Vulcanized Polybutadiene. Swelling and NMR Observation of Stretching

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ABSTRACT: Polymeric gels formed by vulcanized polybutadiene chains are studied by varying the chain molecular weight $\bar{M}_n$, the sulfur concentration c_c^s, and the chain microstructure. The state of maximum swelling is observed from the swelling ratio Q_m; Q_m^{-1} is shown to be a function $f(x)$ of a single variable $x = c_c^s\bar{M}_n - w_c(z_{1,2})$, with $f(0) = 0$. The threshold $w_c(z_{1,2})$ depends upon the vinyl content of the chain microstructure. The effect of uniaxial elongation is observed from the transverse magnetic relaxation of protons attached to polymer chains. The relaxation rate is measured as a function of the stretching ratio λ and the angle between the direction of stretching and the steady magnetic field. A law of transformation of network chain segments, derived from NMR observations, is proposed. Although it does not describe a deformation in affinity with the macroscopic gel deformation, this simple law is also in agreement with the dependence of the retractive force usually observed upon the difference $\lambda - 1/\lambda^2$.

I. Introduction

This work deals with the description and the interpretation of properties of swelling or of stretching observed on vulcanized polybutadiene chains. These effects are induced in systems where the density of cross-links is higher than the density which would correspond to the formation of one covalent bond per chain, on average. The purpose of this work is 2-fold.

(i) The behavior of vulcanized polybutadiene chains in a state of maximum swelling is analyzed in a macroscopic scale. It is attempted to define a relevant variable which relates the amplitude of the effect of maximum swelling to both the density of cross-links and the average chain length.

(ii) Properties of stretching of these systems are analyzed in a macroscopic scale by measuring the modulus of elasticity. They are also described in a semilocal space scale by observing the transverse magnetic relaxation of protons attached to monomeric units. This approach is based upon the assumption that conformational fluctuations of chain segments which give rise to the effect of gel elasticity, at small deformations, must also govern the magnetic relaxation of nuclei linked to these polymer chains. This relaxation process is expected to result from dipole–dipole interactions which exist between nuclear spins. These interactions are expressed as products of spin operators and tensorial functions of orientational coordinates of monomeric units. More precisely, it is now well established that the transverse relaxation of protons is induced by the nonzero average of spin–spin interactions. This property is observed in all polymeric gels, even in the absence of any elongation.[1] The residual interaction of spins results from the anisotropy of rotations of skeletal bonds; the effect of anisotropy is induced by the presence of coupling junctions whether they are cross-links or entanglements. Average end-to-end vectors of segments joining any two consecutive junctions are not equal to zero because cross-links cannot move through one another; consequently, conformational fluctuations of chain segments are permanently nonisotropic. Skeletal bond rotations are also nonisotropic because they are closely associated with conformational fluctuations of chain segments; correspondingly, residual interactions of spins have a permanent character. The effect of anisotropy is enhanced by the uniaxial elongation of a polymeric gel. In this work, the attention is focused mainly upon the deformation of chain segments arising from the stretching of vulcanized chains. It is considered that the NMR observation of the enhancement of the effect of anisotropy which affects rotations of skeletal bonds is necessarily associated with the deformation of chain segments; these two properties are described within a common statistical framework. Consequently, NMR studies are expected to lead to investigations into the property of segment deformation; usually, this is supposed to be in affinity with the macroscopic gel deformation.

The physical system formed by long polymer chains cross-linked at random is currently considered as resulting from the percolation process of units U_N. Each unit is identified with one chain and its functionality f_c is the number N of monomeric units in one chain.[2] The percolation threshold p_c is estimated from the simple relation $p_c \simeq N^{-1}$. The width $|\Delta p_c|$ of the critical domain defined around the threshold p_c is estimated from the relation $|\Delta p_c| \simeq p_c N^{-1/3}$; most systems of vulcanized chains which are studied are outside the range of their critical behavior because of the narrowness of this domain.[3] Consequently, vulcanized chains can be described within the framework of a mean-field approximation.[4] Thus, assuming that the parameter $\epsilon = (p - p_c)/p_c$ is small, several relevant quantities are related to one another. For example, the gel fraction G is expressed as

$$G \propto \epsilon^{\beta} \tag{1}$$

the classical value of the critical exponent β is unity and G is defined by the ratio of the weight of cross-linked chains which form an infinite cluster over the total weight of polymer chains, in the reaction bath. Correspondingly, the modulus of elasticity E associated with small deformations is predicted to vary as

$$E \propto \epsilon^3 \tag{2}$$

for $\epsilon \ll 1$; E and G are related to each other in a simple way, $E \propto G^3$.

Several difficulties are encountered in describing properties of vulcanized chains.

(i) The actual concentration of cross-links is not exactly known when these are formed by sulfur atoms; there is still some uncertainty about the value of the number of sulfur atoms involved in one cross-link.

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(ii) Relations (1) and (2) are not valid anymore when numerical values given to the parameter ϵ are not small. When many cross-links per chain are formed, these relations must be replaced with functions which are not explicitly defined, yet.

(iii) When the concentration of cross-links is progressively increased, the value of the gel fraction G becomes rapidly nearly equal to unity; however, the gelation process is far from being completed. Many cross-links can still be formed, although no chains can be extracted from the vulcanized system. Thus, in this case the variable G is not appropriate to the description of the effect of swelling of the network structure; the effect of stretching must also be correlated to a variable different from G. The modulus of elasticity E is expected to increase until the ideal state where all monomeric units are cross-linked is reached. Correspondingly, the swelling ratio is a decreasing function when the concentration of cross-links is raised. An appropriate variable must be used to describe these properties.

(iv) Finally, the property of elasticity relies upon the law of elongation of characteristic chain segments which define the polymeric gel. This law of deformation must be disclosed from experimental investigations specific to the semilocal space scale which corresponds to the average size of characteristic chain segments (≲50 Å); it is not revealed from formula (2).

Experimental aspects of this study are described in section II. The effect of swelling induced by the osmotic pressure of a good solvent is analyzed in section III. In section V, the principle of the NMR approach is briefly recalled. The law of elongation of characteristic network chain segments is discussed in section VI.

II. Experimental Section

Cross-linked polybutadiene networks were supplied by the Manufacture Française des Pneumatiques Michelin. The cross-linking reaction was carried out with a sulfur cure at four concentrations: 0.5, 0.75, 1, and 1.5%. Molecular weights were determined from gel permeation chromatography. Two chain microstructures were studied. The first one was determined by 42% of monomeric units in the cis-1,4 conformation, 50% in the trans-1,4 conformation, and 8% in the vinyl-1,2 conformation. The second microstructure was determined by 34% of monomeric units in the cis-1,4 conformation, 45% in the trans-1,4 conformation, and 21% in the 1,2-vinyl conformation. For each of these materials, measurements of the modulus of elasticity E were performed from stress–strain data corresponding to a low uniaxial elongation. The temperature was 298 K. Polybutadiene rubber were supplied in sheets of 0.9 mm thickness. They were cut into rectangular strips. The two ends of each strip were firmly stuck with a cyanoacrylate instant adhesive on two pieces of glass. The upper end was connected to a Teflon rod whereas the lower one was fixed. All the device was fitted into a 10-mm-diameter tube. A micrometric-calibrated knurled screw operated the displacement of the Teflon rod, allowing uniaxial extension of the sample parallel to the tube axis. To observe angular properties of the nuclear magnetic relaxation, polybutadiene samples were first stretched and then firmly stuck between two pieces of glass. The uniaxial extension of the sample was perpendicular to the tube axis. The angle between the axis of extension and the steady magnetic field was varied by rotating the sample tube.

