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NMR and Gel Elasticity Interrelationship

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ABSTRACT: This work deals with the spin-system response of nuclei attached to polymer chains in a gel. It is shown that elongation effects and internal fluctuations of chain segments are involved in the gel elasticity and in the relaxation of transverse magnetization, using a phantom network model. Effects of an affine deformation of chain segments on NMR properties are discussed considering a uniaxially strained network structure. The $\lambda - 1/\lambda^2$ dependence of the retractive force is contrasted to the $\lambda^2 - 1/\lambda$ dependence of magnetic relaxation rates (λ is the stretching ratio).

I. Introduction

The purpose of this work is to show that the elasticity property of any polymeric gel can be connected to a specific nuclear magnetic relaxation mechanism. More precisely, internal fluctuations involved in the response of a gel to a weak static strain will be shown to also govern the pseudosolid (solidlike) response of nuclear spins, usually observed in such a system.[1] It is now well established that the dynamics of the transverse magnetization of nuclei attached to polymers may reflect the state of stretching of chain segments in a melt or in a network structure. More generally, a residual energy of tensorial spin–spin interactions has been shown to arise from nonisotropic rotational diffusions of monomeric units, induced by all topological constraints exerted on structural chain segments.[2] These are usually determined from a cutoff in chain fluctuations originating form nodes in a gel or from a dynamic screening effect in a melt.

It is worth emphasizing that the residual energy $\hbar\Delta_r$ of spin–spin interactions is closely related to the asymmetry character of hindered motions of monomer units. Starting from the description of free chain segments where the residual energy is equal to zero, $\hbar\Delta_r$ also corresponds to a reduction of entropy or, more generally, to a volume restriction of phase space associated with all constraints encountered by chain segments embedded in a gel. These constraints concern the presence of nodes and cross-links as well as the existence of monomer unit–monomer unit interactions. It may be stated that the residual energy $\hbar\Delta_r$ reflects the individual fractal character of a given chain segment swollen by all other surrounding segments: the higher the fractal character, the lower the residual energy in a gel. It is recalled that free chain segments in a melt obey a Gaussian statistics;[3] therefore they have a fractional exponent equal to 2. This exponent increases in a gel because of constraints. Accordingly, it is inferred that the residual energy is like the static modulus of elasticity of a gel; it may depend upon two main properties of chain segments: their elongation between nodes $\langle \vec r_e\rangle$ and their configurational fluctuations $\langle (\vec r_e - \langle \vec r_e\rangle)^2\rangle = r_0^2$.

Among the many questions concerning the description of gel systems are (i) the demonstration of the presence of fluctuations of nodes whether these are covalent bonds or not and (ii) the interpretation of an affinity property affecting the average displacements of these nodes under the effect of a weak elongation of a gel.[4]

It will be shown in this work that these two crucial properties are also involved in the spin-system response observed in gels.

II. Simple Description of Elasticity

Ordinary Fluids. The simple description of elasticity used throughout this approach starts from the free-enthalpy function of the system. It relies upon a well-known property concerning ordinary fluids.[5] Considering the free enthalpy function $G(p,T)$ of any fluid, the derivative $(\partial G/\partial V)_T$ is $-\chi$, the isothermal compressibility of the fluid; it is also related to the mean square of fluctuations of the extensive variable V representing the volume:

$$\langle \Delta V^2\rangle = +\chi VkT = -VkT/(\partial G/\partial V)_T \qquad (1)$$

V and T are statistically independent variables. A similar approach can be developed for gel systems.

Gel Systems. (a) Model. The gel system is described as a giant molecule consisting of cross-link points connected by chain segments. Positions of cross-link points in space are denoted $\vec R_j$ ($j = 1, 2, ..., N_c$). It is considered that the gel has no defects, i.e., no dangling chains. All chain segments are attached to cross-links. The functionality is uniform throughout the sample; it is equal to f. It is now assumed that extensive variables used to describe the gel system are end-separation vectors $\vec r_{ij} = \vec R_i - \vec R_j$. The conjugate intensive variables are the internal forces $\vec f_{ij}$; at equilibrium, these obey the relationship

$$\sum_{j=1}^{f} \vec f_{ij} = 0 \qquad (i, j = 1, 2, ..., N_c) \qquad (2)$$

The free-enthalpy function associated with the gel system is called $G(\{\vec f_{ij}\},T)$, where $\{\vec f_{ij}\}$ stands for all internal forces. The function $G(\{\vec f_{ij}\},T)$ is appropriate to the description of fluctuations of cross-link positions in space.[6]

Any average end-separation vector is obtained from the state equations

$$\langle \vec r_{ij}\rangle = \left(\frac{\partial G}{\partial \vec f_{ij}}\right)_T, \qquad (i, j = 1, 2, ..., N_c) \qquad (3)$$

and the correlation function of any two components x_{ij} and y_{lm} of $\vec r_{ij}$ and $\vec r_{lm}$ vectors is given by

$$\langle \Delta x_{ij}\Delta y_{lm}\rangle = \left(\frac{\partial \langle x_{ij}\rangle}{\partial f_{lm}^{y}}\right)kT \qquad (4)$$

where f_{lm}^{y} is the y component of the force $\vec f_{lm}$. Also

$$\langle \Delta x_{ij}\Delta y_{lm}\rangle = \left(\frac{\partial^2 G}{\partial f_{ij}^{x}\partial f_{lm}^{y}}\right)_T kT \qquad (4')$$

