomeric units in the chain segment. To give a quantitative interpretation of the swelling properties of polymeric gels, it is necessary to prove that the mechanism of relaxation of the transverse magnetization of nuclei attached to the network structure is fully governed by this residual interaction of spins; in other words, the dynamics of monomeric units are not perceived from the transverse relaxation. This depends only upon properties of asymmetry of the rotational diffusion of monomeric units. Then, the relaxation function associated with the monomeric unit m reads

$$M_x{}^m(t) = \mathrm{Tr}\{e^{i\langle \mathcal{H}(\mathrm{m})\rangle t} \mathcal{M}_x e^{-i\langle \mathcal{H}(\mathrm{m})\rangle t} \mathcal{M}_x\} \quad (8)$$

Formulas 6 and 8 apply to any tensorial interaction of nuclear spins. They are based on the existence of elementary network chains whatever the real statistical structure of the polymeric gel. The purpose of the NMR approach is to attempt to characterize this structure. A strong experimental evidence for the presence of a residual tensorial interaction of spins is given in this section.

III.1. Effect of Sample Spinning. The observation of the sample spinning effect is used throughout this work to clearly identify the mechanism of relaxation of the transverse magnetization of nuclei attached to end-linked polymer chains. The sample rotation effect was observed from protons located on elementary network chains or from phosphorus nuclei located on nodes.

III.1.a. Phosphorus on Nodes. The resonance spectrum of phosphorus nuclei located on nodes was recorded at 303 K, from the polymeric gel made from the shortest chains ($\overline{M_n}$ = 420 g mol^{-1}). The resonance frequency was 40.5 MHz. The glass transition temperature is 270 K. The spectrum reported in Figure 4a still corresponds to the usual pattern resulting from a powder average of spectra induced by a nonisotropic chemical shift, in the solid state. The width of the spectrum is about 10.7 kHz. The chemical shift tensor is axially symmetric. It is characterized by a parameter determined from the resonance frequency $\nu_0\sigma$ observed in the liquid state: $(3\nu_0\sigma)/2$ = 10.7 kHz and σ = 7.2 kHz. The low-speed sample rotation (1 kHz), at the magic angle, gives rise to conventional side bands (Figure 4b). The narrowing effect of the maximum amplitude line is well perceived when the spinning rate is equal to about 10^3 Hz. The resonance spectrum of phosphorus nuclei was also recorded from polymeric gels made from long chains ($\overline{M_n}$ = 1050 g mol^{-1}). At room temperature, polymer chains are neither in a glassy state nor partially crystallized. Then, a narrow resonance line replaces the broad spectrum as is expected; the width is equal to 180 ± 10 Hz during sample rotation, at 1.2 kHz. In the absence of rotation, the width is equal to 700 ± 60 Hz (Figure 5); similar observations are made at 335 K (Figure 6) where the line width is equal to 400 Hz. This spectrum can be compared with the line width (10^3 Hz) observed in a similar sample at a resonance frequency ν_0 = 81 MHz at 350 K.[6] A field effect is perceived due to the anisotropic chemical shift broadening. It is considered that, in the absence of any rotation, the broadening mechanism is mainly due to the residual interaction of the anisotropic chemical shift. This partial time average is induced by nonisotropic fluctuations of nodes, in space.

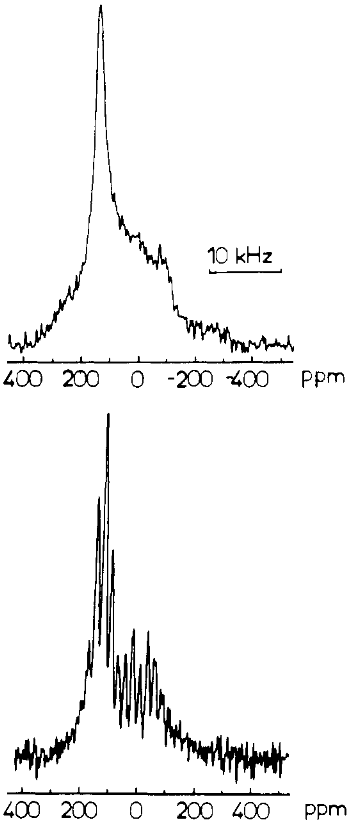

Figure 4. ^{31}P spectrum of PEO network nodes, M_n = 420 g mol^{-1}, at room temperature. (a, top) Without sample rotation. (b, bottom) Sample spinning at magic angle (spinning rate: 1 kHz).

III.1.b. Protons on Elementary Chains. The effect of sample rotation upon the transverse magnetic relaxation of protons was observed in either of two ways: by recording resonance spectra or by forming spin-echoes.

Resonance spectra were recorded from protons attached to PEO gels obtained by end-linking chains characterized by a molecular weight $\overline{M_n}$ = 1050 g mol^{-1}. The spinning rate at the magic angle ranged from 200 to 880 Hz. A typical spectrum reported in Figure 7 was obtained at room temperature. Measured line widths of the central line are 720 and 240 Hz without and with sample rotation, respectively.

