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Effects of Chain Stiffness on NMR Properties. Wiener-Integral Description

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ABSTRACT: This work deals with the description of stiffness effects upon the magnetization relaxation of nuclei attached to polymer chains, in a melt or in a gel. A Wiener-integral approach is used to calculate the residual energy of tensorial spin–spin interactions, taking chain stiffness effects into consideration. It is shown how the effect of chain length competes with that of stiffness. The distribution function of the residual energy existing along a chain segment is calculated in the case where a force is applied to chain ends. It is shown that the usual description of stiffness leads to a residual energy equivalent to that associated with an ideal chain. A local interaction is introduced to modify the residual energy. The case where a chain has fixed end points is considered to illustrate properties of gel systems.

I. Introduction

It is now well established that the magnetic relaxation of nuclei attached to polymer chains can reflect topological constraints resulting either from the presence of entanglements in a melt or from that of cross-links in a covalent gel.[1-3] These constraints induce a diffusional asymmetry of motions of monomeric units which gives rise to a residual energy of tensorial interactions of nuclear spins. The relaxation of the transverse nuclear magnetization is usually found to exhibit a pseudosolid behavior governed by the residual energy of spin–spin interactions. Nonisotropic diffusion processes of segments hence manifest through this specific behavior and the residual energy Δ_e averaged over a whole sample can be considered as pertinent parameters measuring the state of constraints in a polymer whether it is a melt or a covalent gel. The parameter Δ_e has proved a convenient quantity to characterize stretching effects of chain segments resulting either from the isotropic swelling of a gel[4] or from the uniaxial elongation of such a system.[5] These investigations stress the need to quantitatively relate Δ_e not only to collective topological constraints exerted on polymers by one another but also to specific properties of individual chains. More precisely, it is necessary to discriminate the contribution to Δ_e induced by the stiffness of a chain from the contribution due to surrounding obstacles.

The purpose of this work is to propose a continuous chain approach to the description of stiffness effects on NMR properties. The stiffness is actually expected to enhance the steric hindrance affecting skeletal motions of any chain segment with end points fixed in space. According to continuous chain descriptions previously proposed by Edwards[6] and Freed,[7] the polymer will be pictured as the trajectory of a fictitious particle in a three-dimensional space. Furthermore, it will be shown that the residual energy of spin–spin interactions can be given an expression similar to that of the velocity of the fictitious particle. Consequently, the Wiener-type functional integral method will prove well appropriate to the description of NMR properties.

II. Real Chain Description

Eliminating excluded-volume effects throughout this work, the configurational statistics of a single chain will be considered by taking only short-range interactions into consideration. The description of a flexible polymer starts from a simple Gaussian chain model as usual; the nonideal behavior is then introduced through potential functions acting on the configurations. It is now well-known that the statistical description of macromolecules can rely upon

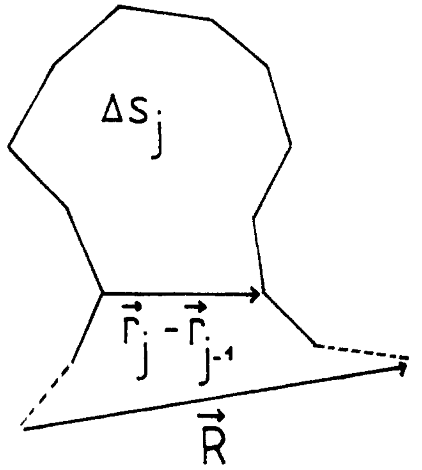


Figure 1. Continuous description is obtained by dividing a chain into Gaussian submolecules of end-separation vectors $\vec{r}_j - \vec{r}_{j-1}$ ($j = 1, 2, ..., N$).

the use of Wiener-type functional integrals.[6] The polymer is represented by a continuous three-dimensional space curve $\vec{r}(s)$, where s measures the contour length along the chain ($0 < s < L$). Stiffness effects have been analyzed in slightly different ways by Saito et al.[8] (STY) and by Freed.[7]

II.1. Chain Stiffness Description. To connect NMR properties to chain stiffness, it is worth recalling how the discrete chain model may give rise to a continuous description. The freely jointed chain is divided into n-equivalent submolecules of contour length Δs_j (Figure 1):

$$\sum_{j=1}^{n} \Delta s_j = L \tag{1}$$

The probability distribution function associated with a submolecule is expressed as

$$P(\vec{r}_j - \vec{r}_{j-1}, \Delta s_j) = (3/2\pi l \Delta s_j)^{-3/2} \exp\left[\frac{-3}{2l\Delta s_j}(\vec{r}_j - \vec{r}_{j-1})^2\right] \tag{2}$$

The continuous description of the whole chain is obtained when the limits $n \to \infty$ and $\Delta s_j \to 0$ are reached. The statistical weight of the end-separation vector $\vec{R}$ is

$$G[\vec{R}] = \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(L)=\vec{R}} D[\vec{r}(s)] \exp(-\beta H_0) \tag{3}$$

with

$$\beta H_0 = \frac{3}{2l}\int_0^L [\vec{r}(s)]^2 \, ds + \beta \int_0^L V[\vec{r}(s)] \, ds$$

and $\beta = 1/kT$; $D[\vec{r}(s)]$ is the usual integration measure over all paths $\vec{r}(s)$, while $V[\vec{r}(s)]$ is a potential energy function acting on every monomeric unit. The function $G[\vec{R}]$ obeys the well-known differential equation

$$\left[\frac{\partial}{\partial L} - \frac{l}{6}\nabla_R^2 + V[\vec{R}]\right] G[\vec{R}] = \delta(\vec{R})\delta(L) \tag{4}$$

In this diffusion equation, the contour length plays the role of a time variable. Several modesl[7,8] have been proposed to account for chain stiffness effects. According to the STY procedure, based on a mechanical point of view, an elastic energy of bending ${}^1/_2\epsilon/R_c^2$ is associated with the rodlike chain. The radius R_c is a quantity defined from the acceleration vector

$$1/R_c = |d\vec{u}/ds| = |d^2\vec{r}/ds^2| \tag{5}$$

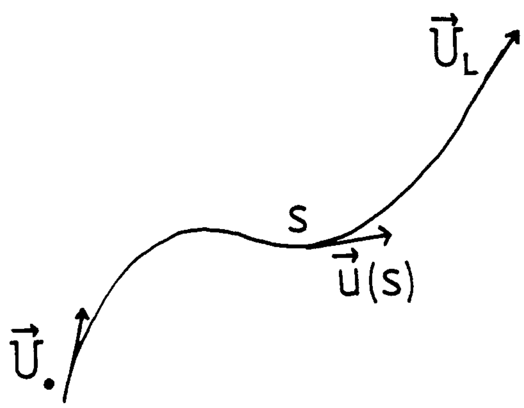


Figure 2. Any submolecule is pictured as a continuous curve. The chain description relies upon velocities $\vec{u}(s)$ when stiffness effects are taken into consideration.