Formula 4′ applies to all components of $\vec r_{ij}$ vectors, defined along x, y, and z axes. For the sake of simplicity but without any loss of generality, it is now assumed that cross-correlation functions are equal to zero:

$$\langle (\Delta x_{ij})^2\rangle = kT\left(\frac{\partial^2 G}{\partial f_{ij}^{x\,2}}\right)_T \qquad (5)$$

From the state equations (3), the free enthalpy can be expressed as an implicit function of the extensive variables $\langle \vec{r}_{ij} \rangle$: $G(\{\langle \vec{r}_{ij} \rangle\},T)$.

(b) Uniaxial Stretching. When the gel system experiences a force applied along the z-axis, its length is multiplied by λ in the direction of the force; to keep the sample volume invariant, its width measured along the directions x or y perpendicular to the force is divided by $\lambda^{1/2}$. The gel system under stretching is described from the free-enthalpy function $G(\{\vec{f}_{ij}\},\lambda,T)$. The affinity property is now applied in the following way. Considering any end-separation vector $\vec{r}_{ij}$, its average components $\langle x_{ij} \rangle$, $\langle y_{ij} \rangle$, and $\langle z_{ij} \rangle$ in the absence of elongation are transformed in affinity with the sample deformation: $\langle u_{ij}(\lambda) \rangle = \langle x_{ij} \rangle / \lambda^{1/2}$, $\langle v_{ij}(\lambda) \rangle = \langle y_{ij} \rangle / \lambda^{1/2}$, and $\langle w_{ij}(\lambda) \rangle = \lambda \langle z_{ij} \rangle$, respectively. This hypothesis implies the following properties of the state equations:

$$\langle u_{ij}(\lambda) \rangle = \frac{\partial G(\{\vec{f}_{ij}\},\lambda,T)}{\partial f_{ij}{}^{x}} = \frac{\partial G(\{\vec{f}_{ij}\},1,T)}{\partial f_{ij}{}^{x}} \Big/ \lambda^{1/2}$$

$$\langle v_{ij}(\lambda) \rangle = \frac{\partial G(\{\vec{f}_{ij}\},\lambda,T)}{\partial f_{ij}{}^{y}} = \frac{\partial G(\{\vec{f}_{ij}\},1,T)}{\partial f_{ij}{}^{y}} \Big/ \lambda^{1/2}$$

$$\langle w_{ij}(\lambda) \rangle = \frac{\partial G(\{\vec{f}_{ij}\},\lambda,T)}{\partial f_{ij}{}^{z}} = \lambda \frac{\partial G(\{\vec{f}_{ij}\},1,T)}{\partial f_{ij}{}^{z}} \tag{6}$$

Intensive variables $\{\vec{f}_{ij}\}$ are functions of average displacements $\langle u_{ij}(\lambda) \rangle$, $\langle v_{ij}(\lambda) \rangle$, and $\langle w_{ij}(\lambda) \rangle$. Now, the derivative $(\partial G/\partial \lambda)_T$ is written as

$$\left(\frac{\partial G}{\partial i} \right)_T = \sum_{i,j} \frac{\partial G}{\partial f_{ij}{}^{z}} \frac{\partial f_{ij}{}^{z}}{\partial \langle w_{ij} \rangle} \frac{\partial \langle w_{ij} \rangle}{\partial i} + \sum_{i,j} \frac{\partial G}{\partial f_{ij}{}^{y}} \frac{\partial f_{ij}{}^{y}}{\partial \langle v_{ij} \rangle} \frac{\partial \langle v_{ij} \rangle}{\partial \lambda} + \sum_{i,j} \frac{\partial G}{\partial f_{ij}{}^{x}} \frac{\partial f_{ij}{}^{x}}{\partial \langle u_{ij} \rangle} \frac{\partial \langle u_{ij} \rangle}{\partial \lambda} \tag{7}$$

where all cross-terms are omitted. Then

$$\left(\frac{\partial G}{\partial \lambda} \right)_T = \sum_{i,j} \langle w_{ij}(\lambda) \rangle \langle z_{ij} \rangle \frac{kT}{\langle \Delta z_{ij}{}^2 \rangle} - \sum_{i,j} \langle v_{ij}(\lambda) \rangle \langle y_{ij} \rangle \frac{kT}{2 \langle \Delta y_{ij}{}^2 \rangle} \lambda^{-3/2} - \sum_{i,j} \langle u_{ij}(\lambda) \rangle \langle x_{ij} \rangle \frac{kT}{2 \langle \Delta x_{ij}{}^2 \rangle} \lambda^{-3/2} \tag{8}$$