The effect of sample spinning was observed in a partially swollen gel to prove that the residual dipole-dipole interaction of protons fully governs the transverse relaxation mechanism, even in the presence of a solvent. The PEO gel, formed from end-linked chains characterized by a molecular weight $\overline{M_n}$ = 3200 g mol^{-1}, was swollen by using a good solvent (CD_2Cl_2); the swelling ratio was Q = 2.8. Magnetic relaxation functions observed during or without sample rotation are shown in Figure 8a. The axis of rotation is perpendicular to the magnetic field direction. Two rotation rates were used: 22 and 60 Hz. The relaxation time scale is increased during sample rotation. The spinning effect is stronger when the spinning rate is increased, as is expected. The tail of the relaxation

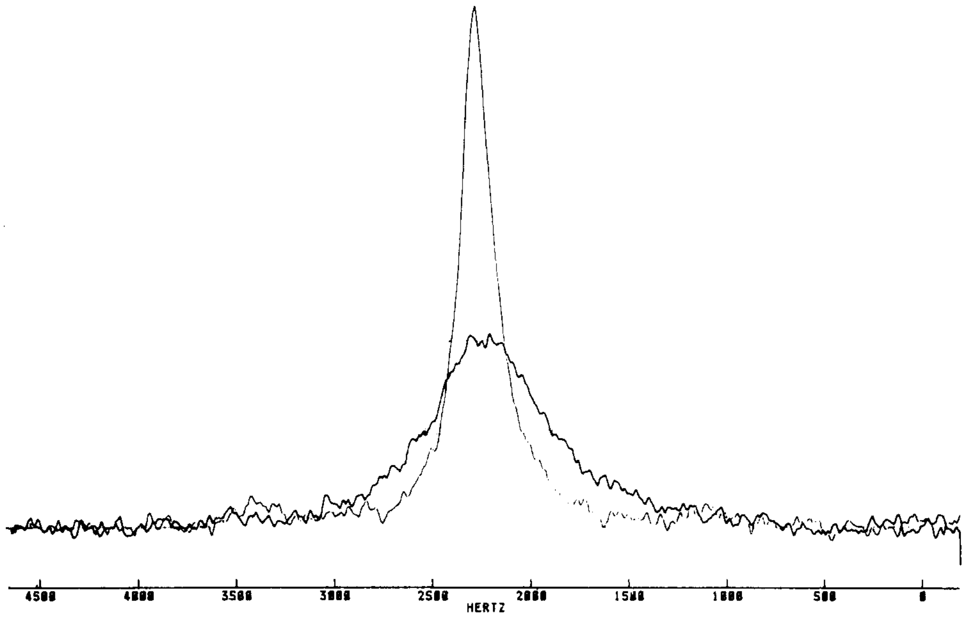

Figure 5. ^{31}P spectrum of PEO network nodes at room temperature for M_n = 1050 g mol^{-1}. Spinning effect at magic angle (spinning rate: 1.2 kHz).

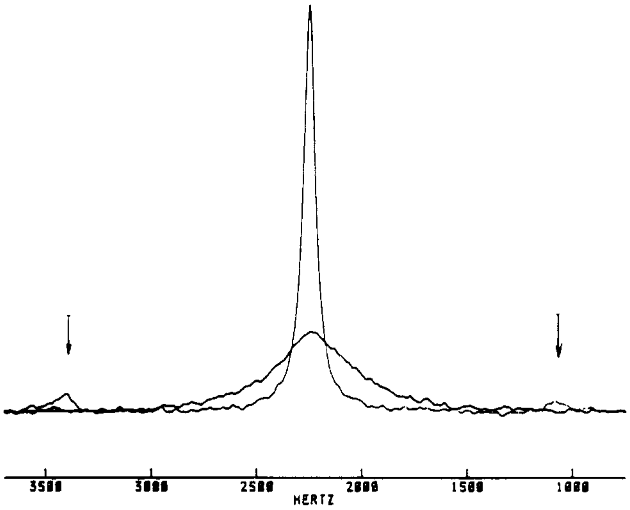

Figure 6. ^{31}P spectrum of PEO network nodes at 335 K for M_n = 1050 g mol^{-1}. Spinning effect at magic angle (spinning rate: 1.1 kHz). Arrows indicate spinning side band positions.

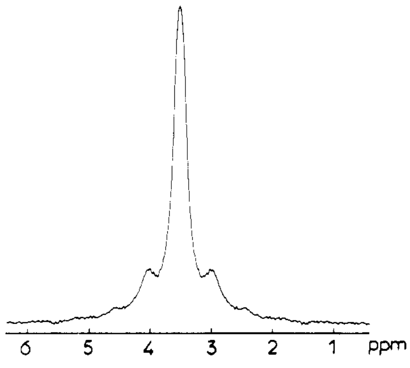

Figure 7. ^1H spectrum of PEO network chains (M_n = 1050 g mol^{-1}): typical spinning effect at magic angle observed at room temperature (spinning rate: 0.55 kHz).

function is lengthened as soon as the rotation speed is equal to 22 Hz. Figure 8b illustrates magnetic relaxation functions of protons observed in glycerol, an ordinary liquid, during or in the absence of sample rotation; no differences can be disclosed because there is no residual interaction.