where $\vec{u}(s)$ is the velocity vector corresponding to the time variable (curvilinear abscissa) s. The parameter ϵ is supposed to depend upon the chemical structure of monomeric units. The partition function is now written down as

$$G[\vec{R}] = \int_{\vec{r}(0)=\vec{0}}^{\vec{r}(L)=\vec{R}} D[\vec{r}(s)] \exp(-\beta H_S) \tag{6}$$

with

$$\beta H_S = \frac{\beta\epsilon}{2}\int_0^L \left(\frac{d^2\vec{r}}{ds^2}\right)^2 ds + \frac{3}{2l}\left(\frac{d\vec{r}}{ds}\right)^2 ds + \beta\int_0^L V[\vec{r}(s)] \, ds$$

In the absence of any potential function, $V[\vec{r}(s)] = 0$, and the partition function may be expressed in terms of the velocity vector $\vec{u}(s) = d\vec{r}/ds$. For given limit conditions applied to end points $\vec{u}(0) = \vec{U}_0$ and $\vec{u}(L) = \vec{U}_L$, attention is now focused upon (Figure 2):

$$G[\vec{U}_0,\vec{U}_L] = \int_{\vec{u}(0)=\vec{U}_0}^{\vec{u}(L)=\vec{U}_L} D[\vec{u}(s)] \times \exp\left\{-\frac{\beta\epsilon}{2}\int_0^L \left(\frac{d\vec{u}}{ds}\right)^2 ds - \frac{3}{2l}\int_0^L \vec{u}^2 \, ds\right\} \tag{7}$$

Since $\vec{u}$ is considered as a velocity, no constraint is applied to its square length, according to the procedure proposed by Freed.[7] $G[\vec{U}_0,\vec{U}_L]$ now satisfies the differential equation

$$\left[\frac{\partial}{\partial L} - \frac{1}{2\beta\epsilon}\vec{\nabla}_{\vec{U}}^2 + \frac{3}{2l}\vec{U}^2\right] G[\vec{U}_0,\vec{U}_L] = \partial(L)\partial(\vec{U}_0 - \vec{U}_L) \tag{8}$$

If $\partial/\partial L$ is replaced by $i\hbar(\partial/\partial t)$, this equation is transformed into the Shrödinger equation associated with a harmonic oscillator.

II.2. Broken Symmetry. Furthermore, considering the potential energy function $V[\vec{r}(s)]$, it is suggested to introduce the velocity vector $\vec{u}(s)$ from partial integrals:

$$\int_0^L V[\vec{r}(s)] \, ds = [sV(s)]_0^L - \int_0^L s \frac{dV}{ds} \, ds \tag{9}$$

The first term of the right-hand part of this equation is included in the normalization constant. Therefore

$$-\int_0^L s \frac{dV}{ds} = \int_0^L s\vec{\gamma}(s)\cdot\vec{u}(s) \, ds \tag{10}$$

with

$$\vec{\gamma}(s) = -\vec{\nabla}_{\vec{r}}(V(\vec{r}(s))) \tag{11}$$

$\vec{\gamma}(s)$ is the force per unit length acting on the monomeric unit located at $\vec{r}(s)$. By analogy with field theory descriptions, a source $\vec{j}$ is defined by

$$\vec{j}(s) = -\beta s \vec{\gamma}(s) \tag{12}$$

Accordingly, the Wiener functional reads

$$G_0[\vec{U}_0,\vec{U}_L,\vec{j}] = \int_{\vec{u}(0)=\vec{U}_0}^{\vec{u}(L)=\vec{U}_L} D[\vec{u}(s)] \exp(-\beta F_0) \tag{13}$$

with

$$\beta F_0 = \frac{\beta\epsilon}{2}\int_0^L \left(\frac{\mathrm{d}\vec{u}}{\mathrm{d}s}\right)^2 \mathrm{d}s + \frac{3}{2l}\int_0^L \vec{u}^2\,\mathrm{d}s - \int_0^L \vec{j}(s)\cdot\vec{u}(s)\,\mathrm{d}s$$

The corresponding differential equation is

$$\left[\frac{\partial}{\partial L} - \frac{1}{2\beta\epsilon}\vec{\nabla}_{\vec{U}}{}^2 + \frac{3}{2l}\vec{U}^2 - \vec{j}\cdot\vec{U}\right] G_0[\vec{U}_0,\vec{U}_L,\vec{j}] = \delta(L)\delta(\vec{U}_0,\vec{U}_L) \tag{14}$$

It illustrates a Markovian process, long-range interactions being neglected. The solution of (14) still has an analytical form:[9]

$$G_0[\vec{U}_0,\vec{U}_L,\vec{j}] = \left[\frac{b}{\pi sh\frac{L}{k}}\right]^{3/2} \exp\{\phi[\vec{U}_0,\vec{U}_L,\vec{j}]\}$$

with

$$K = (\beta\epsilon l/3)^{1/2}, \qquad b = (3\beta\epsilon/4)^{1/2} \tag{15}$$

and

$$\phi[\vec{U}_0,\vec{U}_L,\vec{j}] = \zeta(L,K,b) - \xi(L,K,b)$$

The functions $\zeta(L,K,b)$ and $\xi(L,K,b)$ are defined according to the following expressions:

$$\zeta(L,K,b) = \frac{1}{8b}\int_0^L\int_0^L \mathrm{d}s\,\mathrm{d}s'\,e^{-|s-s'|/K}\vec{j}(s)\cdot\vec{j}(s')$$

and

$$\xi(L,K,b) = \frac{b}{sh\frac{L}{K}}\Big\{(\vec{U}_0{}^2 + \vec{U}_L{}^2)ch\frac{L}{K} - 2\vec{U}_0\cdot\vec{U}_L + 2\vec{A}\cdot(\vec{U}_0 e^{L/K} - \vec{U}_L) + 2\vec{B}\cdot(\vec{U}_L e^{L/K} - \vec{U}_0) + (\vec{A}^2 + \vec{B}^2)e^{L/K} - 2\vec{A}\cdot\vec{B}\Big\}$$

where

$$\vec{A} = \frac{1}{4b}\int_0^L e^{-s/K}\vec{j}(s)\,\mathrm{d}s$$

and

$$\vec{B} = \frac{1}{4b}\int_0^L e^{-(L-s)/K}\vec{j}(s)\,\mathrm{d}s$$

This description may be illustrated by considering two forces $\vec{f}$ and $-\vec{f}$ applied to chain ends; the corresponding potential energy function is written as $-\vec{f}\cdot\vec{R}$, with $\vec{R}$ the end-separation vector of the chain defined by

$$\vec{R} = \int_0^L \vec{u}(s)\,\mathrm{d}s$$

The Boltzmann factor associated with $\vec{f}$ is

$$\exp(\beta\vec{f}\cdot\vec{R}) = \exp\left(\int_0^L \beta\vec{f}\cdot\vec{u}(s)\,\mathrm{d}s\right) \tag{16}$$

Accordingly, the source $\vec{j} = \beta\vec{f}$ is indpendent of s. Such a source will be studied in next sections.