In accordance with the phantom network model, mean-square fluctuations are supposed to be independent of λ for slight deformations:[1]

$$\sum_{i,j} \langle \Delta z_{ij}{}^2 \rangle = \sum_{i,j} \langle \Delta y_{ij}{}^2 \rangle = \sum_{i,j} \langle \Delta x_{ij}{}^2 \rangle = \sum_{i,j} \langle \Delta \vec{r}_{ij}{}^2 \rangle / 3 \tag{9}$$

Also, it is assumed that $\sum \langle x_{ij} \rangle^2 = \sum \langle y_{ij} \rangle^2 = \sum \langle z_{ij} \rangle^2$. Then, in the same way

$$\left(\frac{\partial G}{L_0 \partial \lambda} \right)_T = \frac{kT}{L_0} (\lambda - 1/\lambda^2) \sum_{i,j} \frac{\langle \bar{r}_{ij} \rangle^2}{\langle \Delta \vec{r}_{ij}{}^2 \rangle} \tag{10}$$

with L_0 the initial length of the gel ($\lambda = 1$). Therefore, the force per unit initial area, corresponding to the elongation λ, is given by

$$\left(\frac{\partial G}{V_0{}^{\partial \lambda}} \right)_T = \frac{kT}{V_0} (\lambda - 1/\lambda^2) \sum_{i,j} \frac{\langle \vec{r}_{ij} \rangle^2}{\langle \Delta \vec{r}_{ij}{}^2 \rangle} \tag{11}$$

where V_3 is the gel volume supposed to be invariant. The summation extends over all chains, ν in number. Let the expression

$$\nu(\langle \vec{r}_{ij} \rangle^2 / \langle \Delta \vec{r}_{ij}{}^2 \rangle)$$

denote the summation $\sum_{ij} \langle \vec{r}_{ij} \rangle^2 / \langle \Delta \vec{r}_{ij}{}^2 \rangle$; then

$$f(\lambda) = \left(\frac{\partial G}{V_0{}^{\partial \lambda}} \right)_T = kT(\lambda - 1/\lambda^2) \frac{\nu}{V_0} \left(\frac{\langle \vec{r}_{ij} \rangle^2}{\langle \Delta \vec{r}_{ij}{}^2 \rangle} \right) \tag{12}$$

The above formula is equivalent to usual expressions proposed to describe small elongation of gels, in the simplest way.[1] Connections of the elasticity property of a gel with the response of nuclear spins attached to polymer chains will be discussed in the next section.

III. Transverse Magnetic Relaxation

It may be worth briefly recalling the way NMR is sued to investigate elementary chain properties in network structures.

Partial Motional Averaging. A given elementary chain is considered with a fixed end-separation vector $\vec{r}_{i,j}$ whatever the origins of the constraint applied to the segment. Instantaneous orientations of any skeletal bond a obey a distribution function compatible with the end-separation vector $\vec{r}_{i,j}$: $\mathcal{P}(\vec{r}_{i,j};\vec{a})$. Monomer units undergo nonisotropic rotational diffusions.

It is first considered that the elementary chain is in a frozen state like the glassy state. Then the static distribution of orientations of bonds within a chain segment is also given by $\mathcal{P}(\vec{r}_{ij};\vec{a})$; it now describes an ensemble average instead of a time average. The average extends over all elementary chains characterized by the same end-separation vector $\vec{r}_{i,j}$. Neglecting dipole–dipole interactions between spins ($I = {}^1/_2$) located on different chain segments, a second moment $\mu_2{}^{s}(\vec{r}_{i,i})$ and a fourth one $\mu_4{}^{s}(\vec{r}_{i,j})$ are associated with the dynamics of the transverse nuclear magnetization defined along the chain. They are calculated according to usual formulas, taking dipole–dipole interactions $\mathcal{H}_{i,j}{}^{D}$ existing within a chain segment into consideration.[7] Then turning back to the case where random motions of monomeric units occur while end-separation vectors are fixed, the second moment is invariant whereas the fourth moment is expressed as

$$\mu_4{}^{m}(\vec{r}_{i,j}) = \mu_4{}^{s}(\vec{r}_{i,j}) - \mu_2{}^{s}(\vec{r}_{i,j}) \Gamma^{\circ\circ}{}_{e}(0) \tag{13}$$

when $\Gamma^{\circ\circ}{}_{e}(0)$ represents the second time derivative of the correlation function describing random motions of monomeric units, whatever the complexity of these motions. Also, the first-order average of dipole–dipole interactions is not equal to zero: there is a residual energy of dipole–dipole interactions $\hbar \mathcal{H}_{i,j}{}^{e}$. For the sake of simplicity, the analysis is now restricted to noninteracting proton pairs. The first-order average leads to a splitting of resonance frequencies: $\omega_0 \pm \epsilon_{i,j}{}^{e}$ (ω_0 is the Larmor frequency of protons); $\epsilon_{i,j}{}^{e}$ will be expressed subsequently. The second moment associated with $\epsilon_{i,j}{}^{e}$ is $\mu_2{}^{e}(\vec{r}_{i,j}) = (\epsilon_{i,j}{}^{e})^2$. A well-resolved doublet of resonance lines is obtained whenever the following inequality is satisfied:

$$(\mu_2{}^{s}(\vec{r}_{i,j}) - \mu_2{}^{e}(\vec{r}_{i,j}))^2 \ll \mu_4{}^{s}(\vec{r}_{i,j}) - \mu_2{}^{s}(\vec{r}_{i,j}) \Gamma^{\circ\circ}{}_{e}(0) - (\epsilon_{i,j}{}^{e})^4 \tag{14}$$