III.2. Pseudosolid Spin–Echoes. Pseudosolid spin–echoes are specific to the presence of residual interaction.[9] The time reversal effect is induced by applying a $\pi/2$ rotation to the spin system when the magnetization is aligned along the x axis in the rotating frame. The rotation operator applied to $\langle \mathcal{H}_T(m) \rangle_{ij}$ gives $\langle \tilde{\mathcal{H}}_T(m) \rangle_{ij}$ such that

$$[\langle \tilde{\mathcal{H}}_T(m) \rangle_{ij}, \mathcal{M}_x] = -[\langle \mathcal{H}_T(m) \rangle_{ij}, \mathcal{M}_x] \qquad (9)$$

and

$$[\langle \tilde{\mathcal{H}}_T(m) \rangle_{ij}, \langle \mathcal{H}_T(m) \rangle_{ij}] \neq 0 \qquad (9')$$

A pseudosolid spin–echo (PSOSE) formed from the pulse sequence $(\pi/2)/y$, $(\pi/2)/x$ is described according to the formula

$$E(t,\tau) = \mathrm{Tr}\,\{\tilde{\mathcal{M}}_x(-t+\tau)\mathcal{M}_x(\tau)\} \qquad (10)$$

in which

$$\mathcal{M}_x(t) = \exp(i\langle \mathcal{H}_T(m) \rangle_{ij}t)\mathcal{M}_x \exp(-i\langle \mathcal{H}_T(m) \rangle_{ij})t$$

and $\tilde{\mathcal{M}}_x(t)$ is obtained by replacing $\langle \mathcal{H}_T(m) \rangle_{ij}$ with $\langle \tilde{\mathcal{H}}_T(m) \rangle_{ij}$.

III.2.a. Specific Properties. Two main properties characterize any PSOSE; they are derived from formulas 9 and 9′. First, the slope $\partial E(t=\tau_+,\tau)\partial t$ is opposite to the slope $\mathrm{d}M_x(t=\tau_+)/\mathrm{d}t$. Then, the intersection of two pseudosolid echoes formed at times $\tau + \eta$ and $\tau - \eta$, respectively, is observed at $t = 2\tau$; the expression

$$E(2\tau, \tau+\eta) = \mathrm{Tr}\,\{\tilde{\mathcal{M}}_x(-\tau+\eta)\mathcal{M}_x(\tau+\eta)\}$$

is equal to

$$E(2\tau, \tau-\eta) = \mathrm{Tr}\,\{\tilde{\mathcal{M}}_x(-\tau-\eta)\mathcal{M}_x(\tau-\eta)\}$$

PSOSE properties are illustrated in Figure 9. Echoes were observed from a PEO gel formed from end-linked chains characterized by a molecular weight $\overline{M_n}$ = 2100 g mol^{-1}. Measurements were performed while the gel was in a state of maximum swelling; the swelling ratio was Q_m = 6.6. Well-shaped pseudosolid echoes are reported. They obey properties specific to a relaxation function fully governed by a residual tensorial interaction of spins. Slopes $\partial E(t=\tau_+,\tau)/\partial t$ are illustrated in Figure 9.

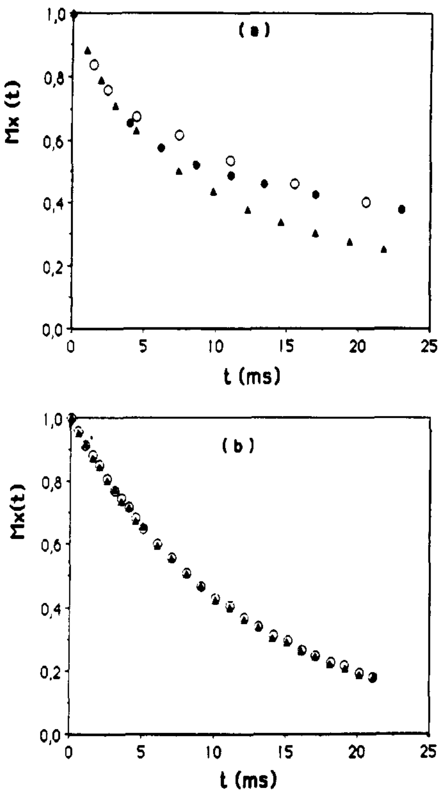

Figure 8. Spinning sample effect on proton spin–echo relaxation decays observed at room temperature. The angle between B_0 and the rotation axis was 90°. (a) PEO network: M_n = 3200 g mol^{-1} and Q = 2.8. (▲) Without sample rotation, (●) spinning rate equal to 22 Hz and (○) spinning rate equal to 60 Hz. (b) Liquid glycerol: (▲) sample without rotation, (○) spinning rate equal to 50 Hz.

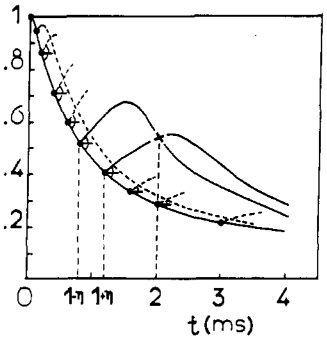

Figure 9. Proton pseudosolid spin–echo observed from PEO network (M_n = 2100 g mol^{-1}) observed at room temperature and $Q = Q_m$ = 6.6. Intersection (τ = 1 ms, η = 0.2 ms) and slope properties of E(t, τ) are also shown.

The observation of such echoes demonstrates that elementary network chains forming a polymeric gel are in a state of weak elongation whether they are observed in a dry system or in a swollen one.

III.2.b. Relaxation Function Derivative. The formation of a PSOSE at a time τ leads to a convenient way to determine the slope d$M_x(t)$/dt at $t = \tau$. This property has already been reported in an earlier study.[9] The experimental value of the slope is obtained by drawing the curve $S(t, \tau)$ representing the ratio

$$S(t, \tau) = (E(t, \tau) - M_x(t))/2(t-\tau) \qquad (11)$$

Then, the experimental limit of this ratio is equal to d$M_x(t{=}\tau)$/dt (Figure 10a). Two relaxation function derivatives are illustrated in Figure 10b. They were observed from a partially swollen gel (Q = 2.6) and from a fully swollen gel (Q_m = 6.6); the elementary chain molecular weight is $\overline{M_n}$ = 2100 g mol^{-1}. Continuous curves were drawn from a numerical description of $M_x(t)$; they are compared with experimental points obtained according to the direct way described above. The agreement between the two curves reinforces the observation of a residual tensorial interaction existing in PEO gels, like in many other polymeric gels whether they are formed from end-linked chains or vulcanized chains.