NMR experiments were performed using a CXP 100 Bruker spectrometer operating at 60 MHz. All relaxation functions were measured by using Carr–Purcell spin–echo sequences. Pseudo-solid echoes have been described elsewhere.[5] They are formed from the following pulse sequence:

$$[(\pi/2)/y] - \tau/2 - (\pi/y) - \tau/2 - [(\pi/2)/-x] - \tau_1/2 - (\pi/y) - \tau_1 - (\pi/y) - \tau_1(\pi/-y) - \tau_1(\pi/-y)$$

Table I
Characterization of Vulcanized Polybutadiene Chains

microstructure	M_n	M_w	ν_c^s	Q_m	E, MPa
21%, 1,2-vinyl 45% trans 34% cis	130 000	150 000	0.5	20.4	
			0.75	7.8	
			1	6.3	
			1.5	4.7	
	210 000	280 000	0.5	8.7	
			0.75	5.3	
	270 000	360 000	0.5	6.6	
			0.75	4.9	
			1	4.4	
			1.5	3.9	
8% 1,2-vinyl 50% trans 42% cis	250 000	267 000	0.5	9.7	0.42
			1	4.9	0.70
	363 000	480 000	0.5	6.7	0.63
			1	4.4	0.9

Polybutadiene rubbers were swollen by using cyclohexane. Values of the swelling ratio and the modulus of elasticity are given in Table I.

III. State of Maximum Swelling

In this section, a set of systems of cross-linked polybutadiene chains characterized by different microstructures, different chain lengths, and different concentrations of sulfur atoms is used to analyze the effect of swelling, induced by the osmotic pressure of a good solvent. The state of maximum swelling is observed in the case where many cross-links per chain are formed: the amount of polymer extracted by washing the system of cross-linked chains is negligible. Consequently, it cannot be considered that the parameter $\epsilon = |p - p_c|/p_c$ is given a small value. Relevant variables used to describe properties of these polymeric gels are not simply proportional to ϵ^y where y would be an appropriate exponent. It is attempted to define experimentally a relevant variable which can be used to describe a network structure in the state of maximum swelling. This variable must take the concentration of cross-links and the average chain molecular weight into consideration. It is of interest to define a standard variable even though the function which relates the swelling ratio Q_m to this variable is not known explicitly; Q_m is the ratio of the volume V_m of the swollen gel over the volume V_0 of the dry gel.

III.1. State of Gelation. Let c_c denote the concentration of cross-links per gram of polymer; then the concentration of sulfur per gram of polymer is expressed as

$$c_c^s = c_c x_s M_s / \mathcal{A}$$

x_s is the mean number of sulfur atoms per cross-link; $\mathcal{A}$ is Avogadro's number, and M_s is the gram-atom weight of one sulfur atom. The total number of monomeric units in 1 g of polymer is $\mathcal{N}_m = \mathcal{A}/M_m$; M_m is the molar weight of one monomeric unit. The state of gelation of one system of cross-linked chains is described in the following way. It is considered that the system of vulcanized chains results from the reaction of units U_N formed by polymer chains with difunctional units V_2 formed by cross-links. One U_N unit contains a number of U groups equal to the number N of monomeric units in one chain; the functionality of one unit is $f = N$. One V_2 unit contains two V groups; the reaction occurs exclusively between U and V. The initial number of U groups is equal to $\mathcal{N}_m$; the initial number of V groups is equal to $2c_c$. The state of gelation is characterized by the fraction ϕ_c of all V groups which have reacted and by the fraction ϕ_m of all monomeric units which have participated in the formation of cross-links. Then, ϕ_m and ϕ_c obey the relation

$$2c_c\phi_c = \phi_m\mathcal{N}_m \tag{3}$$

According to the description of the formation of polymeric gels proposed by Flory,[2] the probability p to form one cross-link is expressed as

$$p = \phi_m\phi_c \tag{4}$$

p is also called the branching coefficient. The parameter $\epsilon = |p - p_c|/p_c$ is written as

$$\epsilon = \left(\frac{2c_c\phi_c^{\ 2}}{\mathcal{N}_m} - \frac{\zeta}{N}\right)\Big/\frac{\zeta}{N} \tag{5}$$

with $p_c = \zeta N^{-1}$. It is well-known that the value of p_c is very sensitive to the model which is chosen to describe the percolation process. In this study, p_c is supposed to be proportional to N^{-1}. When all cross-links are formed, the fraction ϕ_c is equal to unity and the parameter ϵ is written as

$$\epsilon = \frac{2c_cN}{\zeta\mathcal{N}_m} - 1 \tag{5$'$}$$

The parameter ϵ is also expressed as

$$\epsilon = \frac{2c_c^s\bar{M}_n}{x_sM_s\zeta} - 1 \tag{6}$$

Consequently, the swelling ratio Q_M is expected to be a function of the parameter ϵ whatever the complex structure of this function.

III.2. Maximum Swelling Ratio. The inverse of the square of the swelling ratio Q_m is represented as a function of the variable $c_c^s\bar{M}_n$ in Figure 1. Numerical values are reported in Table I. Two curves can be drawn; they correspond to two different chain microstructures.[6] The vinyl content $z_{1,2}$ corresponding to curve A is 20%, while it is equal to 8% for curve B. It is considered that the experimental variable w which can be used to describe the effect of swelling is

$$w = c_c^s\bar{M}_n - W_c(z_{1,2}) \tag{7}$$

where $W_c(z_{1,2})$ is a limiting value which depends upon the chain microstructure: $W_c(z_{1,2}) = 5 \times 10^2$ g mol^{-1} for curve A and 8.5×10^2 g mol^{-1} for curve B. The limiting value of the product $c_c^s\bar{M}_n$ is equal to $M_sx_s\zeta(z_{1,2})/2$. The empirical variable w is made equal to the parameter ϵ by assuming that $W_c(z_{1,2})$ is equal to $\zeta M_sx_s/2$. However, it cannot be considered that the number x_s of sulfur atoms per cross-link is a function of the chain microstructure. It is suggested to assume that ζ depends upon the chain microstructure. The threshold of percolation is actually sensitive to both N^{-1} and the chain stiffness reflected by the characteristic ratio C_∞ which depends upon the chain microstructure. Numerical values are $\zeta x_s = 32$ for $z_{1,2} =$ 20% and $\zeta x_s = 54$ for $z_{1,2} = 8\%$. The physical meaning of the variation of x_s as a function of the vinyl content is still unexplained. It is not expected to determine exactly the number of sulfur atoms involved in one cross-link from the swelling effect of vulcanized chains; there is also some uncertainty about the experimental value of the threshold of percolation.