The above well-known inequality determines the condition necessary to observe a partial motional narrowing effect of dipole–dipole interactions. The effect of hindered diffusional rotations of monomeric units amounts to the elimination of the $\mu_2{}^{s} - \mu_2{}^{e}$ part of the second moment $\mu_2{}^{s}(\vec{r}_{i,j})$. Then, the well-defined splitting $2\epsilon_{i,j}{}^{e}$ becomes the parameter of investigations of properties of the gel system. The NMR approach described throughout this study will rely upon this fundamental property, induced by a partial motional averaging process of spin–spin interactions. The nuclear magnetization associated with a proton pair attached to a given chain segment is simply written as

$$M_x^{\mathrm{e}}(t,\vec{r}_{i,j}) = \tfrac{1}{2}\exp(\pm i\epsilon_{i,j}^{\mathrm{e}}t) \tag{15}$$

Transfer of NMR Properties. Considering again noninteracting proton pairs, the general expression of the splitting parameter $\epsilon_{i,j}^{\mathrm{e}}$ is

$$\epsilon_{i,j}^{\mathrm{e}}(\vec{r}_{i,j}) = (3\gamma^2\bar{h}/4b^3)3\vec{r}_{i,j}^{\,2}(3\cos^2\theta_{i,j} - 1)/5\mathrm{Le}^2 \tag{16}$$

It is a function of both the orientation $\theta_{i,j}$ of the end-separation vector $\vec{r}_{i,j}$ and the ratio $|\vec{r}_{i,j}|/\mathrm{Le}$; Le is the contour length of the chain segment. The dipole–dipole interaction of two protons separated by a distance b is $3\gamma^2\bar{h}/4b^3$. The ratio $|\vec{r}_{i,j}|/\mathrm{Le}$ gives an illustration of the competitive roles played by the chain length and the chain extension, in the stretching effect. It also illustrates the sensitivity of NMR properties to the fractal character of a chain segment. When the segment (i,j) is completely stretched ($|\vec{r}_{i,j}| = \mathrm{Le}$), it has no fractal character, and the dipole–dipole interaction within a proton pair is maximum. When the segment is slightly stretched ($|\vec{r}_{i,j}| = 0$), the residual energy is reduced by the factor $|\vec{r}_{i,j}|^2\mathrm{Le}^2$; the fractal character is maximum and the fractal exponent is $D = 2$. More generally, the parameter $\epsilon_{i,j}^{\mathrm{e}}$ reflects not only elongation effects but also all topological constraints which hinder monomeric unit motions.

Formula 16 applies to real Gaussian chains. It actually describes a transfer of NMR properties from the local space scale associated with any monomeric unit to the semilocal space scale determined by end-separation vectors $\vec{r}_{i,j}$. Details about the dynamics of monomeric units are completely ignored; we are only interested in the asymmetry property of the rotational motions. This asymmetry character is mainly governed by the elongation vector $\vec{r}_{i,j}$.

More generally, but without entering into a description too detailed, the second moment $\mu_2^{\mathrm{s}}(\vec{r}_{i,j})$ associated with all proton groups attached along a given chain segment is reduced to $\mu_2^{\mathrm{e}}(\vec{r}_{i,j})$, with

$$\mu_2^{\mathrm{e}}(\vec{r}_{i,j}) = \mathrm{Tr}\,\{[\mathcal{H}_{i,j}^{\mathrm{e}},M_{\mathrm{x}}]\}^2/\mathrm{Tr}\,\{M_{\mathrm{x}}^2\} \tag{17}$$

M_{x} is the transverse magnetization operator.

The part $\mu_2^{\mathrm{s}}(\vec{r}_{i,j}) - \mu_2^{\mathrm{e}}(\vec{r}_{i,j})$ is reduced by random motions of monomeric units, provided that the part $\mu_4^{\mathrm{m}}(\vec{r}_{i,j}) - \mu^{\mathrm{e}}(\vec{r}_{i,j})$ of the fourth moment is strong enough compared with $(\mu_2^{\mathrm{s}}(\vec{r}_{i,j}) - \mu_2^{\mathrm{e}}(\vec{r}_{i,j}))^2$; $\mu_4^{\mathrm{e}}(\vec{r}_{i,j})$ is defined in an usual way from the residual interaction $\mathcal{H}_{i,j}^{\mathrm{e}}$. When this condition is fulfilled, it can be considered that the transverse magnetization dynamics is purely governed by the residual energy of spin–spin interactions $h\mathcal{H}_{i,j}^{\mathrm{e}}$:

$$M_{\mathrm{x}}^{\mathrm{e}}(t;\vec{r}_{i,j}) = \mathrm{Tr}\,\{e^{i\mathcal{H}_{i,j}^{\mathrm{e}}t}M_{\mathrm{x}}e^{-i\mathcal{H}_{i,j}^{\mathrm{e}}t}M_{\mathrm{x}}\}/\mathrm{Tr}\,\{M_{\mathrm{x}}^2\} \tag{18}$$

Several cases must now be discussed, depending upon the model chosen to describe gel systems.