III. Residual Energy of Spin-Spin Dipolar Interactions

NMR properties will be described according to the following model. Considering a freely jointed chain segment, every skeletal bond $\vec{l}$ is supposed to carry one proton pair. Nuclear magnetic interactions between different proton pairs are neglected. The dipole–dipole coupling of nuclear spins existing within a proton pair is called $\mathcal{H}_\mathrm{D}$ and the corresponding Hamiltonian is written as

$$\hbar\mathcal{H} = \hbar\mathcal{H}_\mathrm{Z} + \hbar\mathcal{H}_\mathrm{D}$$

$\hbar\mathcal{H}_\mathrm{Z}$ is the Zeeman energy of a proton pair in the steady magnetic field $\vec{B}_0$. Also, for two nuclear spins $\vec{I}_1$ and $\vec{I}_2$

$$\hbar\mathcal{H}_\mathrm{D} = \hbar(\vec{I}^1\cdot\vec{I}^2 - 3I_\mathrm{Z}{}^1 I_\mathrm{Z}{}^2)A_{12}$$

with

$$A_{12} = \gamma^2\hbar(3\cos^2\theta_{\vec{l}} - 1)/2a^3 \tag{17}$$

$\theta_{\vec{l}}$ is the angle between the directions of a link $\vec{l}$ and that of the steady magnetic field $\vec{B}_0$; γ is the gyromagnetic ratio of a proton. The two spins are separated by a distance a.

The relaxation function of the transverse magnetization $M_x(t)$ in the rotating frame is known to be expressed by

$$M_x{}^0(t) = Tr\{M_x(t)M_x\}/Tr\{M_x{}^2\} \tag{18}$$

with

$$M_x(t) = e^{i\mathcal{H}_\mathrm{D}t}M_x e^{-i\mathcal{H}_\mathrm{D}t}$$

M_x is the spin operator representing a proton pair.[10] The spin-system response of a proton pair has been extensively described[11]

$$M_x{}^0(t) = \cos(\epsilon_0(\vec{l})t) \tag{18'}$$

with

$$\epsilon_0(\vec{l}) = 3\gamma^2\hbar(3\cos^2\theta_{\vec{l}} - 1)/4a^3$$

It is now assumed that the freely jointed chain segment pictures a submolecule with a fixed end-separation vector $\vec{r}_j - \vec{r}_{j-1}$; then, the spin-system response $M_x{}^0(t)$ must be averaged over all bond orientations compatible with the end-separation vector $\vec{r}_j - \vec{r}_{j-1}$. Accordingly, the relaxation function is expressed as

$$\langle M_x{}^0(t)\rangle = \cos\{t\langle\epsilon_0(\vec{l})\rangle_\mathrm{orien}\} \tag{19}$$

$\langle\epsilon_0(\vec{l})\rangle_\mathrm{orien}$ corresponds to the first-order term of a cumulant series expansion. It has been already shown that this first-order term gives a satisfactory spin-system response.[11] The average $\langle\epsilon_0(\vec{l})\rangle_\mathrm{orien}$ is expressed as

$$\langle\epsilon_0(\vec{l})\rangle_\mathrm{orien} = \frac{3\gamma^2\hbar}{4a^3}(3\cos^2[\theta(\vec{r}_j - \vec{r}_{j-1})] - 1)\mathcal{L}^*\left(\frac{3|\vec{r}_j - \vec{r}_{j-1}|}{\Delta s_j}\right) \tag{20}$$

$\theta(\vec{r}_j - \vec{r}_{j-1})$ is the angle which the end-separation vector $\vec{r}_j - \vec{r}_{j-1}$ makes with the steady magnetic field $\vec{B}_0$ (Figure 3). The function $\mathcal{L}^*(x)$ is defined by

$$\mathcal{L}^*(x) = 1 + \frac{3}{x^2} - \frac{3}{x}\coth x \tag{21}$$

and for small x values

$$\mathcal{L}^*(x) \simeq x^2/15$$

$\langle\epsilon_0(\vec{l})\rangle_\mathrm{orien}$ is the residual energy of spin–spin interactions resulting from nonisotropic motions of skeletal bonds. The deviation from isotropic motions is associated with the

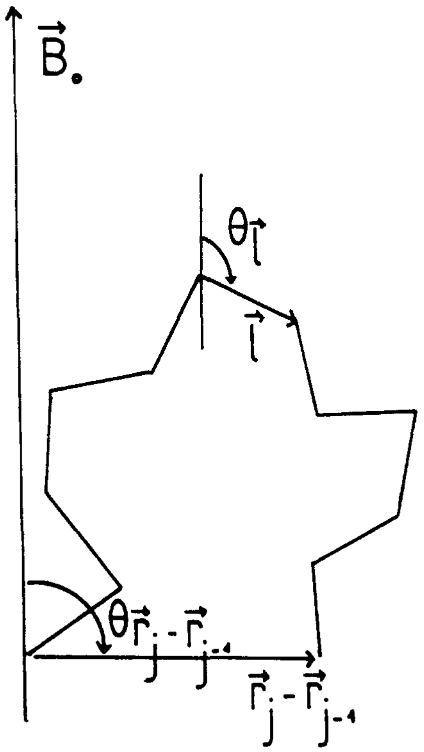


Figure 3. NMR model of a submolecule consists of freely connected skeletal bonds $\vec{l}$. The end-separation vector $\vec{r}_j - \vec{r}_{j-1}$ is fixed.

end-separation vector $\vec{r}_j - \vec{r}_{j-1}$. In the continuous limit $\Delta s_j \rightarrow 0$, the residual energy depends upon the velocity vector $\vec{u}(s)$

$$\hbar D(s) = \hbar \langle \epsilon_0(\vec{l}) \rangle_{\text{orien}} = \left(\frac{3\gamma^2 \hbar}{4a^3} \right)^2 (3 \cos^2 \theta_{\vec{u}(s)} - 1) 3[\vec{u}(s)]^2/5 \quad (22)$$

$\theta_{\vec{u}(s)}$ is the angle which the velocity vector $\vec{u}(s)$ makes with the magnetic field $\vec{B}_0$. The mean value of $D(s)$ will be calculated in next sections, taking stiffness effects into consideration.