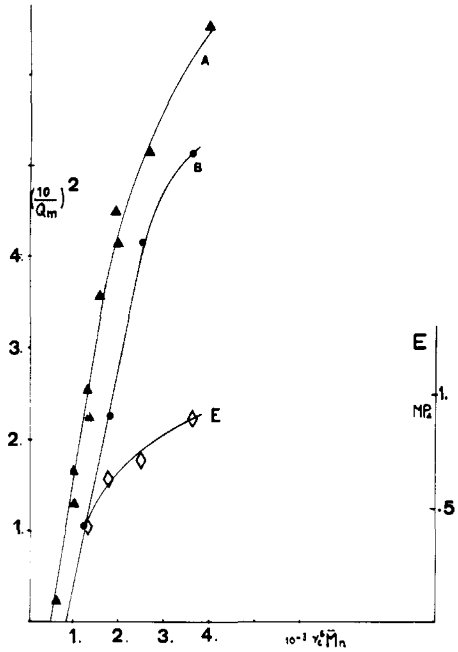

Figure 1. Variations of the square of the inverse of the swelling ratio Q_m reported as a function of the variable $\nu_c^3\bar{M}_n$. Vinyl contents of the chain microstructures are $z_{1,2} = 20\%$ (▲) and $z_{1,2} = 8\%$ (●). The modulus of elasticity E corresponds to $z_{1,2} = 8\%$ (◇).

It is proposed to describe the swelling effect of vulcanized polybutadiene chains by using the relevant variables $w = c_c^s\bar{M}_n - W_c(z_{1,2})$. The swelling ratio Q_m is a function which is still unknown explicitly

$$Q_m = f(c_c^s\bar{M}_n - W_c(z_{1,2}))$$

It is well-known that the swelling effect results from the collective behavior of correlation domains determined by characteristic network chain segments; the framework of the description of percolation processes takes this collective aspects into consideration.[7] It is seen from Figure 1 that an empirical expression of the function can be given for the range $0.5 \times 10^3 \lesssim c_c^s\bar{M}_n \lesssim 2 \times 10^3$: $Q_M \propto \epsilon^{-1/2}$. Another function must be used when the concentration of cross-links is higher.

IV. Gel Elasticity

In this section, a simple description of the property of gel elasticity is given to show how it is sensitive to the law of deformation of characteristic network chain segments. This law of deformation is also perceived from NMR; it relates the property of elasticity to the magnetic relaxation of protons attached to polymer chains.

IV.1. Fluctuations of Coupling Junctions. It is supposed that any polymeric gel consists of chain segments determined by coupling junctions $(...i...j...)$; these nodes are pictured as points defined by their coordinates $(...\vec{R}_i...\vec{R}_j...)$. Let $\vec{r}_{ij}$ denote the end-to-end vector of a chain segment (i,j). It is assumed that coupling junctions can fluctuate in space. The state of equilibrium of the gel is defined from all average end-to-end vectors $\langle\vec{r}_{ij}\rangle$. Accordingly, it is convenient to describe gel properties from the free enthalpy $G(T,\{\vec{f}_{ij}\})$. The force $\vec{f}_{ij}$ is the conjugate variable of $\vec{r}_{ij}$. At equilibrium

$$\text{(i)}\ \langle\vec{r}_{ij}\rangle = \left(\frac{\partial G}{\partial\vec{f}_{ij}}\right)_T \tag{8}$$

and

$$\text{(ii)} \sum_j \vec{f}_{ij} = \vec{0}, \quad f_{ij} \neq \vec{0} \tag{8'}$$

The sum is extended over all segments issuing from the node i.

IV.2. Stretching Effect. It is then considered that the free enthalpy of the gel system becomes an implicit function of the stretching ratio λ when the network structure is submitted to a uniaxial elongation. Let $G^{\lambda}(T,\{f_{ij}\})$ denote this free enthalpy. Under the effect of stretching $\vec{r}_{ij}$ vectors are transformed into $\vec{u}_{ij}$ vectors. This effect is described according to the expression

$$\frac{\partial G^{\lambda}}{\partial \lambda} = \sum_{i,j} \sum_{l,p} \left(\frac{\partial G^{\lambda}}{\partial \vec{f}_{ij}} \right)_T \frac{\partial \vec{f}_{ij}}{\partial \langle \vec{u}_{lp} \rangle} \frac{\partial \langle \vec{u}_{lp} \rangle}{\partial \lambda} \tag{9}$$

Formula (9) clearly illustrates the main problems encountered in studying polymeric gels.

(i) The state of internal deformation is represented by the first derivative of the product:

$$\langle \vec{u}_{ij} \rangle = \left(\frac{\partial G^{\lambda}}{\partial \vec{f}_{ij}} \right)_T \tag{10}$$

End-to-end vectors $\langle \vec{u}_{ij} \rangle$ obviously differ from $\langle \vec{r}_{ij} \rangle$ vectors defined in the absence of stretching.

(ii) Amplitudes of fluctuations occurring in the gel system are defined by

$$\frac{kT}{\langle \Delta u_{lp}^{\alpha} \Delta u_{ij}^{\beta} \rangle} = \frac{\partial f_{ij}^{\alpha}}{\partial \langle u_{lp}^{\beta} \rangle} \tag{11}$$

α and β represnet x, y, and z components of vectors and forces,[8] Δu_{lp}^{α} is equal to $u_{lp}^{\alpha} - \langle u_{lp}^{\alpha} \rangle$. Amplitudes of fluctuations are not easily estimated. They are supposed to be independent of λ in the case of small elongations.[9,10]

$$\langle \Delta u_{lp}^{\alpha} \Delta u_{ij}^{\beta} \rangle = \langle \Delta r_{lp}^{\alpha} \Delta r_{ij}^{\beta} \rangle \tag{12}$$

(iii) Variations of internal deformations upon the amplitude of the macroscopic elongation are taken into consideration in the last derivative of formula (9). Formula (9) simply shows that the modulus of elasticity E is increased when the stretching of end-to-end vectors is increased and/or when amplitudes of fluctuations are reduced.

IV.3. Affine Internal Deformation. If it is assumed that cross-fluctuations concerning different components of a given end-to-end vector as well as different vectors, are stochastically independent from one another, formula (12) is expressed in a simple way:

$$\frac{\partial G^{\lambda}}{\partial \lambda} = kT \sum_{i,j} \left\{ \frac{1}{\langle (\Delta r_{ij}^{z})^2 \rangle} \frac{\partial}{\partial \lambda} \langle u_{ij}^{z} \rangle^2 + \frac{1}{\langle (\Delta r_{ij}^{y})^2 \rangle} \frac{\partial}{\partial \lambda} \langle u_{ij}^{y} \rangle^2 + \frac{1}{\langle (\Delta r_{ij}^{x})^2 \rangle} \frac{\partial}{\partial \lambda} \langle u_{ij}^{x} \rangle^2 \right\} \tag{13}$$

The well-observed $(\lambda - 1/\lambda^2)$ dependence of the retractive force is obtained by assuming that

$$u_{ij}^{z} = \lambda r_{ij}^{z} \quad \text{and} \quad u_{ij}^{x} = r_{ij}^{x}/\sqrt{\lambda} \tag{14}$$

and that

$$\sum_{i,j} \langle r_{ij}^{x} \rangle^2 / \langle (\Delta r_{ij}^{x})^2 \rangle = \sum_{i,j} \langle r_{ij}^{y} \rangle^2 / \langle (\Delta r_{ij}^{y})^2 \rangle = \sum_{i,j} \langle r_{ij}^{z} \rangle^2 / \langle (\Delta r_{ij}^{z})^2 \rangle \tag{14'}$$

$$\frac{\partial G^{\lambda}}{\partial \lambda} = (\lambda - 1/\lambda^2) \nu_e {\xi_e}^2 kT / 3\Delta {\xi_e}^2 \tag{15}$$

with

$$\sum_{i,j} \langle r_{ij}^{x} \rangle^2 / \langle (\Delta r_{ij}^{x})^2 \rangle = \nu_e {\xi_e}^2 / 3\Delta {\xi_e}^2 \tag{16}$$

ν_e is the number of active chain segments.