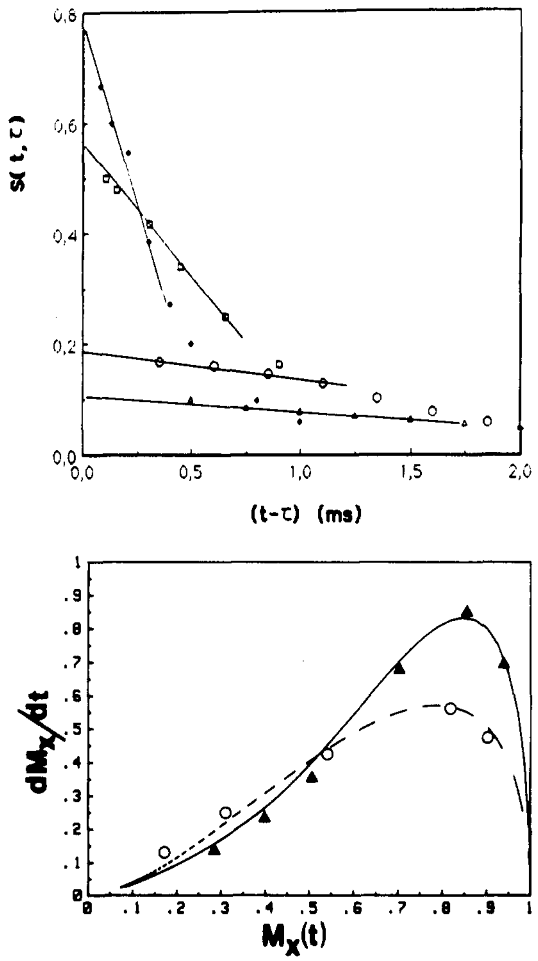

Figure 10. Proton relaxation function derivative. (a, top) Measured from the limit value of $S(t, \tau)$ at $t = \tau$. M_n = 2100 g mol^{-1} and $Q = Q_m$; τ = 0.2 (◆), 0.6 (□), 1.2 (○), and 2 ms (△). (b, bottom) Comparison between measured derivatives and derivatives calculated from numerical fits (formula 15). Q = 2.2 (○) and $Q = Q_m$ (▲).

III.3. Temperature Variations. No effect was found to result from variations of the temperature of samples, within the range 303–350 K. This is illustrated from a PEO network structure formed from a chain precursor characterized by a molecular weight $\overline{M_n}$ = 2100 g mol^{-1}. Relaxation functions of the partially swollen gel (Q = 2.6) are reported in Figure 11a; they correspond to two temperatures. These functions are similar to one another. Relaxation functions of the fully swollen gel (Q = 6.6) were also recorded to disclose possible effects of temperature variations due to the presence of a large amount of solvent. However, no changes of this function can be disclosed from Figure 11b.

IV. Swelling Properties

Before starting NMR investigations into the properties of polymeric gels, it is necessary to describe their behavior in a state of maximum swelling. The dependence of the maximum swelling ratio Q_m upon the molecular weight of the chain precursor is reported in Figure 12. Two ranges

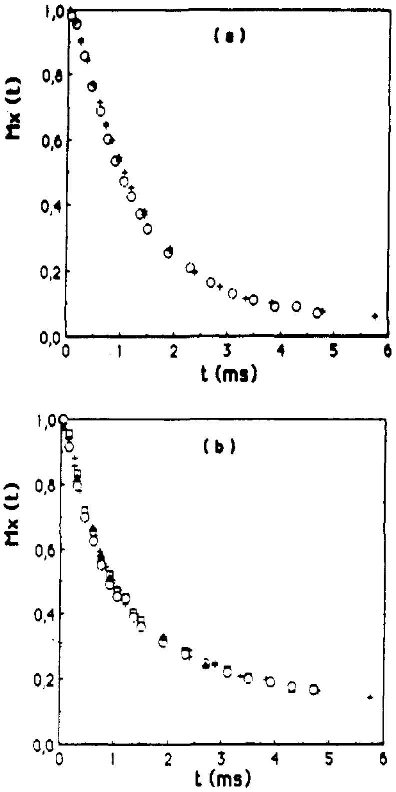

Figure 11. Temperature effect on proton spin-echo relaxation ($\overline{M}_n$ = 2100 g mol^{-1}). (a) Q = 2.2; T = 303 K (+) and T = 350 K (○). (b) $Q = Q_m$ = 6.6; T = 303 K (+), T = 318 K (▲), T = 335 K (□), and T = 346 K (○).