Frozen Cross-Links. Noninteracting proton pairs are considered again. In the case where it is supposed that cross-links do not fluctuate at all, end-separation vectors obey a distribution function $\Pi(\vec{r}_{i,j})$, describing the whole gel system; NMR properties result from the isotropic average of nonisotropic effects associated with every elementary chain. Then, the second moment of the spectrum is given by $(\epsilon_{i,j}^{\mathrm{e}})^2$ and the fourth moment also corresponds to

$$\int \Pi(\vec{r}_{i,j})(\epsilon_{i,j}^{\mathrm{e}})^{2n}\,\mathrm{d}\vec{r}_{i,j} \qquad n = 1, 2 \tag{19}$$

More generally, the dynamics of the transverse magnetization observed in such a gel system is given by

$$M_{\mathrm{x}}^{G}(t) = \int \Pi(\vec{r}_{i,j})\cos(\epsilon_{i,j}^{\mathrm{e}}t)\,\mathrm{d}\vec{r}_{i,j} \tag{20}$$

It reflects the distribution of vectors joining cross-link points. The response $M_{\mathrm{x}}^{G}(t)$ has been already calculated in the case of a Gaussian distribution of $\vec{r}_{i,j}$ vectors:[2]

$$M_{\mathrm{x}}^{G}(t) = \left(\frac{1 + 3\theta^2 + U(\theta)}{2(U(\theta))^2}\right)^{1/2} \tag{21}$$

with

$$U(\theta) = ((1 + 3\theta^2)^2 + 4\theta^6)^{1/2}$$

and

$$\theta = t(0.6\Delta_G{}^2a^2/3\mathrm{Le}^2)^{1/2}$$

a is the mean skeletal bond length and $\Delta_G = 0.67\gamma^2\bar{h}/b^3$ is the second moment which would be observed in a glassy state.

The case of nonfluctuating cross-links has no equivalent description within the framework of analysis of gel system properties presented in section II. This simplest theory of gel elasticity is known to be independent of internal properties of elementary chains. It only depends upon the number of cross-links per unit volume.[9]

Fluctuating Cross-Links. It is now supposed that positions of cross-link points fluctuate in time. This assumption implies that end-separation vectors are time dependent: $\vec{r}_{i,j}(t)$. The determination of the crucial role played by cross-link fluctuations and the characterization of the rate of these fluctuations are two main problems encountered nowadays, in the description of the mechanical response of gels. Considering the response of spins attached to polymer chains, two main cases can be considered depending upon the rate of cross-link fluctuations.

(a) Rapidly Fluctuating Cross-Links. Observing a given chain segment, characterized by an end-separation vector $\vec{r}_{i,j}$, there is a residual energy $\epsilon_{i,j}^{\mathrm{e}}(\vec{r}_{i,j})$, as given by formula 16. Assuming now that cross-links fluctuate in time, there is a new residual energy $\epsilon_{i,j}^{\mathrm{f}}$ corresponding to these fluctuations:

$$\epsilon_{i,j}^{\mathrm{f}} = \langle\langle\epsilon_{i,j}^{\mathrm{e}}\rangle\rangle_{\mathrm{f}}$$

where the symbol $\langle\langle\ \rangle\rangle$ stands for a double time average affecting motions of monomeric units.

When fluctuations are fast enough, i.e., when the rate of fluctuations τ_{f}^{-1} is higher than $|\epsilon_{i,j}^{\mathrm{e}} - \epsilon_{i,j}^{\mathrm{f}}|$, they induce a partial motional averaging effect perceived from NMR.

The dipole–dipole energy is more reduced; however, it is not averaged to zero:

$$\epsilon_{i,j}^{\mathrm{f}} = (3\gamma^2\bar{h}/4b^3)3\langle\vec{r}_{i,j}\rangle_{\mathrm{f}}^2(3\cos^2\theta_{i,j}^{\mathrm{f}} - 1)/5\mathrm{Le}^2 \tag{22}$$

The dynamics of the transverse magnetization observed in such a system is described by

$$M_{\mathrm{x}}(t) = \int \Pi_f(\langle\vec{r}_{i,j}\rangle_{\mathrm{f}})\cos\{\epsilon_{i,j}^{\mathrm{e}}(\langle\vec{r}_{i,j}\rangle_{\mathrm{f}})t\}\,\mathrm{d}\langle\vec{r}_{i,j}\rangle_{\mathrm{f}} \tag{23}$$

The distribution of average end-separation vectors $\langle\vec{r}_{i,j}\rangle_{\mathrm{f}}$ is perceived from NMR. A Gaussian distribution can be used to describe all average end-separation vectors. However, no information is obtained about internal fluctuations of chain segments involved in gel elasticity.