IV. Average Quantities of a Chain System

It will be shown in section V that the zero-order function G_0 derived from the simple bending energy (13) cannot account for strong stiffness effects. Accordingly, an additional contribution $V[\vec{u}(s)]$ is introduced into the free energy F. The description of stiffness effects is generalized by defining a new statistical weight function:

$$G[\vec{U}_0,\vec{U}_L,\vec{j}] = \int_{\vec{U}_0}^{\vec{U}_L} D[\vec{u}(s)] \exp(-\beta F) \quad (23)$$

with

$$\beta F = \beta F_0 + \int_0^L V[\vec{u}(s)] \, \mathrm{d}s$$

The function $G[\vec{U}_0,\vec{U}_L,\vec{j}]$ now resembles a Landau–Ginzburg–Wilson functional (n vector model with $n = 3$, $d = 1$). Nevertheless the differential equations they obey are different because of the finite length of the polymer chain.

Whatever the complex structure of the free energy F, the average value of any given function $\psi[\vec{u}(s)]$ of $\vec{u}(s)$ is simply defined by

$$\langle \psi[\vec{u}(s)] \rangle = \frac{\int_{\vec{U}_0}^{\vec{U}_L} D[\vec{u}(s)] \psi[\vec{u}(s)] \exp(-\beta F)}{\int_{\vec{U}_0}^{\vec{U}_L} D[\vec{u}(s)] \exp(-\beta F)} \quad (24)$$

or

$$\langle \psi[\vec{u}(s)] \rangle = [G[\vec{U}_0,\vec{U}_L,\vec{j}]]^{-1} \psi\left[\frac{\delta}{\delta_{\vec{j}(s)}} \right] G[\vec{U}_0,\vec{U}_L,\vec{j}] \quad (25)$$

IV.1. State Equation. The velocity vector $\vec{u}(s)$ is averaged by using

$$\langle \vec{u}(s) \rangle = \frac{\delta}{\delta_{\vec{j}(s)}} \ln G[\vec{U}_0,\vec{U}_L,\vec{j}] \quad (26)$$

It gives the equation of state of a stiff chain. A link with more usual concepts is established, relating $\langle \vec{u}(s) \rangle$ to the average end-to-end vector $\langle \vec{R} \rangle$:

$$\langle \vec{R} \rangle = \int_0^L \langle \vec{u}(s) \rangle \, \mathrm{d}s \quad (27)$$

IV.2. Residual Energy of Dipolar Coupling of Nuclear Spins. The quantity $D(s)$ is defined at any point of the polymer by

$$D(s) = \Delta_G \langle (3 \cos \theta_{\vec{u}(s)}{}^2 - 1) \mathcal{L}^*(3|\vec{u}(s)|) \rangle \quad (28)$$

with

$$\Delta_G = 3\gamma^2/4a^3$$

Starting from the series expansion of $\mathcal{L}^*(x)$, it is now possible to express $D(s)$ as a functional form

$$\mathcal{L}^*(3|\vec{u}(s)|) = \frac{3}{5}\vec{u}^2(s) - \frac{18}{35}(-\vec{u}^2(s))^2 + \ldots$$

$(\vec{u}^2(s))^2$ is associated with $\delta^4/\delta_{\vec{j}^4(s)}$. However, a simplification is suitable, if the source is weak. Since $\ln G(\vec{U}_0,\vec{U}_L,\vec{j})$ is at least quadratic in $\vec{j}$ (formula 15), $\langle \vec{u}(s) \rangle$ is at least linear in $\vec{j}$. Consequently, it is possible to neglect $(\vec{u}^2(s))^2$ compared with $\vec{u}^2(s)$ in the average values. Now we deal with

$$D(s) = \Delta_G \left\langle \frac{3}{5}(2u_z{}^2(s) - u_x{}^2(s) - u_y{}^2(s)) \right\rangle = \mathbf{M}_{\text{pl}} \left[\frac{\delta^2 \ln G}{\delta_{j_{\text{p}}(s)} \delta_{j_{\text{l}}(s)}} + \frac{\delta \ln G}{\delta_{j_{\text{p}}(s)}} \frac{\delta \ln G}{\delta_{j_{\text{l}}(s)}} \right] \quad (29)$$

$\mathbf{M}_{\text{pl}}$ is a matrix defined by

$$\mathbf{M}_{\text{pl}} = \frac{3}{5}\Delta_G \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}$$

It is clearly seen that formula 29 consists of two terms which have different physical meanings. The first-order derivative $\delta \ln G/\delta_{j_{\text{p}}(s)}$ is related to the state equation, while the second-order derivative $\delta^2 \ln G/\delta_{j_{\text{p}}(s)}\delta_{j_{\text{l}}(s)}$ is analogous to a one-point correlation function. Both terms are sensitive to a symmetry break.

V. Chain with Free End Orientations

Since the analytical expression for $G(\vec{U}_0,\vec{U}_L,\vec{j})$ is known (eq 15), the formula

$$G(\vec{U}_0,\vec{U}_L,\vec{j}) = e^{-\int^L{}_0 V(\delta/\delta_{\vec{j}(s)}) \mathrm{d}s} G_0(\vec{U}_0,\vec{U}_L,\vec{j}) \quad (30)$$

allows us to calculate $\mathrm{G}(\vec{\mathrm{U}}_0,\vec{\mathrm{U}}_\mathrm{L},\vec{j})$. If the orientations of the chain ends are not hindered, an interesting simplification occurs. Using usual notations, let the new partition functions be defined by

$$Z_0(\vec{j}) = \int \mathrm{d}\vec{U}_0 \, G_0(\vec{U}_0{=}\vec{U}_L,\vec{j}) = Z_0(\vec{j}{=}\vec{\mathrm{O}}) e^{\mathrm{W}_0(\vec{j})} \quad (31)$$

$$Z(\vec{j}) = \int \mathrm{d}\vec{U}_0 \, G(\vec{U}_0{=}\vec{U}_L,\vec{j}) = Z(\vec{j}{=}\vec{\mathrm{O}}) e^{W(\vec{j})} \quad (32)$$

$W_0(j)$ can be expressed in the form

$$W_0(\vec{j}) = \frac{1}{2}\int_0^L\int_0^L j_p(s_1)j_l(s_2)\Delta(s_1,s_2)\,\mathrm{d}s_1\,\mathrm{d}s_2 \qquad (33)$$

$$\Delta^{pl}(s_1,s_2) = \delta^{pl}\,\frac{ch\left\{\left(|s_1 - s_2| - \frac{1}{2}\right)\frac{1}{K}\right\}}{4bsh\frac{L}{2K}} = \Delta^{pl}\Delta(s_1,s_2)$$

δ^{pl} is the Kronecker symbol. K and b depend on the flexibility; they were already expressed in section II.