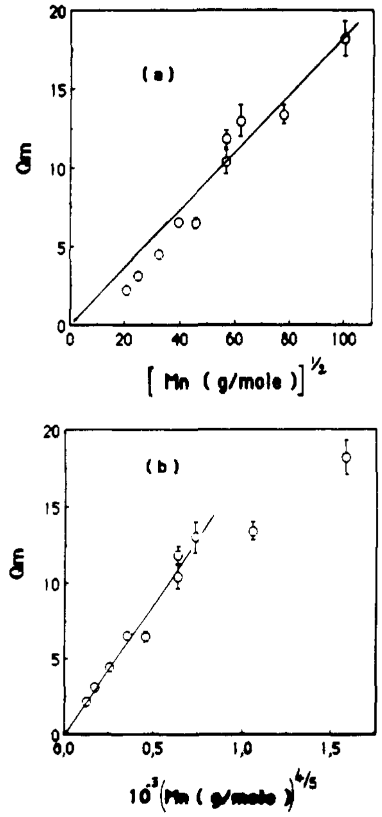

Figure 12. (a) Equilibrium swelling of PEO networks versus the square root of the precursor chain length. (b) Equilibrium swelling Q_m versus $\overline{M}_n$.

of variations are defined. For $\overline{M}_n < 3 \times 10^3$ g mol^{-1}, Q_m is found to be a linear function of $\overline{M}_n^{4/5}$. For $\overline{M}_n > 3 \times 10^3$ g mol^{-1}, a linear variation of Q_m is observed as a function of the square root $\overline{M}_n^{1/2}$. In both cases, the straight lines go through the origin of coordinates. These two laws of variations of Q_m are interpreted in the following way. For $\overline{M}_n \leq 3 \times 10^3$ g mol^{-1}, the volume fraction of solvent ν_s in the reaction bath, prior to the gelation process, is in the range where chain precursors start overlapping. The statistical structure of solutions near the C^* concentration is trapped by the end-linking reaction; then, it governs the state of maximum swelling induced by adding any good solvent. Consequently, Q_m^{-1} is proportional to the crossover concentration C^*, which depends upon the chain molecular weight according to the power law $C^* \propto \overline{M}_n^{-4/5}$. Each correlation domain that contributes to the swelling process is determined roughly by an entire chain precursor. For $\overline{M}_n \geq 3 \times 10^3$ g mol^{-1}, chain precursors overlap in the reaction bath. Random structures of solution result from statistical domains characterized by a coherence length $\xi \propto \upsilon_c^{-1}$, as is well-known from the description of concentrated polymer solutions.[5] If it is supposed that these statistical domains are trapped during the gelation process, then in the state of maximum swelling they are swollen by a good solvent. If they obey a condition of packing, the swelling ratio Q_m is expressed as $\upsilon_c^{-1.6}$ It should be independent of the chain molecular weight; this is in contradiction with experimental results. It is considered that a branched structure is trapped by the cross-linking reaction. It is formed from units determined by statistical domains in solution; the total number of monomeric units $\mathcal{N}_t$ in the branched structure is proportional to $\overline{N}_n$, the number of monomeric units in one chain precursor. Then, the swelling ratio is expressed as $Q_m \propto \overline{M}_n^{1/2}/\upsilon_c^{-1.6}$. This property will be described in a subsequent paper.

V. Relaxation Function of Partially Swollen Gels

Most relaxation functions of the transverse magnetization of nuclei attached to the polymeric system cannot be represented by simple exponential functions. Consequently, the quantitative interpretation of NMR properties observed in swollen gels cannot rely upon one parameter arbitrarily defined from the relaxation function. It is necessary to give a mathematical description of this function considered as a whole.

V.1. Relaxation Function. The elementary spin system that determines the NMR properties of PEO gels is one proton pair. Consequently, the relaxation function is supposed to be built from the basic response of a two-spin system ($I = {}^1/_2$):

$$m_x(t, \vec{r}_{ij}) = \cos\,[\Delta_G t(3\cos^2\theta(\vec{r}_{ij}) - 1)r_{ij}^2/L_{ij}^2] \qquad (12)$$

Δ_G is the dipole–dipole interaction in the absence of any motion; $\vec{r}_{ij}$ is the end-to-end vector of one elementary chain while L_{ij} is the contour length of this segment. Then, the relaxation function observed over the whole polymeric gel is expressed as

$$M_x(t) = \int m_x(t, \vec{r}_{ij})\, \mathcal{G}(\vec{r}_{ij})\, \mathrm{d}^3\vec{r}_{ij} \qquad (13)$$

The gel function $\mathcal{G}(\vec{r}_{ij})$ is the probability distribution function that describes properties of elementary network chains throughout the PEO gels under observation.

V.2. Gel Function. The probability distribution function that is chosen to describe the progressive swelling of systems formed from end-linked PEO chains consists of two parts:

$$\mathcal{G}(\vec{r}_{ij}) = p_s\mathcal{P}_1(\vec{r}_{ij}/\sigma_1) + (1-p_s)\mathcal{P}_2(\vec{r}_{ij}/\sigma_2) \quad (14)$$

$\mathcal{P}_1$ and $\mathcal{P}_2$ are Gaussian functions characterized by different mean square widths σ_1^2 and σ_2^2, respectively; p_s is a weight factor. The functions $\mathcal{P}_1$ and $\mathcal{P}_2$ are supposed to represent two populations of protons, located near cross-links or in the center of chain segments, for example. Then, the transverse relaxation function is expressed as a sum of two functions:

$$M_x(t) = p_s\mathcal{R}_1(t) + (1-p_s)\mathcal{R}_2(t) \quad (15)$$

where the function $\mathcal{R}_\alpha(t)$ (α = 1, 2) is defined as

$$\mathcal{R}_\alpha(t) = (1 + \Delta_\alpha^{\ 2}t^2 + r(\Delta_\alpha t))^{1/2}/\sqrt{2}r(\Delta\alpha t) \quad (16)$$

with

$$r(\Delta_\alpha t) = ((1 + \Delta_\alpha^{\ 2}t^2)^2 + 4(\Delta_\alpha t)^6/27)^{1/2} \quad (16')$$

α = 1, 2.