(b) Slowly Fluctuating Cross-Links. In this section, it is assumed that cross-link points slowly fluctuate, i.e., the rate of fluctuations τ_f^{-1} is small compared with $|\epsilon_{i,j}^{\mathrm{e}} - \epsilon_{i,j}^{\mathrm{f}}|$. There is no possible additional motional averaging effect observed from NMR. As a characteristic property of NMR, fluctuations are perceived in space instead of being perceived in time. Considering two consecutive nodes i and j, the distribution function of instantaneous end-separation vectors $\vec{r}_{i,j}$ is used as a distribution function of static end-separation vectors, to calculate NMR properties. The average of the spin-system response observed in a whole gel is obtained in two steps. The spin-system response associated with a given vector $\vec{r}_{i,j}$ is first considered. The second moment induced by the residual energy governing the magnetization dynamics is expressed as

$$M_2^{\mathrm{r}}(i,j) = \langle \mu_2^{\mathrm{e}}(\vec{r}_{i,j}) \rangle \tag{24}$$

or

$$M_2^{\mathrm{r}}(i,j) = \langle (\epsilon_{i,j}^{\mathrm{e}})^2 \rangle \tag{24'}$$

for a proton pair. The average extends over all end-separation vectors concerning cross-links i and j. It is calculated by assuming that the distribution function of $\vec{r}_{i,j}$ vectors is Gaussian. Then

$$M_2^{\mathrm{r}}(i,j) = 1.22(\gamma^4\hbar^2/b^6)(\langle z_{i,j}^4\rangle - \langle z_{i,j}^2\rangle^2)/\mathrm{Le}^4 \tag{25}$$

where $z_{i,j}$ is one of the three cartesian coordinates of the stretching vector $\vec{r}_{i,j}$.

Let $\langle \Delta\vec{r}_{i,j}^{\,2}\rangle/3$ denote the average quantity $\langle (z_{i,j} - \langle z_{i,j}\rangle)^2\rangle$; $M_2(i,j)$ is easily shown to be equal to

$$M_2(i,j) = 2.43(\gamma^4\hbar^2/b_6)\frac{\langle \Delta\vec{r}^{\,2}_{i,j}\rangle}{3\mathrm{Le}^4}\left(\frac{\langle \Delta\vec{r}_{i,j}^{\,2}\rangle}{3} + 2\langle z_{i,j}\rangle^2\right) \tag{26}$$

The second step of the average is extended over all chains in a gel

$$M_2^{\mathrm{r}} = M_2^{\mathrm{r}}(i,j) = 2.43\frac{(\gamma^4\hbar^2/b^6)}{\nu\mathrm{Le}^4}\sum_{i,j}\frac{\langle \Delta\vec{r}_{i,j}^{\,2}\rangle}{3}\left(\frac{\langle \Delta\vec{r}_{i,j}^{\,2}\rangle}{3} + \frac{2\langle \vec{r}_{i,j}\rangle^2}{3}\right) \tag{27}$$

The second moment M_2^{r} observed on the whole gel system is dependent on internal chain segment fluctuations and also on the stretching state of chains, in the absence of gel elongation. Quantities determining M_2^{r} also define the elasticity constant given by formula 12.

Small Gel Elongation. Only effects of chain stretching induced by the gel elongation will be considered throughout the present analysis. The possible enhancement of orientational effects of monomeric units will be left aside.[9] The direction of the force is parallel to that of the steady magnetic field $\vec{B}_0$.

(a) No Cross-Link Fluctuations. When there are no fluctuations of nodes, whatever their exact nature, the residual energy within a chain segment (i,j) is simply expressed by assuming that the displacements are in affinity with the macroscopic deformation of the gel:

$$\epsilon_{i,j}^{\mathrm{e}} = (2\lambda^2 z_{i,j}^2 - y_{i,j}^2/\lambda - x_{i,j}^2/\lambda)/\mathrm{Le}^2 \tag{28}$$

when it is extended over all chains segments, it is not equalo to zero:

$$\nu^{-1}\sum_{i,j}\epsilon_{i,j}^{\mathrm{e}} = 2(\lambda^2 - 1/\lambda)\nu^{-1}\sum_{i,j} z_{i,j}^2 \tag{29}$$

Also, the second moment resulting from the residual energy is expressed as

$$M_2^{\mathrm{r}} = 0.09(\gamma^4\hbar^2/b^6)a^2(3\lambda^4 - 2\lambda + 2/\lambda^2)/\mathrm{Le}^2 \tag{30}$$

The distribution function of end-separation vectors is supposed to be Gaussian.