The modulus of elasticity E derived from the retractive force calculated by unit area of the gel section perpendicular to the force, in the initial state, is

$$E = \frac{\nu_e}{V_0} \frac{{\xi_e}^2}{3\Delta {\xi_e}^2} kT \tag{17}$$

V_0 is the initial volume of the network structure. The ratio $\xi_e^2/\Delta\xi_e^2$ is a measure of both the state of stretching of elementary chains in the absence of any elongation of the gel and the state of fluctuations of coupling junctions. The larger the stretching of elementary chains in the initial state and correspondingly the smaller the amplitude of fluctuations, the higher the modulus of elasticity. A simple idea underlies the description of elasticity: the increase of constraints exerted on chain segments increases the modulus of elasticity, whatever the nature of these constraints. The above description is in accordance with the phantom network model.[9] It illustrates clearly the role played by $\langle \vec{r}_{ij} \rangle$ end-to-end vectors which are also involved in NMR properties.

V. Proton Relaxation in Polymeric Gels

It is now well established that all relaxation functions of protons observed in polymeric gels are fully governed by the residual dipole–dipole interactions of nuclear spins.[5,11]

Considering a polymeric gel, it is supposed that all nodes fluctuate in time. Then, the end-to-end vector $\vec{r}_{ij}$ of one chain segment (i,j) fluctuates. The observation of a residual interaction of spins indicates that the time average $\langle \vec{r}_{ij} \rangle$ of $\vec{r}_{ij}$ is not equal to zero. There is a probability distribution function $\mathcal{G}(\langle \vec{r}_{ij} \rangle / \zeta_{ij})$ of the mean vector $\langle \vec{r}_{ij} \rangle$, defined throughout the polymeric gel. The use of this function replaces the sum over all vectors in formula (16). It obeys the relation

$$\int \mathcal{G}(\langle \vec{r}_{ij} \rangle / \zeta_{ij}) \langle \vec{r}_{ij} \rangle \, \mathrm{d}\langle \vec{r}_{ij} \rangle = 0 \tag{18}$$

in the absence of any deformation. The time average $\langle \vec{r}_{ij} \rangle$ of $\vec{r}_{ij}$ must not be confused with the space average of $\langle \vec{r}_{ij} \rangle$.

NMR properties are interpreted by considering first the relaxation function associated with a single network chain segment (i,j); then a space average is carried out over the ensemble of chain segments in a gel.

V.1. Residual Dipole–Dipole Interaction. A network chain segment (i,j) is considered; its end-to-end vector $\langle \vec{r}_{ij} \rangle$ is fixed in space. Then, monomeric units which belong to this segment undergo a nonisotropic rotational diffusion.[12] Consequently, tensorial interactions which exist between all nuclei attached to the chain segment are not averaged to zero. There is a residual energy of dipole–dipole interactions $h\epsilon_{ij}$. Assuming tht fluctuations which occur within the chain segment have an axial symmetry around the mean end-to-end vector $\langle \vec{r}_{ij} \rangle$, the residual interaction of spins associated with any proton pair located on one monomeric unit can be expressed in a quite general way as

$$h\epsilon_{ij}^{0} = 0.3\Delta_G h(2\langle z_{ij}\rangle^2 - \langle y_{ij}\rangle^2 - \langle x_{ij}\rangle^2)a^2\Lambda/\sigma_{ij}^4 \tag{19}$$

a is the mean skeletal bond length and Δ_G is the spin–spin interaction corresponding to a fully extended chain. This formula applies to any flexible polymer chain whatever the complex structure of its monomeric units; the mean-square end-to-end distance σ_{ij}^2 is calculated in the absence of any external constraint. The factor Λ is called the parameter of second-order stiffness

$$\Lambda = 3.75\sum_{n,m,p} \langle(3(a_p^z)^2 - a^2)a_m^z a_n^z\rangle_0/a^4N_{ij} \tag{20}$$

$\Lambda = 1$ for ideal chains; N_{ij} is the number of skeletal bonds in the chain segments (i,j). Terms in Λ are equal to zero whenever the contour length between skeletal bonds a_p and a_m or a_m and a_n is too large. The normalized transverse magnetic relaxation function associated with the segment (i,j) is expressed as

$$m_x^{ij}(t) = \cos\{\epsilon_{ij}(\langle\vec{r}_{ij}\rangle)t\} \tag{21}$$

Deformations of network chain segments are perceived from the above relaxation function taking formula (6) into consideration. Formula (8) has been established by assuming that interactions between nuclear spins located on different chain segments are negligible; it has been already shown that these interactions are actually negligible by comparing observations made from ^{13}C nuclei with those made from protons. The relaxation function $M_x(t)$ observed from the sample gel is obtained by carrying out a space average of $m_x^{ij}(t)$ over all chain segments.

V.2. Local Diffusional Asymmetry. The residual dipole–dipole interaction of spins results from the asymmetry of the local diffusion of monomeric units. The existence of $\epsilon_{ij}(\langle\vec{r}_{ij}\rangle)$ amounts to consider that each skeletal bond is subjected to a potential energy

$$W(\vec{a}, \langle\vec{r}_{ij}\rangle) = 3\vec{a}\langle\vec{r}_{ij}\rangle kT/\sigma_{ij}^2 \tag{22}$$

and

$$\langle\vec{a}\rangle = \langle\vec{r}_{ij}\rangle/N_{ij} \tag{22'}$$

For a Gaussian chain

$$W(\vec{a}\langle\vec{r}_{ij}\rangle) = 3\vec{a}\langle\vec{r}_{ij}\rangle kT/N_{ij}a^2C_\infty \tag{23}$$

while

$$\epsilon_{ij}(\langle\vec{r}_{ij}\rangle) \propto \Delta_G\Lambda\langle\vec{r}_{ij}\rangle^2/N_{ij}^2C_\infty a^2 \tag{23'}$$