V.1. Effects of Weak Chain Stiffness. The equation of state reads as

$$\langle u_p(s)\rangle = \frac{\delta W_0}{\delta_{j_p(s)}} = \int_0^L j_p(s)\Delta(s,s')\,\mathrm{d}s' \qquad (34)$$

The ideal chain equation of state is obtained when the source $\vec{j}$ is set equal to $\beta\vec{f}$; as was shown in section II.2 this source corresponds to external forces $\vec{f}$ and $-\vec{j}$ applied to chain ends:

$$\langle u_p(s)\rangle = \beta\frac{l}{3}f_p$$

or

$$\langle\vec{R}\rangle = \frac{\beta lL}{3}\vec{f} \qquad (35)$$

This simple result suggests a relationship between the use of W_0 and the freely jointed chain model. The residual energy of tensorial interactions is calculated in the Appendix. It obeys the equality

$$(3\cos^2\theta_{\vec{u}(s)} - 1)\mathcal{L}^*(3|\vec{u}(s)|) = (3\cos^2\theta_{\vec{R}} - 1)\mathcal{L}^*\left(3\frac{|\langle\vec{R}\rangle|}{L}\right) \qquad (36)$$

The residual energy is a function of the stretching vector $\langle\vec{R}\rangle$. There is no stiffness effect on NMR properties when chain ends have free orientations.

V.2. Effects of Strong Stiffness. This section deals with stiffness effects. It was shown that the chain statistics are Gaussian, when the limit-conditions are relaxed and $\vec{j}$ is taken as a constant.

To induce deviations from ideality, more terms must be introduced in the free energy, as was suggested in section IV. Following Landau–Ginzburg–Wilson, it seems reasonable to propose a local interaction characterized by a symmetry $O(3)$:

$$V[\vec{u}] = \frac{g}{4!}(\vec{u}^2)^2$$

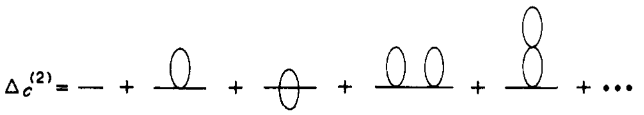
Then $W(\vec{j})$ can be expanded as

$$W(\vec{j}) = \sum_{N=2}^{\infty}\frac{1}{N!}\int_0^L \cdots \int_0^L \cdots \int_0^L \mathrm{d}s_1 \ldots \mathrm{d}s_N\, j(s_1)\ldots j(s_N)\Delta_c^{(N)}(s_1, \ldots, s_N) \qquad (37)$$

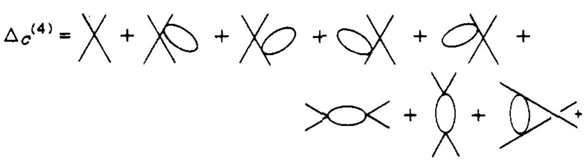
The component indexes with respect to $\vec{j}$ are omitted. For the sake of simplicity, formula 33 is written as

$$W(\vec{j}) = \sum_{N=2}^{\infty}\frac{1}{N!}\langle\langle j(1)\ldots j(N)\Delta_c^{(N)}(1, \ldots, N)\rangle\rangle_{1,\ldots,N} \qquad (38)$$

$\langle\langle\,\rangle\rangle_{1,\ldots,N}$ means an integration over all variables $s_1, \ldots, s_N$. $W(\vec{j})$ is analogous to the functional generatrix of the N-point correlation function. Considering the proposed interaction, we obtain the following perturbation expansion, expressed in terms of graphs:



(39)



(40)

The calculation rules are almost identical with those of the ϕ^4 theory (self-interacting scalar field). (i) each vertex is associated with a g factor; (ii) each line represents a function

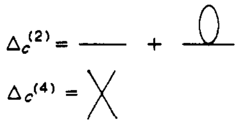
$$\Delta(1,2) = \frac{ch\left\{\left(|s_1 - s_2| - \frac{L}{2}\right)/K\right\}}{4bsh(L/2K)}$$

(iii) an integration over the internal lines has to be performed; (iv) each graph corresponds to a symmetry factor, which takes the vector character of $\vec{u}(s)$ into consideration.

The g expansion has to be cut at an order compatible with the chosen approximation. The residual energy is written as

$$\hbar D(s) = \hbar\Delta_G\left\langle(3\cos^2\theta_{\vec{u}(s)} - 1)\frac{3}{5}\vec{u}^2(s)\right\rangle \qquad (41)$$

To the first order



(42)

The tadpole includes the symmetry factor $(n + 2)/6 = {}^5/_6$, where n is the number of components of $\vec{u}(s)$. Then, the first terms of the function $W(\vec{j})$ are written as

$$W(\vec{j}) = \frac{1}{2}\langle\langle\vec{j}(1)\cdot\vec{j}(2)\Delta(1,2)\rangle\rangle_{1,2} + \frac{5}{12}g\langle\langle\vec{j}(1)\cdot\vec{j}(2)\Delta(1,3)\Delta(3,3)\Delta(3,2)\rangle\rangle_{1,2,3} - \frac{1}{4!}\frac{9}{3}\langle\langle[(\vec{j}(1)\cdot\vec{j}(2))(\vec{j}(3)\cdot\vec{j}(4)) + \mathrm{perm}]\Delta(1,5)\Delta(2,5)\Delta(3,5)\Delta(3,5)\Delta(4,5)\rangle\rangle_{1,2,3,4,5} \qquad (43)$$

First terms of the first derivative are also known

$$\frac{\delta W}{\delta j_K(s_1)} = \langle\langle j^K(2)\Delta(1,2)\rangle\rangle_2 + \frac{5}{6}g\langle\langle j^K(2)\Delta(1,3)\Delta(3,3)\Delta(3,2)\rangle\rangle_{2,3} - \frac{1}{3!}g\langle\langle j^K(2)(\vec{j}(3)\cdot\vec{j}(4))\Delta(1,5)\Delta(2,5)\Delta(3,5)\Delta(4,5)\rangle\rangle_{2,3,4,5} \qquad (44)$$

while the second derivative is expressed as

$$\frac{\delta^2 W}{\delta j_K(s_1)\delta j_l(s_1)} = \delta^{Kl}\left[\Delta(1,1) + \frac{5}{6}g\right]\langle\langle\Delta^2(1,3)\Delta(3,3)\rangle\rangle_3 - \frac{1}{3!}g\langle\langle(\delta^{Kl}\vec{j}(3)\cdot\vec{j}(4) + 2j^K(3)j^l(4))\Delta^2(1,5)\cdot\Delta(3,5)\Delta(4,5)\rangle\rangle_{3,4,5} \qquad (45)$$

$$M_{Kl}\frac{\delta^2 W}{\delta j_L(s_1)\delta j_l(s_1)} = -\Delta_G\frac{9}{5}\langle\langle[2j_z(3)j_z(4) - j_x(3)j_x(4) - j_y(3)j_y(4)]\cdot\Delta^2(1,5)\Delta(3,5)\Delta(4,5)\rangle\rangle_{3,4,5} \qquad (46)$$