The function $\mathcal{R}_\alpha(t)$ has already proved to be well appropriate for the description of NMR properties observed in molten polybutadiene.[10] Typical relaxation functions are reported in Figure 13. In Figure 13a, relaxation functions correspond to two states of swelling (Q = 2.2 and Q_m = 6.6); the effect of swelling does not induce a monotonous evolution which applies along the whole relaxation function. In Figure 13b, the strong effect of swelling upon NMR properties is illustrated from a gel formed from a precursor chain characterized by a chain molecular weight $\overline{M_n}$ = 6000 g mol^{-1}. The swelling ratio is Q = 12; the time scale is 100 ms. Pseudosolid spin-echoes are observed along the whole relaxation function. The long tail corresponds to slightly stretched chain segments. The relaxation curve $M_x(t)$, given by formula 15, is shown to fit experimental results in Figure 13. The values assigned to the parameters are p_s = 0.81, Δ_1 = 0.71, and Δ_2 = 2.8 ms^{-1} for curve 13a′. For curve 13a″, p_s = 0.36, Δ_1 = 0.4, and Δ_2 = 2.1 ms^{-1}. For curve 13b, the parameter values are p_s = 0.56, Δ_1 = 0.043, and Δ_2 = 1.2 ms^{-1}. The agreement between experimental results and theoretical curves is fairly good, although experimental relaxation functions may have very different shapes and very different time scales of evolution.

V.3. Progressive Swelling of Gels. The progressive swelling of PEO gels was studied by adding small amounts of a good solvent until the state of maximum swelling was reached. Each step of the partial swelling was characterized by a relaxation function $M_x(t)$. Then, an intrinsic NMR parameter was defined by

$$\Sigma = M_2^{\ 3/2}/M_4^{\ 1/2} \quad (17)$$

in which

$$M_2 = (\mathrm{d}^2M_x(t)/\mathrm{d}t^2)_{t=0} \quad (18)$$

and

$$M_4 = (\mathrm{d}^4M_x(t)/\mathrm{d}t^4)_{t=0} \quad (18')$$

These quantities are derived from the fitting procedure

$$M_2 = 3p_s\Delta_1^{\ 2} + 3(1-p_s)\Delta_2^{\ 2}$$

and

$$M_4 = 81p_s\Delta_1^{\ 4} + 81(1-p_s)\Delta_2^{\ 4}$$

Parameters M_2 and M_4 are not obtained from direct differentiation of data. It is assumed that the relaxation function is entirely described by formula 15; therefore, the initial derivatives are defined from this function. Typical variations of the parameter Σ as a function of the ratio of partial swelling Q are reported in Figure 14. The three curves correspond to three different molecular weights of chain precursor, $\overline{M_n}$ = 1050, 2100, and 3200 g mol^{-1}. All curves exhibit a similar behavior.

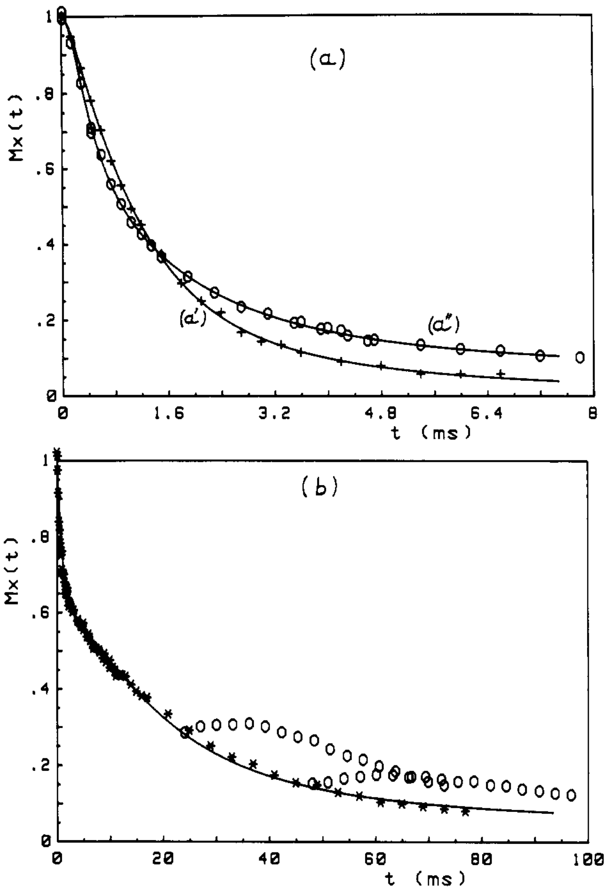

Figure 13. Swelling effect on proton spin–echo decay. (a) M_n = 2100 g mol^{-1}; Q = 2.2 (+) and Q = 6.6 (○). (b) M_n = 6000 g mol^{-1} and Q = 12; relaxation decay (*) and pseudosolid spin-echo (○). The continuous curves are obtained from a theoretical fit based on formula 15: (a′) p_s = 0.81, Δ_1 = 0.71 ms^{-1}, Δ_2 = 2.8 ms^{-1} for Q = 2.2; (a″) p_s = 0.36, Δ_1 = 0.40 ms^{-1}, Δ_2 = 2.1 ms^{-1} for Q = 6.6; (b) p_s = 0.56, Δ_1 = 0.043 ms^{-1}, Δ_2 = 1.2 ms^{-1}.

(i) A decrease of the relaxation rate Σ is first observed until the swelling ratio reaches the value $Q \simeq 2.5$ or 3. This first step is supposed to reflect a disengagement of elementary network chains from one another whatever their exact nature. It is considered that they obey a Gaussian statistic.