The distribution of $\langle\vec{r}_{ij}\rangle$ is isotropic in the absence of any deformation; consequently, the space average of ϵ_{ij} over the whole gel is equal to zero, but what is observed from NMR is a space average of $m_x^{ij}(t)$ The foregoing description applies to all nuclei undergoing tensorial magnetic interactions. Typical spin systems may be formed from one ^{13}C nucleus in dipole–dipole interaction with one or two protons. Proton pairs (CH_2) or methyl groups are also convenient spin systems.[9] The quadrupolar interaction of one deuterium nucleus with an electric field gradient also reflects properties associated with chain segments. The present description will rely upon the proton transverse relaxation; however, as is shown in this work, experimental results parallel those obtained from ^{13}C nuclei or deuterium nuclei as long as averaged angular properties of monomeric units are considered. Upon observation of the magnetic resonance of deuterium nuclei, vulcanized chains have recently been studied in two ways. According to one of these two ways, deuterium atoms are attached to small solvent molecules (C_6D_6); the polymeric network structure is slightly swollen and then stretched (the polymeric fraction is $\phi = 0.9$). A nonisotropic rotational diffusion of small molecules results from the effect of stretching; this property is disclosed from a resonance line doublet.[13] The splitting $\Delta\Omega$ is an increasing function of the elongation. According to the other way, polymer chains are partly deuterated to analyze the states of deformation near cross-links or in the center parts of network chain segments.[14] In both cases, NMR parameters are found to be dependent upon the relevant variable of stretching $\lambda^2 - 1/\lambda$; $\lambda = L/L_0$ is the stretching ratio defined from the lengths L and L_0 of the stretched and unstretched samples, respectively.

The NMR approach reported in this work is based upon the analysis of the transverse magnetic relaxation of protons attached to polybutadiene chain.[11]

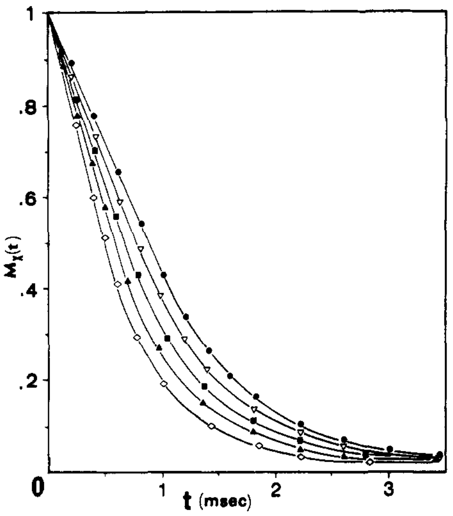

Figure 2. Proton transverse relaxation functions recorded at room temperature. Numerical values of the stretching ratio λ are 1 (●), 1.2 (▽), 1.4 (■), 1.6 (▲), and 1.9 (◇).

VI. NMR and Gel Elongation

In this section, the effect of a small extension of a gel is analyzed in a molecular scale from NMR.

VI.1. Elasticity of Vulcanized Chains. In addition to the swelling ratio Q_m, the modulus of elasticity E was measured in the case of polybutadiene chains with a vinyl content $z_{1,2}$ equal to 8% (Figure 1); the curve drawn in Figure 1 shows that the variable w is again appropriate to the description of the state of gelation of vulcanized chains. However, considering formulae (15) and (16), the variable w does not appear directly from the ratio $\sum_{i,j}\langle r_{ij}^x\rangle^2/\langle(\Delta r_{ij}^x)^2\rangle$. Therefore, this ratio must be a function more complicated than a simple front factor proportional to ν_e or c_c^s. The collective behavior of correlation domains which arise from the percolation process must be taken into consideration to calculate the sum $\sum_{i,j}\langle r_{ij}^x\rangle^2/\langle(\Delta r_{ij}^x)^2\rangle$.

VI.2. Pseudo-solid Magnetic Relaxation. The uniaxial deformation of cross-linked chains is well perceived from the transverse magnetic relaxation of protons attached to polybutadiene chains. This effect is illustrated in Figure 2 where relaxation functions corresponding to values of the stretching ratio λ equal to 1, 1.2, 1.4, 1.6, and 1.9 are drawn. The great sensitivity of proteons leads to accurate measurements of relaxation parameters. The chain molecular weight is $\bar{M}_n = 2.67 \times 10^5$, the sulfur

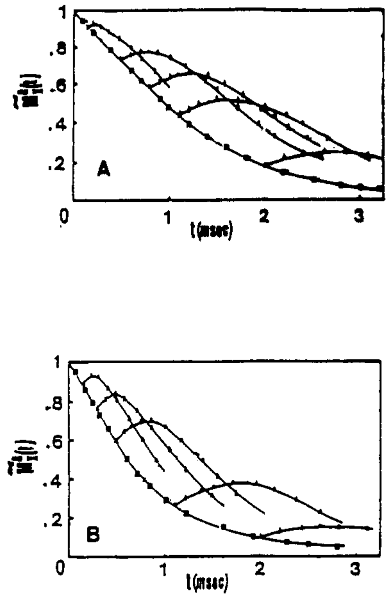

Figure 3. Pseudo-solid spin echoes observed from vulcanized polybutadiene. The chain molecular weight is $\bar{M}_n = 2.5 \times 10^5$; the sulfur concentration is $c_c^3 = 5\%$ (w/w) (vinyl content $z_{1,2} = 8\%$). Numerical values of the stretching ratio λ are 1 (A) and 2.5 (B).

concentration is 10^{-2} g (w/w), and the content of monomeric units in the 1,2-vinyl conformation is 8%.

In accordance with the description given in section V, pseudo-solid spin echoes can be formed (Figure 3). They reflect the existence of a residual interaction of spins. The transverse magnetic relaxation of protons is entirely governed by this residual interaction.

VI.3. $\lambda^2 - 1/\lambda$ Dependence. Each magnetic relaxation function is easily characterized from the slope σ_0 of the tangent drawn at the initial time $t = 0$ of the transverse relaxation function; variations of the ratio σ/σ_0 are reported in Figure 4 as a function of the variable of stretching $\lambda^2 - 1/\lambda$; σ_0 is measured in the absence of any deformation. Two values are given to the angle which the direction of stretching makes with the magnetic field B_0: $\theta = 0$ or $\theta = \pi/2$. The ratio $(\sigma - \sigma_0)/\sigma_0$ is exactly proportional to the variable $\lambda^2 - 1/\lambda$. A similar property is observed from deuteriated systems; it is in accordance with many other studies on oriented polymeric systems.

VI.4. Angular Dependence. Magnetic relaxation functions observed when the angle θ is varied by keeping the stretching ratio at a constant value $\lambda = 1.95$ are reported in Figure 5. Effects of angular variations are perceived without any ambiguity. Variations of the slope of the initial tangent to the relaxation function are shown in Figure 6. Several values are given to the stretchig ratio: $\lambda = 1.2, 1.5, 1.7$, and 1.95. The main feature perceived in Figure 6 concerns the value of the relaxation parameter σ measured at the magic angle $\theta_0 = 54°44'$; this value is independent of the stretching ratio and is equal to the slope observed in the absence of any deformation.