This last term vanishes with g, leading to the Gaussian limit. In that case, the single contribution to $D(s)$ arises

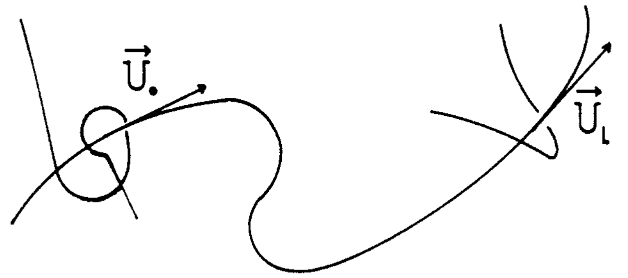


Figure 4. Entanglements are supposed to hinder chain-end orientations; this constraint is conveniently illustrated by fixing end velocities $\vec{U}_0$ and $\vec{U}_L$.

from $\langle\vec{u}(s)\rangle$, i.e., from the first derivatives of ln G.

V.3. State Equation. Using

$$\langle\langle\Delta(1,2)\rangle\rangle_2 = l/3 \tag{47}$$

and

$$\langle\langle\Delta(1,3)\Delta(3,3)\Delta(3,2)\rangle\rangle_{2,3} = \frac{l^3}{54}\,\frac{1}{K}\coth\frac{L}{2K} \tag{48}$$

and also

$$\langle\langle\Delta(1,5)\Delta(2,5)\Delta(3,5)\Delta(4,5)\rangle\rangle_{2,3,4,5} = l^4/81 \tag{49}$$

the average value of $\vec{u}$ is expressed as

$$\langle\vec{u}\rangle = \frac{\beta\vec{f}l}{3}\left[1 + \frac{5}{108}\,\frac{l}{K}(lg)\coth\frac{L}{2K} - \frac{(lg)}{162}(\beta\vec{f}l)^2\right] \tag{50}$$

The above formula clearly shows cross-effects of the energy of binding and the local interaction $V(\vec{u})$ upon the average stretching vector $\langle\vec{R}\rangle$ of a chain. Also, the linear response to the local potential $V(\vec{u})$ depends upon the square of the applied force $\vec{f}$.

V.4. Residual Energy of Dipolar Coupling. Since

$$\langle\langle\Delta^2(1,5)\Delta(3,5)\Delta(4,5)\rangle\rangle_{3,4,5} = \frac{l^4}{324}\,\frac{1}{K}\left(\frac{L/2K}{sh^2L/2K} + \coth\frac{L}{2K}\right) \tag{51}$$

then

$$D(s) = \frac{(\beta l\vec{f})^2}{15}(3\cos^2\theta_{\vec{f}} - 1) \times \left[1 + \frac{lg}{108}\,\frac{l}{K}\left(9\coth\frac{L}{2K} - \frac{L/2K}{sh^2L/2K}\right) - \frac{lg}{81}(\beta l\vec{f})^2\right]\Delta_G \tag{52}$$

The results are independent of s. When the source is uniform, the translational invariance is satisfied. If the chain is very flexible ($K \rightarrow 0$)

$$D(s) \simeq \frac{(\beta\vec{f}l)^2}{15}(3\cos^2\theta_{\vec{f}} - 1)\left[1 + \frac{1}{12}(lg)\frac{l}{K} - \left(\frac{lg}{81}\right)(\beta\vec{f}l)^2\right]\Delta_G \tag{53}$$

$$\langle\vec{u}(s)\rangle \simeq \frac{(\beta\vec{f}l)}{3}\left[1 + \frac{5}{108}\,\frac{l}{K}(lg) - \left(\frac{lg}{162}\right)(\beta\vec{f}l)^2\right] \tag{54}$$

A decrease of K simultaneously increases $\langle\vec{u}(s)\rangle$ and $D(s)$, as expected; for a given $\vec{f}$, average values of submolecule end-to-end distance are more important when the chain is very flexible than in the case of very stiff chains. This results from the fact that bent configurations with stretched bonds are allowed.

VI. Entanglement Effects

For the sake of simplicity, it was supposed in section IV that velocities associated with chain ends have no restricted values. Considering that a submolecule is determined by entanglements in molten systems or by cross-links in gels, it is now assumed that chain end velocities are fixed vectors. When $\vec{U}_0$ and $\vec{U}_L$ are fixed, $\langle\vec{u}(s)\rangle$ and $D(s)$ values can be calculated for all s, using the $G_0(\vec{U}_0,\vec{U}_L,\vec{j})$ distribution (15). It is not necessary to introduce a local interaction $V(u)$ anymore. Three simple cases will be discussed in the following sections (Figure 4): (i) $\vec{U}_0 = \vec{U}_L = \vec{0}$; (ii) $\vec{U}_0 = -\vec{U}_{\mathrm{L}}$; (iii) $\vec{U}_0 = \vec{U}_L \neq \vec{0}$. From eq 15, the average value of the velocity is expressed as

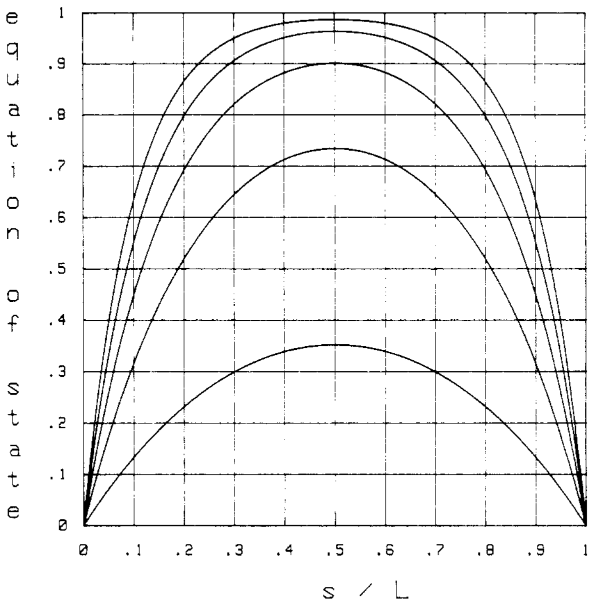


Figure 5. Local state equation $\langle\vec{u}(s)\rangle$ according to formula 57. The curves also reflect the residual dipolar coupling behavior when the chain contour length s varies from 0 to L. Maximum values are shifted up when stiffness effects are increased. Values of L/K correspond to 2, 4, 6, 8, and 10 from the lower to the upper curve.