(ii) When the polymer volume fraction becomes smaller than about 0.4, the relaxation rate Σ starts increasing in a monotonous way until the state of maximum swelling is reached. This second step is supposed to reflect a smooth transition from a state where a Gaussian statistic applies because excluded volume effects are screened to a state where these effects govern the swelling process of PEO gels.

V.4. Crossover Concentration. It is worth analyzing properties of the state of swelling corresponding to the minimum of the relaxation rate $\Sigma_{\min}$ observed during the progressive swelling of any PEO gel. Although the value of $Q_{\min}$ associated with $\Sigma_{\min}$ is not determined with great accuracy, the dependence of $\Sigma_{\min}^{\ -1}$ upon the molecular weight $\overline{M_n}$ of the chain precursor can be well illustrated from the straight line drawn in Figure 15a. A qualitative interpretation of this linear dependence can be given in

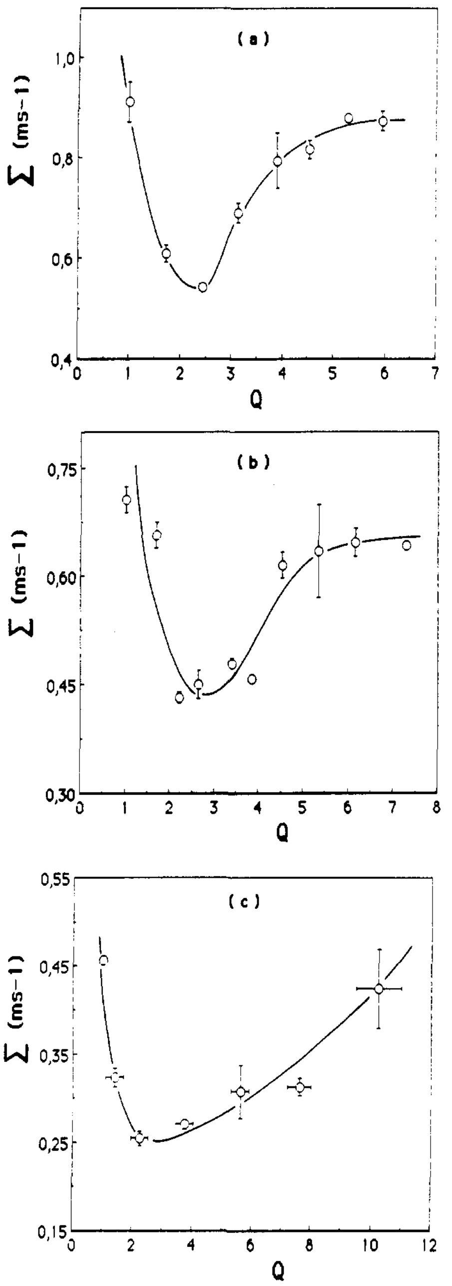

Figure 14. Relaxation rate $\Sigma(Q)$ (formula 17): a two-step swelling process. (a) M_n = 1050 g mol^{-1}. (b) M_n = 2100 g mol^{-1}. (c) M_n = 3200 g mol^{-1}.

accordance with formula 12. The strength of the residual interaction corresponding to statistical segments that obey Gaussian statistics is estimated from

$$|\epsilon_e| \simeq \Delta_G (r_{ij}{}^g)^2/(L_{ij}{}^g)^2$$

or

$$\Sigma_{min} \propto |\epsilon_e| \simeq \Delta_G/L_{ij}{}^g \qquad (19)$$

$L_{ij}{}^g$ and $r_{ij}{}^g$ are the contour length and the end-to-end vector of the chain segment which defines any statistical domain, whatever the exact nature of this domain. The main consequence of the observation of a linear dependence is that $L_{ij}{}^g$ is proportional to $\overline{M_n}$. In other words, statistical domains perceived from NMR are not determined from the concentration of synthesis but from the molecular weight of the chain precursor. Therefore, in the case where statistical domains would obey a property of packing condition, Q_{min} should be expressed as

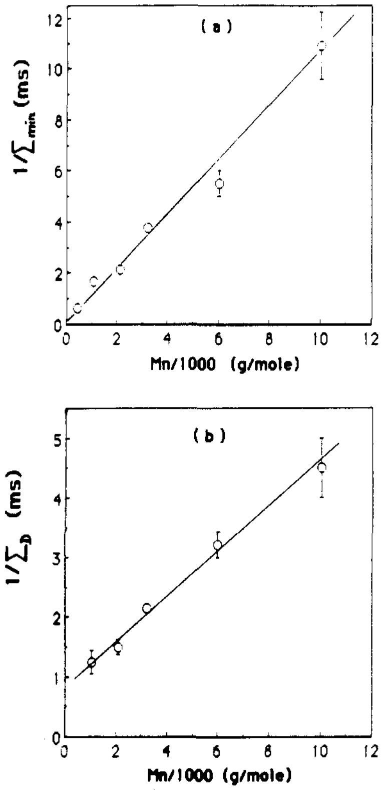

Figure 15. Relaxation time Σ^{-1} versus the precursor chain length. (a) $\Sigma_{min}{}^{-1}$ at room temperature. (b) $\Sigma_D{}^{-1}$ at T = 330 K.

$$Q_{min} \propto L_{ij}{}^{1/2} \qquad (19')$$

or

$$Q_{min} \propto M_n{}^{1/2}$$

However, it is found experimentally that Q_{min} hardly varies with $\overline{M_n}$; it is nearly constant: $2 < Q_{min} < 3$. It is considered that Q_{min} corresponds to the so-called C^{**} concentration of crossover between the concentration range where solution properties are described from three-body interactions to the concentration range where these properties are described from two-body interactions.[5] Accordingly, Q_{min} must not be dependent upon chain length variations. It is considered that statistical domains observed from NMR are distinct from those responsible for the partial swelling effect of PEO gels.