VI.5. Deformation of NMR Network Chain Segments. Variations of the ratio σ/σ_0 as a function of the variable of stretching $\lambda^2 - 1/\lambda$ are reported in Figure 7; they correspond to different values given to the angle θ between the magnetic field and the direction of stretching. Results reported in Figures 6 and 7 are crucial; they serve as a basis for the interpretation of NMR properties. According to experimental results shown in Figures 4, 6, and 7, the relaxation rate of the transverse magnetization of protons must be written as

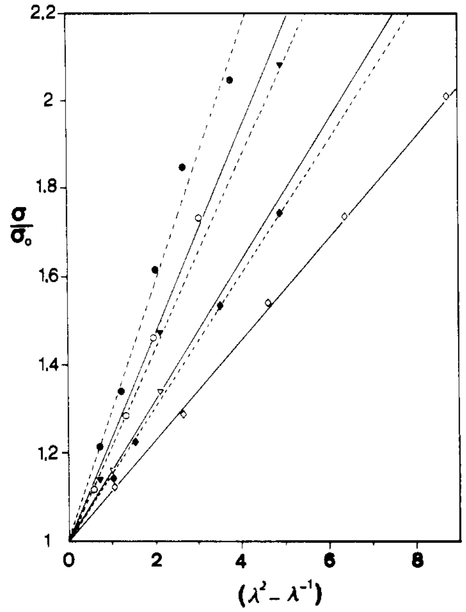

Figure 4. Ratio σ/σ_0 represented as a function of the variable of stretching $\lambda^2 - 1/\lambda$ (σ_0 corresponds to $\lambda = 1$). σ is the tangent drawn at the initial time of the proton relaxation function. Samples are characterized by: $\bar{M}_n = 2.5 \times 10^5$, $c_c^s = 0.5\%$ (◇,◆); $\bar{M}_n = 3.6 \times 10^5$, $c_c^s = 0.5\%$ (▽,▼); $\bar{M}_n = 2.5 \times 10^5$, $c_c^s = 1\%$ (○, ●). Open symbols correspond to $\theta = \pi/2$, while closed symbols correspond to $\theta = 0°$.

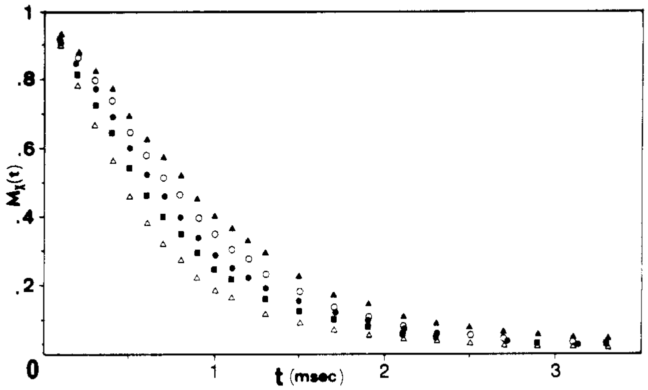

Figure 5. Effect of sample orientation with respect to the steady magnetic field. ($\bar{M}_n = 2.5 \times 10^5$, $\nu_c^s = 1\%$). Numerical values of θ are 0° (△), 22° (■), 51° (▲), 68° (○), and 90° (●). Proton relaxation functions were recorded at room temperature; the stretching ratio is $\lambda = 1.95$.

$$\sigma = \sigma_0 + (\lambda^2 - 1/\lambda)|3\cos^2\theta - 1|\kappa(c_c^s) \qquad (24)$$

the slope of straight lines drawn in Figure 4 is a function of the concentration of cross-links c_c^s. The effect of gel stretching is disclosed as a simple addition to the relaxation rate σ_0 observed in the absence of any deformation. Taking formula (6) into consideration, the residual interaction of spins must be expressed as a function of deformed end-to-end vectors of network chain segments whatever their exact definition.

VI.5a. Laboratory Reference Frame. The deformation of elementary network chain segments is first analyzed in the reference frame $OXYZ$, associated with the steady magnetic field $\vec{B}_0$. The Z-axis is parallel to the direction of the field $\vec{B}_0$. The expression of the residual interaction must consist of two contributions, in accordance with the empirical formula (24). These two contributions are analyzed in the following way. One skeletal bond $\vec{a}$ is considered; it belongs to the chain segment (i,j)

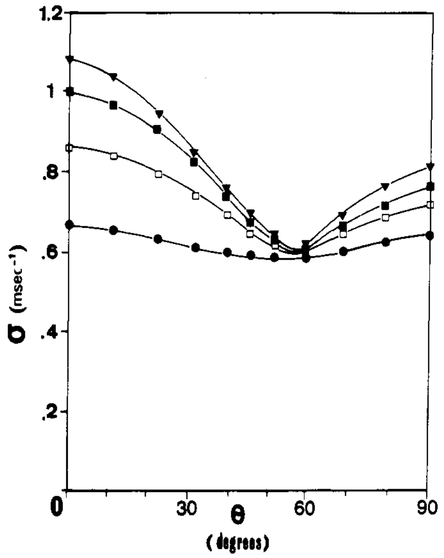

Figure 6. Angular variations of the relaxation rate (initial tangent to the relaxation function). Numerical values of the stretching ratio λ are 1.2 (●), 1.5 (□), 1.7 (▽), and 1.95 (▲). ($\bar{M}_n = 2.5 \times 10^5$, $c_c^s = 1\%$).

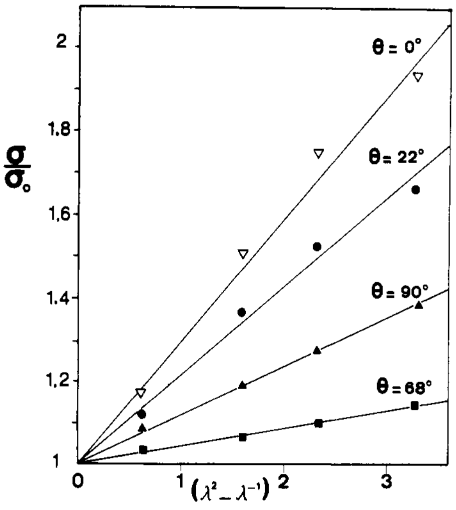

Figure 7. Ratio σ/σ_0 reported as a function of the variable of stretching $\lambda^2 - 1/\lambda$. Several numerical values are given to the angle θ between the direction of elongation and the study magnetic field ($\bar{M}_n = 2.5 \times 10^5$; sulfur concentration $c_c^s = 1\%$).

characterized by the mean end-to-end vector $\langle \vec{r}_{ij} \rangle$, and it makes the angle $\beta(\vec{a})$ with the magnetic field $\vec{B}_0$. Then, the mean value of the angular function $(3 \cos^2 [\beta(\vec{a})] - 1)$ must consist of two contributions. The first one gives rise to the residual interaction which is called $\epsilon_{ij}^0(\langle \vec{r}_{ij} \rangle)$; it is associated with mean end-to-end vectors which exist in the absence of any uniaxial deformation of the polymeric gel. It is written as

$$\epsilon_{ij}^0(\langle \vec{r}_{ij} \rangle) = 0.3\Lambda\Delta_G \langle \vec{r}_{ij} \rangle^2 a^2 (3 \cos^2 \Psi_{ij} - 1)/\sigma_{ij}^4 \qquad (25)$$

This expression corresponds to an axial symmetry of fluctuations which occur around the mean vector $\langle \vec{r}_{ij} \rangle$; Ψ_{ij} is the angle which $\langle \vec{r}_{ij} \rangle$ makes with the magnetic field $\vec{B}_0$. The contribution $\epsilon_{ij}^0(\langle \vec{r}_{ij} \rangle)$ leads to the relaxation rate σ_0 which is observed in the absence or in the presence of a uniaxial deformation. The other contribution to the mean value of the angular function $(3 \cos^2 [\beta(\vec{a})] - 1)$ gives rise to the additional residual interaction which is called $\Delta\epsilon_{ij}(\langle \vec{r}_{ij} \rangle)$. It arises from the effect of stretching. It must reflect the law of deformation of network chain segments. It is conveniently analyzed in the sample reference frame.