(b) Rapidly Fluctuating Cross-Links. In the case of rapidly fluctuating cross-links, the residual energy of spin–spin interactions assigned to a given chain segment (i,j) reads

$$\epsilon_{i,j}^{\mathrm{e}} = 0.45(\gamma^2\hbar/b^3)(\langle 2w_{i,j}^2(\lambda)\rangle - \langle v_{i,j}^2(\lambda)\rangle - \langle u_{i,j}^2(\lambda)\rangle)/\mathrm{Le}^2 \tag{31}$$

The residual energy is averaged over the whole gel system, assuming that the affinity property applies to average end-separation vectors:

$$\nu^{-1}\sum_{i,j}\epsilon_{i,j}^{\mathrm{e}} = 0.9(\gamma^2\hbar/b^3)(\lambda^2 - 1/\lambda)\nu^{-1}\sum_{i,j}\langle z_{i,j}\rangle^2/\mathrm{Le}^2 \tag{32}$$

The second moment is expressed by formula 30, provided that the distribution function of average elongation vectors is Gaussian.

(c) Slowly Fluctuating Cross-Links. The effect of slow fluctuations of cross-links is to introduce internal chain segment fluctuations and chain elongations:

$$M_2^{\mathrm{r}} = \frac{0.21\gamma^4\hbar^2/b^6}{\mathrm{Le}^4}\left\{(12\lambda^4 + 8/\lambda^2 - 8\lambda)\nu^{-1}\sum_{i,j}\frac{\langle \Delta\vec{r}_{i,j}^{\,2}\rangle}{3}\left(\frac{\langle \Delta\vec{r}_{i,j}^{\,2}\rangle}{3} + 2\langle z_{i,j}\rangle^2\right) + 4(\lambda^2 - 1/\lambda)^2\nu^{-1}\sum_{i,j}\langle z_{i,j}\rangle^4\right\} \tag{33}$$

IV. Discussion

The above description can be illustrated from the observation of the transverse magnetic relaxation of noninteracting two-spin systems ($I = {}^1/_2$) or from quadrupolar nuclei ($I = 1$).[10-12] It is worth emphasizing that most experimental results concerning NMR properties observed in uniaxially strained network structures show a linear dependence of the residual tensorial energy upon the expression $\lambda^2 - 1/\lambda$. Slight deviations from this linear dependence have not been definitely assigned to the nonaffine nature of chain deformation. Actually, intrinsic NMR properties, like the mathematical structure of the relaxation function, may be also affected by increasing strain; then it cannot be considered that the relaxation rate is derived in an invariant way from experimental results, whatever the strain strength.

Surprisingly enough the linear variation of the residual energy of spin–spin interactions with respect to the expression $\lambda^2 - 1/\lambda$ well applies to proton pairs although they interact with one another. This property has been observed in uniaxially strained polybutadiene networks corresponding to several cross-link concentrations.[12] Furthermore, a similar result is obtained from uniaxially strained silica–siloxane mixtures.[13] The dynamics of three-spin systems ($I = {}^1/_2$) associated with methyl groups attached to siloxane chains is known to parallel that of proton pairs; therefore, the state of stretching of chain segments is probed in the same way by observing either proton pairs or methyl groups.[2] Silica particles are randomly shaped and there are about 100 polymer chains bound to one particle. When the concentration of particles is high enough and the length of siloxane chains is suitable, an infinite cluster is formed. It behaves like a conventional gel system. Although cross-links are far from being pictured as points, the retractive force per unit initial cross-section obeys a linear dependence upon the expression $\lambda - 1/\lambda^2$. This property is equivalent to the dependence upon $\lambda^2 - 1/\lambda$ observed from NMR. Consequently, the specific dependence of the transverse magnetic relaxation rate upon the difference $\lambda^2 - 1/\lambda$ is considered as strong evidence for affine deformation of elastically effective chains, whatever the exact nature of nodes. It affects any chain segment as a whole. In accordance with formula 33, the dependence upon $\lambda^2 - 1/\lambda$ is obtained by assuming that elongation effects determined by $\langle z_{i,j}\rangle^2$ dominate over fluctuation effects determined by $\langle \Delta r_{i,j}^2\rangle$. It must be noted that the relaxation rate dependence upon λ is contrasted to that of the retractive force $f(\lambda)$ since it varies as $\lambda^2 - 1/\lambda$ instead of $\lambda - 1/\lambda^2$.

In accordance with the analysis presented in section II, this nearly general NMR property can be given a framework of description broader than that developed in section III. The transverse nuclear magnetization M_x of the whole gel system is supposed to be a function of $\{\vec{r}_{i,j}\}$ vectors. At a given time t, the derivative of $M_x(t)$ with respect to the stretching ratio λ is expressed as

$$\frac{\partial M_x(t)}{\partial \lambda} = \sum_{i,j} \frac{\partial M_x}{\partial \langle w_{i,j}\rangle} \langle z_{i,j}\rangle - \sum_{i,j} \frac{\partial M_x}{\partial \langle v_{i,j}\rangle} \langle y_{i,j}\rangle / 2\lambda^{3/2} - \sum_{i,j} \frac{\partial M_x}{\partial \langle u_{i,j}\rangle} \langle x_{i,j}\rangle / 2\lambda^{3/2} \quad (34)$$