The value of the inverse of the relaxation rate $\Sigma_D{}^{-1}$ observed in dry gels is reported in Figure 15b as a function of $\overline{M_n}$, for comparison with the evolution of $\Sigma_{min}{}^{-1}$.

V.5. State of Maximum Swelling. Properties of the state maximum swelling can also be investigated from the relaxation rate of the transverse magnetization, in the following way. Variations of the relaxation time $\Sigma_m{}^{-1}$ observed as a function of the swelling ratio are reported in Figure 16. Two ranges of variations are determined in accordance with the two ranges observed from the maximum swelling ratio. For $\overline{M_n} < 3000$ g mol^{-1}, the relaxation time $\Sigma_m{}^{-1}$ is a linear function of Q_m in accordance with formula 3, a property already observed in other polymeric gels. For $\overline{M_n} > 3000$ g mol^{-1}, the relaxation time $\Sigma_m{}^{-1}$ is a linear function of $Q_m{}^{2.8}$ (Figure 16b). The two straight lines are found to go through the origin of coordinates. This dependence is interpreted in the following way. According to formula 13, the inverse of the time scale of variations of the magnetization of protons is given by the

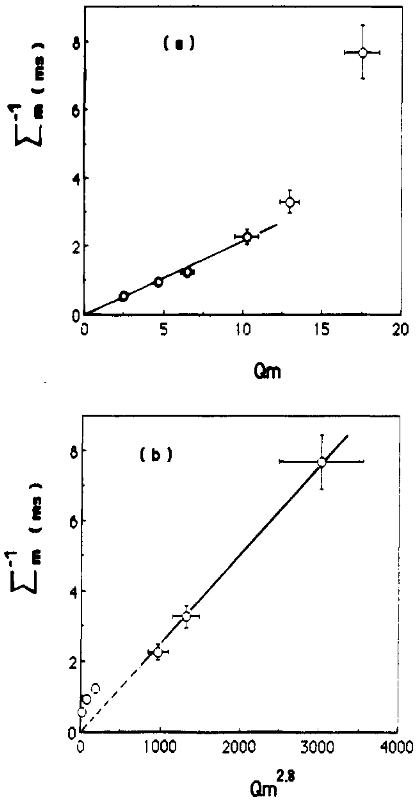

Figure 16. (a) Relaxation time Σ_m^{-1} versus the equilibrium swelling ratio. (b) Relaxation time Σ_m^{-1} versus $Q_m^{14/5}$.

general expression

$$\Sigma \propto a^2 \zeta_{ij}^2 / \sigma_{ij}^4 \qquad (20)$$

The width of the gel function $\mathcal{G}(\mathbf{r}_{ij}/\zeta_{ij})$ is given by ζ_{ij}, while σ_{ij}^2 is the mean square end-to-end distance of any segment formed from N_{ij} skeletal bonds; $\sigma_{ij}^2 = a^2N^{2\nu}$ with $\nu = {}^1/_2$ or ${}^3/_5$ for a Gaussian segment or a segment swollen by an excluded volume effect, respectively.

In the state of maximum swelling, the width of the gel function is dilated by a scaling factor equal to $Q_m^{1/3}N_{ij}^{1/3}$ if segments perceived from NMR obey a packing condition; then,

$$\Sigma_m \propto a^2 Q_m^{2/3} N_{ij}^{2/3} / N_{ij}^{4\nu} \qquad (20')$$

with $Q_m \propto N_{ij}^{1/2}$. Therefore, the scaling factor of the time scale of the relaxation function is proportional to $N_{ij}^{4\nu-1}$ or $Q_m^{8\nu-2}$. This dependence upon Q_m observed from three measurements is considered, of course, as a preliminary result.

VI. Conclusion

The transverse magnetic relaxation of protons attached to end-linked poly(ethylene oxide) chains is fully governed by the residual interaction of spins. The magnetic relaxation function can be given a quantitative description that reveals several features. The first one concerns the two-step progressive swelling of the trifunctional PEO gels. A disinterpersion of chains is first observed upon addition of solvent. A minimum of the proton relaxation rate is reached at a polymer volume fraction independent of chain precursor molecular weight and ranging between 0.33 and 0.4; the inverse of the minimum of the relaxation rate is proportional to the chain molecular weight. This result shows that network chain segments observed from NMR are different from those that govern the state of partial swelling of PEO gels. An entire chain precursor is perceived from NMR.

Another feature concerns the state of maximum swelling of PEO gels. Both the swelling ratio and the proton relaxation rate exhibit a strong molecular weight dependence. Although the determination of exponents is not easy over a range of molecular weights going from 400 to 10^4 g mol^{-1}, two domains of variations can be considered. Within the range going from 400 to 3000 g mol^{-1}, the swelling ratio is proportional to $\overline{M}_n^{4/5}$; correspondingly, the relaxation rate is proportional to $\overline{M}_n^{-4/5}$, as is expected ($\overline{M}_n$ is the chain precursor molecular weight). Within the range going from 3000 to 10 000 g mol^{-1}, the swelling ratio is proportional to $\overline{M}_n^{1/2}$ while the relaxation rate is proportional to $\overline{M}_n^{-14/5}$, as expected if the swollen gel is described as a branched structure.

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