$$\langle\vec{u}(s)\rangle = \frac{\delta\phi[\vec{U}_0,\vec{U}_L,\vec{j}]}{\delta\vec{j}(s)} \tag{55}$$

By eliminating all terms independent of $\vec{j}$, the function $\phi[\vec{U}_0,\vec{U}_L,\vec{j}]$ can be rewritten in the form

$$\phi[\vec{U}_0,\vec{U}_L,\vec{j}] = \zeta(L,K,b) - \xi^*(L,K,b) \tag{56}$$

with

$$\xi^*(L,K,b) = \frac{b}{sh(L/K)}|2\vec{A}\cdot(\vec{U}_0e^{L/K} - \vec{U}_L) + 2\vec{B}\cdot(\vec{U}_Le^{L/K} - \vec{U}_0) + (\vec{A} + \vec{B})e^{L/K} - 2\vec{A}\cdot\vec{B}|$$

The foregoing formula includes both terms linear with respect to $\vec{j}$ and quadratic ones. They give rise to a dependence of $\langle\vec{u}(s)\rangle$ proportional to $\vec{U}_0$ and $\vec{U}_L$. Furthermore, a part proportional to $\vec{j}$ also comes from the derivatives of $\vec{A}^2$, $\vec{H}^2$, and $\vec{A}\cdot\vec{B}$.

VI.1. $\vec{U}_0 = \vec{U}_L = \vec{0}$. According to this first possible description of entanglements, chain ends are not fixed but the first and the last submolecules are free to fluctuate in space provided their end-to-end vectors remain close to zero. Correspondingly, a physical illustration is obtained when a $\vec{j}$ force acts on a particular without initial velocity; then

$$\langle\vec{u}(s)\rangle = \frac{\beta l\vec{f}}{3}\left[1 - \frac{ch\{1/K(s - L/2)\}}{ch(L/2K)}\right] \tag{57}$$

The first term reflects the ideal behavior of the chain; the stiffness effect is described as a correction. This correction induces an s dependence. Formula 57 exhibits a $L/2$

symmetry, as expected, with a maximum in the middle of the chain. $\langle \vec{u}(s)\rangle$ depends on the ratio K/L; thus, the stiffness competes with the effect of chain length. An increase of K (or a decrease of K) shifts the maximum toward higher values (Figure 5). Applying eq 25

$$\langle \vec{R}\rangle = \frac{\beta l L}{3}\vec{f}\left(1 - 2\frac{K}{L}th\frac{L}{2K}\right) \tag{58}$$

The limit case $K/L \to 0$ leads to

$$\langle \vec{R}\rangle \to \frac{\beta l L}{3}\vec{f}_2$$

corresponding to the ideal behavior.

Considering now the average dipolar coupling, since we deal with $G_0(\vec{U}_0,\vec{U}_L,\vec{j})$ instead of $G(\vec{U}_0,\vec{U}_L,\vec{j})$, $D(s)$ reflects the $\langle \vec{u}(s)\rangle^2$ behavior.

$$D(s) = \frac{(\beta l\vec{f})^2}{15}(3\cos^2\theta_{\vec{f}} - 1)\left(1 - \frac{ch\{1/K(s - L/2)\}}{ch(L/2K)}\right)^2\Delta_G \tag{59}$$

This function shows a maximum in the middle of the chain, which can be understood in the following way; the model relies upon a first decomposition into submolecules, of end-to-end vectors $\vec{r}_j - \vec{r}_{j-1}$ (see section II.1). In the continuous limit, the velocity vector $\vec{u}(s)$ is defined by

$$\langle \vec{u}(s)\rangle = \lim_{\Delta s_j \to 0}\frac{\vec{r}_j - \vec{r}_{j-1}}{\Delta s_j}$$

The existence of a maximum only means that starting from chain end conditions $\vec{U}(0) = \vec{U}(L) = \vec{0}$, the fictitious velocity must be different from zero for $s \neq 0$ or $s \neq L$ to describe the stretched state of a chain. It is maximum in the middle of the chain because of a symmetry property. The resulting bond extension is raised by an increase of K or a reduction of L.

VI.2. $\vec{U}_0 = -\vec{U}_L$. A description complementary to the previous one is now discussed: $\vec{f} = \vec{0}$ and nonvanishing values for $\vec{U}_0 = -\vec{U}_L = \vec{U}_a$. It is supposed that entanglements hinder chain-end orientations.

With opposite velocities $\vec{U}_0 = -\vec{U}_L = \vec{U}_a$, the average velocity has the simple expression:

$$\langle \vec{u}(s)\rangle = \frac{sh\{(L/2 - s)1/K\}}{sh(L/2K)}\vec{U}_a \tag{60}$$

The state equation is $\langle \vec{R}\rangle = \vec{0}$. It corresponds to a loop. Also

$$D(s) = \vec{U}_a{}^2(3\cos^2\theta_{\vec{U}_a} - 1)\left[\frac{sh\{(L/2 - s)1/K\}}{sh(L/2K)}\right]^2\Delta_G \tag{61}$$

To make a comparison of the quantity D_S with experimental results, an average over $\vec{U}_a$ vectors should be carried out by using a distribution of vectors specific of the polymer system. The residual energy is now equal to zero in the middle of the chain because of an antisymmetry property.

VI.3. $-\vec{U}_0 = \vec{U}_L = \vec{U}_S$. With equal velocities $\vec{U}_0 = \vec{U}_L = \vec{U}_S$, the average velocity also has a simple expression:

$$\langle \vec{u}(s)\rangle = \frac{ch\{(L/2 - s)1/K\}}{ch(L/2K)}\vec{U}_S \tag{62}$$

The state equation of the chain is now written as

$$\langle R\rangle = 2Kth(L/2K)$$

while the residual energy corresponds to

$$D(s) = \vec{U}_S{}^2(3\cos^2\theta_{\vec{U}_S} - 1)\left[\frac{ch\{(L/2 - s)1/K\}}{ch(L/2K)}\right]^2\Delta_G \tag{63}$$

The residual dipolar coupling is minimum when $s = L/2$, as expected. Formula 63 shows that deviations from isotropic motions are stronger at chain ends than in the middle of the submolecule. This property results from the stiffness of the chain; motions are necessarily more hindered near chain ends than in the center of the chain; thus $\vec{u}(s)$ and $D(s)$ are minimum for $s = L/2$.