When a relaxation rate is experimentally found to vary as a $\lambda^2 - 1/\lambda$, its derivative is a function of $2\lambda + 1/\lambda^2$. Compared with equation 34, such a result implies that

$$\frac{1}{2\lambda} \sum_{i,j} \frac{\partial M_x}{\partial \langle w_{i,j}\rangle} = -(\lambda^{1/2}) \sum_{i,j} \frac{\partial M_x}{\partial \langle v_{i,j}\rangle} = -(\lambda^{1/2}) \sum_{i,j} \frac{\partial M_x}{\partial \langle u_{i,j}\rangle} \quad (35)$$

These equalities correspond to $\partial M_x/\partial\langle w_{i,j}\rangle = \langle w_{i,j}\rangle$-$\partial M_x/\partial\langle v_{i,j}\rangle = -\langle v_{i,j}\rangle$, and $\partial M_x/\partial\langle u_{i,j}\rangle = -\langle u_{i,j}\rangle$, respectively. Accordingly, the magnetization $M_x(t)$ is a function of $2\langle w_{i,j}\rangle^2 - \langle v_{i,j}\rangle^2 - \langle u_{i,j}\rangle^2$ as a whole. Furthermore, the observation of a $\lambda^2 - 1/\lambda$ linear dependence indicates that slow fluctuations of nodes occur in gel systems. Their relaxation rate is probably smaller than 10^{-3} rad·s^{-1} in cross-linked polybutadiene, for example. An affine property applies to the displacements of nodes in gels uniaxially stretched.

V. Conclusion

The present analysis illustrates the relationship existing between the retractive force characterizing a gel system under stretching and the relaxation rate of the transverse magnetization of nuclei attached to polymer chains. More precisely, elongation effects of chain segments connecting nodes and internal fluctuations are involved in both the spin-system response and the retractive force. Also, the nature of the dependence of the magnetic relaxation rate upon the stretching ratio may help in discriminating several gel models from one another. The observed $\lambda^2 - 1/\lambda$ linear dependence of relaxation rates is in accordance with the phantom network model which corresponds to an affine deformation of elastically effective chains and to fluctuations independent of the gel elongation. NMR investigations concern the response of statistical structural units to macroscopic deformations of a gel. This semi-local approach to gel elasticity complements the description derived from mechanical measurements. NMR is very sensitive to the individual fractal character of chain segments resulting from monomer unit–monomer unit interactions and elongation. The $\lambda^2 - 1/\lambda$ dependence of relaxation rates indicates that any chain segment is affected by an affine deformation as a whole, whatever the nature of nodes.

References and Notes

(1) Staverman, A. J. *Adv. Polym. Sci.* **1982**, *44*, 73.
(2) Cohen-Addad, J. P. *J. Phys. (Les Vlis, Fr.)* **1982**, *43*, 1509.
(3) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(4) Flory, J. P. *Br. Polym. J.* **1985**, *17*, 96.
(5) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Pergamon Press: New York, 1958.
(6) Callen, H. B. *Thermodynamics*; Wiley: New York, 1966.
(7) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: London, 1961.
(8) Flory, J. P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, N. Y., 1953.
(9) Erman, B.; Monnerie, L. *Macromolecules* **1985**, *18*, 1985.
(10) Deloche, B.; Samulski, E. *Macromolecules* **1981**, *14*, 575.
(11) Gromski, W.; Stadler, R.; Jacobi, M. M. *Macromolecules* **1984**, *17*, 741.
(12) Cohen-Addad, J. P.; Huchot, Ph.; Viallat, A. *Polym. Bull.* **1988**, *19*, 257.
(13) Cohen-Addad, J. P.; Huchot, Ph. *Polymer*, submitted for publication.

Measurement of Homonuclear Coupling Constants Associated with Poly(vinyl fluoride) by ^{19}F Two-Dimensional *J*-Resolved Spectroscopy

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ABSTRACT: NMR spectroscopy provides insight into the conformation of synthetic polymers since the magnitudes of the homonuclear scalar coupling constants are sensitive to changes in the average chain conformation. These coupling constants are difficult to extract from conventional spectra since the lines are broad and poorly resolved. Two-dimensional *J*-resolved spectroscopy has been used to measure the ^{19}F scalar coupling constants associated with poly(vinyl fluoride). The magnitude of the scalar coupling constants, and hence the average local conformation, is shown to depend markedly on the local stereochemistry of the coupled fluorines. The local conformation is only slightly affected by the relative stereochemistry of neighboring vinyl fluoride units.

Introduction

NMR spectroscopy is a powerful probe into the microstructure and chain conformation of synthetic polymers because the NMR parameters are sensitive to local structural variations. In particular, homonuclear scalar coupling constants are of interest since the magnitudes of the coupling constants are dependent upon the local chain conformation. However, these coupling constants often are difficult to measure from conventional spectra due to unresolved sequence effects on the NMR parameters that

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