VI.5b. Sample Reference Frame. The additional contribution results from an orientational perturbation of monomeric units; it must account for the $(3 \cos^2 \theta - 1)$ dependence, observed in the laboratory reference frame. In accordance with the transformation of spherical harmonics, this dependence implies that the $\Delta\epsilon_{ij}$ additional contribution must be characterized by an axial symmetry around the direction of the force $\vec{f}$ which is applied to the gel. This is clearly illustrated from the average values of the following set of spherical harmonics $Y_2^m(\vec{a})$ associated with the bond $\vec{a}$ which belongs to the segment (i,j). In the sample reference frame, the average values are expressed as

$$\langle Y_2^0(\vec{a}) \rangle_{ij} = 0.3 Y_2^0(\langle \vec{r}_{ij} \rangle)\Lambda \langle r_{ij} \rangle^2 a^2/\sigma_{ij}^4 + \left(\frac{5}{4\pi}\right)^{1/2} g_{ij}(\lambda) \qquad (26)$$

and

$$\langle Y_2^m(\vec{a}) \rangle_{ij} = 0.3 Y_2^m(\langle \vec{r}_{ij} \rangle)\Lambda \langle r_{ij} \rangle^2 a^2/\sigma_{ij}^4 \qquad m \neq 0 \qquad (26')$$

$\langle\ \rangle_{ij}$ denotes the angular average obtained when the mean end-to-end vector of the segment (i,j) is equal to $\langle \vec{r}_{ij} \rangle$; $Y_2^m(\langle \vec{r}_{ij} \rangle)$ depends upon the angular coordinates of the vector $\langle \vec{r}_{ij} \rangle$, defined in the sample reference frame. The function $g_{ij}(\lambda)$ is introduced to account for the observed dependence upon λ. It gives rise to the contribution $\Delta\epsilon_{ij}(\langle \vec{r}_{ij} \rangle)$. Then, in the laboratory reference frame, the transformation of spherical harmonics leads to

$$\langle 3 \cos^2 \beta(\vec{a}) - 1 \rangle_{ij} = 0.3\Lambda(3 \cos^2 \Psi_{ij} - 1)\langle \vec{r}_{ij} \rangle^2 a^2/\sigma_{ij}^4 + (3 \cos^2 \theta - 1) g_{ij}(\lambda) \qquad (27)$$

In the sample reference frame, $\langle \vec{u}_{ij} \rangle$ is the mean vector resulting from the law of transformation of the vector $\langle \vec{r}_{ij} \rangle$ and the residual interaction of spins is expressed as

$$\epsilon_{ij}(\langle u_{ij} \rangle) = 0.3\Lambda\Delta_G(2\langle r_{ij}^z \rangle^2 - \langle r_{ij}^x \rangle^2 - \langle r_{ij}^y \rangle^2)a^2/\sigma_{ij}^4 + \Delta_G g_{ij}(\lambda) \qquad (28)$$

In formula (28) the effect of stretching upon the three components is observed as a whole.

VI.5c. Dependence upon the Stretching Ratio. The existence of relations (26) and (26′) suggests the following law of transformation for each component.

$$\langle u_{ij}^z \rangle^2 = \langle r_{ij}^z \rangle^2 + \Gamma_{ij}(\lambda) \qquad (29)$$

$$\langle r_{ij}^y \rangle^2 = \langle u_{ij}^y \rangle^2 + \gamma_{ij}(\lambda) \qquad (29')$$

and

$$\langle r_{ij}^x \rangle^2 = \langle u_{ij}^x \rangle^2 + \gamma_{ij}(\lambda) \qquad (29'')$$

where $\Gamma_{ij}(\lambda)$ and $\gamma_{ij}(\lambda)$ are positive functions of λ which concern a given network chain segment (i,j). These functions must account for the $\lambda^2 - 1/\lambda$ dependence observed from NMR and for the $\lambda - 1/\lambda^2$ dependence of the retractive force. Formulae (13), (15), and (24) lead to the following definitions of $\Gamma_{ij}(\lambda)$ and $\gamma_{ij}(\lambda)$:

$$\Gamma_{ij}(\lambda) = (\lambda^2 - 1)\chi_{ij} \qquad (30)$$

and

$$\gamma_{ij}(\lambda) = (1 - 1/\lambda)\chi_{ij} \qquad (30')$$

The same factor χ_{ij} applies to x, y, and z components; it is discussed in the next section. Then

$$g_{ij}(\lambda) = 0.6\Lambda(\Gamma_{ij}(\lambda) + \gamma_{ij}(\lambda))a^2/\sigma_{ij}^4 \qquad (31)$$

or

$$g_{ij}(\lambda) = 0.6\Lambda(\lambda^2 - 1/\lambda)\chi_{ij}a^2/\sigma_{ij}^4 \qquad (32)$$

and, for the modulus of elasticity

$$E = 6kT\sum_{i,j}\chi_{ij}/\langle\Delta r_{ij}^x\rangle^2 \qquad (33)$$

This law of deformation of end vectors conciliates NMR results and the $\lambda - 1/\lambda^2$ dependence of the property of elasticity. It is considered that NMR properties originate in the fluctuations which give rise to the property of elasticity. The residual interaction of spins is written as

$$\epsilon_{ij}(\langle\vec{u}_{ij}\rangle) = 0.3\Lambda\Delta_G(2\langle u_{ij}^z\rangle^2 - \langle u_{ij}^x\rangle^2 - \langle u_{ij}^x\rangle^2)a^2/\sigma_{ij}^4 \qquad (34)$$

Relations (29), (30), and (29″) do not correspond to the property of affinity described by relations (17). It is considered that the effect of stretching appears only as an additional property of the relaxation rate which is related to a vector of deformation $\Delta\vec{r}_{ij} = \langle\vec{u}_{ij}\rangle - \langle\vec{r}_{ij}\rangle$. However, the apparent $\lambda - 1/\lambda^2$ dependence of the retractive force is well described.