VII. Conclusion

The purpose of this work was to give a theoretical analysis of stiffness effects upon NMR properties observed from the transverse magnetization of nuclei attached to polymer chains. This description concerns entangled chains in a melt or cross-linked chains in a covalent gel. More generally, the analysis corresponds to polymer chains experiencing topological constraints. These were supposed to only apply to chain ends. The presence of topological constraints necessarily gives rise to nonisotropic motions of monomeric units. These deviations from isotropic rotations generate a residual energy of tensorial spin–spin interactions. Stiffness effects were analyzed through this residual energy. The present theoretical approach clearly shows that chain stiffness actually governs the relaxation behavior of the magnetization. However, predicted properties strongly depend upon limit conditions concerning chain ends.

Considering an external force applied to a chain, two cases were discussed: (i) When there is no orientational constraints concerning chain ends, the usual description of stiffness does not lead to any effect on NMR properties; the expression of the residual energy is that of an ideal chain. An additional local interaction must be taken into consideration to effect the residual energy of spins, but this energy is constant along the chain. (ii) When the limit condition corresponds to a negligible stretching of chain ends, the residual energy obeys a distribution function along the chain. The effect of chain length competes with that of the stiffness.

When there is no external force applied to a chain, a distribution of the residual energy is still defined along the chain. Its expression depends upon limit conditions concerning chain ends; the effect of chain length still competes with that of stiffness.

Appendix

Formula 36 is proven in the following way. Using the $\mathcal{L}^*(x)$ series expansion

$$\mathcal{L}^*(x) = (\vec{u}(s))^2\sum_{n=0}^{\infty}a_n(\vec{u}^2(s))^n$$

The average is calculated by assuming that submolecules of chain ends have free orientations; therefore

$$(3\cos^2\theta_{\vec{u}(s)} - 1)\mathcal{L}^*(3\vec{u}(s)) = (2u_z{}^2(s) - u_x{}^2(s) - u_y{}^2(s))\sum_{n=0}^{\infty}a_n(\vec{u}^2(s))^n$$

This can also be expressed as

$$e^{-W_0}\left[2\frac{\delta^2}{\delta j_z{}^2(s)} - \frac{\delta^2}{\delta j_x{}^2(s)} - \frac{\delta^2}{\delta j_y{}^2(s)}\right)\sum_{n=0}^{\infty}a_n\frac{\delta^{2n}}{\delta\vec{j}(s)^{2n}}e^{W_0} = \left[2\left(\frac{\delta W_0}{\delta j_z(s)}\right)^2 - \left(\frac{\delta W_0}{\delta j_x(s)}\right)^2 - \left(\frac{\delta W_0}{\delta j_y(s)}\right)^2\right]\sum_{n=0}^{\infty}a_n\left(\frac{\delta W_0}{\delta\vec{j}(s)}\right)^{2n}$$

with $\delta W_0/\delta\vec{j}(s) = \beta l\vec{f}/3$ and $\vec{R} = (\beta L l/3)\vec{f}$. Then

$$(3\cos^2\theta_{\vec{u}(s)} - 1)\mathcal{L}^*(3|\vec{u}(s)|) = (3\cos^2\theta_{\vec{f}} - 1)\mathcal{L}^*\left(3\frac{\beta l\vec{f}}{3}\right) = (3\cos^2\theta_{\vec{R}} - 1)\mathcal{L}^*\left(3\frac{|\vec{R}|}{L}\right)$$

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NMR Approach to the Characterization of the Swelling Process of Polyethylene Networks

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ABSTRACT: Statistical properties of irregular polyethylene networks of different cross-link densities were probed by determining their gel fraction and equilibrium swelling ratio and by measuring the magnetic relaxation of protons. Experimental results were in agreement with the description of the vulcanization of linear chains within a percolation framework leading to a G^{-1} dependence of the equilibrium swelling ratio Q_m. A parametrized assay function was formed to fit the observed relaxation functions. The fit yielded the second and fourth moment behavior of the resonance line. Evidence for a two-step swelling behavior of the PE networks in the presence of a swelling agent (xylene) is given. The second moment of the relaxation functions observed in networks swollen at equilibrium was shown to be independent of the cross-link density. This result was assigned to the existence of a submolecule perceived from NMR with a size smaller than the average distance between cross-links in the polymer gel.

I. Introduction

This work deals with the statistical structure of randomly cross-linked networks obtained from the gelation process of long linear polymer chains. Vulcanization processes of linear chains in the bulk polymer may be pictured either by a classical branching process giving rise to treelike structures or by a percolation process on an infinite renormalized lattice generating on infinite cluster above the percolation threshold. Renormalization consists in taking the primary chain radius for the lattice parameter and the molecular weight Z for the functionality. For vulcanization in contrast with gelation of polyfunctional monomers, both descriptions are not in conflict but give coherent and complementary results.[1]

The swelling behavior of an irregular gel strongly depends on its functionality and cross-link density.[2] A picture of the swelling process must take into account the fractal dimension of the network and of the network strands in the dry state and in the presence of a solvent. A theoretical treatment within a percolation framework relating the equilibrium swelling to the gel fraction near the gelation threshold has recently been developed.[3]

Determining the statistical structural units is one of the major problems in describing the gel system. The gel behavior is sensitive to the average properties of these statistical domains. In a system of vulcanized chains, the coexistence of entanglements and cross-links is a further complication. Trapped entanglements are known to play a major part in the swelling process of cross-linked networks by acting as additional constraints.[4]

The investigation of quantum coherence properties of the transverse relaxation function has proved to be a convenient tool to probe the gel structure on a semilocal space scale.[5]

It has been shown that the fractal structure of chain segments statistically determined by two consecutive junctions whether they are temporary entanglements or covalent bridges can be investigated by the residual energy Δr of spin–spin interactions. This residual energy results from nonisotropic rotational diffusions of proton pairs attached to polymer chains. The NMR technique thus yields information on all hindrance effects exerted on chain segments.

The state of stretching of a given elementary chain may be reflected by the transverse magnetic relaxation function: it has been shown that the residual energy Δ_r of dipole–dipole interactions of proton spins attached to a chain of fixed end separation vector r_e is expressed as a function of both $|r_e|$ and the number of skeletal bonds Ne in the chain segments. For small extensions, Δ_r is known to be given by

$$\hbar\Delta_r \propto \hbar\Delta_G\frac{|r_e|^2}{\mathrm{Ne}^2a^2} \qquad (1)$$

where Δ_G is the dipole-dipole interaction observed in the glassy state and a is the monomer unit length.[6] The purpose of this paper is to get a picture of the swelling process of weakly cross-linked polyethylene networks as it is perceived in a macroscopic scale by equilibrium swelling ratio and in a microscopic scale by its magnetic relaxation response. We probed the statistical properties of chain segments in dry and swollen polyethylene networks covering a wide range of cross-link densities. It was necessary to include observations at intermediate swelling

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