VI.6. Variations of Entropy. Although the law of deformation of each component does not obey a property of affinity, the transformation of any vector $\vec{r}_{ij}$ into u_{ij} can occur in a continuous way:

$$\vec{r}_{ij}(L_{ij}) = \int_0^{L_{ij}}\vec{v}_{ij}(s)\,\mathrm{d}s \qquad (35)$$

The transformation induced by the stretching is associated with a vector $\Delta\vec{v}_{ij}(s)$. Then

$$\langle(u_{ij}^z)^2\rangle = \langle(r_{ij}^z)^2\rangle + \int_0^{L_{ij}}\mathrm{d}s_1\int_0^{L_{ij}}\mathrm{d}s_2\,\langle\Delta v_{ij}^z(s_1)\,\Delta v_{ij}^z(s_2)\rangle \qquad (36)$$

with the relation

$$\int\int\langle\Delta v_{ij}^z(s_1)\,\Delta v_{ij}^z(s_2)\rangle\,\mathrm{d}s_1\,\mathrm{d}s_2 = (\lambda^2 - 1)bL_{ij} \qquad (37)$$

the factor of proportionality b is a characteristic length of the polymer segment. In the same way

$$\lim_{L_{ij}\to\infty}\frac{1}{L_{ij}}\int\int\langle\Delta v_{ij}^{x,y}(s_1)\,\Delta v_{ij}^{x,y}(s_2)\rangle\,\mathrm{d}s_1\,\mathrm{d}s_2 = (1 - 1/\lambda)b \qquad (38)$$

with

$$\langle(r_{ij}^{x,y})^2\rangle = \langle(u_{ij}^{x,y})^2\rangle + \int_0^{L_{ij}}\int_0^{L_{ij}}\mathrm{d}s_1\,\mathrm{d}s_2\,\langle\Delta v_{ij}^{x,y}(s_1)\,\Delta v_{ij}^{x,y}(s_2)\rangle \qquad (39)$$

Considering the usual hypothesis which is the basis for the description of the property of elasticity at small deformations

$$\langle(\Delta u_{ij}^\alpha)^2\rangle = \langle(\Delta r_{ij}^\alpha)^2\rangle \qquad \alpha = x, y, \text{ or } z \qquad (40)$$

or

$$\langle(u_{ij}^\alpha)^2\rangle - \langle(r_{ij}^\alpha)^2\rangle = \langle u_{ij}^\alpha\rangle^2 - \langle r_{ij}^\alpha\rangle^2 \qquad (41)$$

The relations of deformation (29), (29′), and (29″) are identified with relations (36) and (38) with $\chi_{ij} = bL_{ij}$.

The dependence upon λ of the variation of entropy associated with the chain segment (i,j) is in accordance with the usual descriptions.[8,9]

$$\Delta s_{ij} = -k(\lambda^2 + 2/\lambda - 3)bL_{ij}/\sigma_{ij}^2 \qquad (42)$$

In the laboratory reference frame, the residual interaction is expressed as

$$\{\epsilon_{ij}(\langle\vec{u}_{ij}\rangle)\}_{OXYZ} = \epsilon_{ij}(\langle\vec{r}_{ij}\rangle) + 0.6\Lambda\Delta_G/3\cos^2\theta - 1/(\lambda^2 - 1/\lambda)ba^2/L_{ij}\lambda_c^{\,2} \qquad (43)$$

where $\lambda_c = aC_\infty$ is the Kuhn step length.

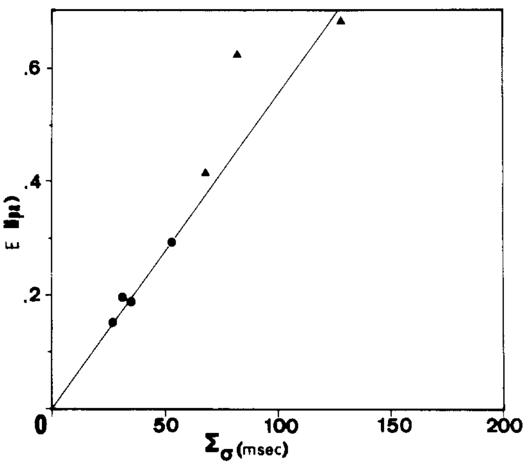

Figure 8. Modulus of elasticity of vulcanized chains reported as a function of the factor of proportionality κ of the NMR parameter σ upon the variable $\lambda^2 - 1/\lambda$. Polybutadiene samples (▲) and poly(dimethylsiloxane) ones (●) are described in the text.

Table II
Characterization of Vulcanized PDMS Chains

vinyl concn, ppm	E, MPa	vinyl concn, ppm	E, MPa
700	0.155	1200[a]	0.180
2100	0.295	2100[b]	0.190

[a] Sample obtained by mixing chains with a 700 ppm vinyl content with chains with a vinyl content equal to 2100 ppm. [b] Sample obtained by mixing chains with a 700 ppm vinyl content with chains with a vinyl content equal to 4500 ppm.

VI.7. NMR–Elasticity Interrelationship. Although the law of deformation described by relations (29), (29′), and (29″) is supposed to apply to network chain segments perceived from NMR, it may be of interest to attempt to relate the property of elasticity to the magnetic relaxation of protons. On the one hand, the factor Σ associated with the $\lambda^2 - 1/\lambda$ dependence in formula (24) is proportional to the inverse of the contour length $L_{ij} = aN_{ij}$; the mean value of N_{ij} is $N_c = \mathcal{A}/\nu_c M_b$ (ν_c is the concentration of cross-links per gram). On the other hand, the modulus of elasticity expressed according to formula (28) is proportional to the ratio ν_e/ν_c which is roughly estimated from the ratio $\rho\mathcal{A}/N_c M_b$ (ρ is the pure polymer density). Consequently, the parameters E and κ must be related to each other. This is illustrated in Figure 8 where NMR results are compared with elasticity measurements. Results concerning four vulcanized poly(dimethylsiloxane) chains are reported in addition to those observed from polybutadiene chains. Without entering into experimental details, cross-links of PDMS chains are formed from vinyl side chains ($\bar{M}_n = 3.2 \times 10^5$). Concentrations of vinyl groups are reported in Table II. A straight line can be reasonably drawn through experimental points; it goes through the origin of coordinates. It is considered that Figure 8 gives evidence experimentally for the strong relationship which exists between elasticity and the transverse nuclear magnetic relaxation in a polymeric gel. However, the scatter in the polybutadiene data does not permit us to assert that the straight line drawn in Figure 8 illustrates a very general property.

VI.8. Field of Asymmetry. Systems of vulcanized chains perceived from NMR can be pictured in the following way.

(i) In the absence of any deformation, a distribution of nonzero end-to-end vectors of network chain segments is observed from NMR. Any nonzero end-to-end vector creates a field of anisotropy which applies to monomeric units which form this network chain segment. A scattering of the directions of different fields of asymmetry occurs because polymer chains are swollen by one another. However, the high sensitivity of NMR permits us to disclose the nonisotropic local diffusion of monomeric units in any polymeric gel.

(ii) When a uniaxial deformation is applied to the system of vulcanized chains, a uniform field of asymmetry is applied to all monomeric units in addition to the effect of anisotropy which exists prior to the deformation of each chain segment. This additional field manifests itself through a residual average of tensorial functions of orientational coordinates of small molecules or monomeric units. The strength of the effect of asymmetry appears through the function $(\lambda^2 - 1/\lambda)/N_c$ where λ is the stretching ratio and N_c is the average number of skeletal bonds per cross-link.

This picture applies to small deformations only; the additional field of asymmetry must be considered as the linear expansion of a more complex function used to describe strong deformations. This interpretation can be viewed as the reduction of entropy which accompanies the well-known effect of sedimentation. Starting from a uniform distribution of particles in a solution, then the gravity leads to an effect of sedimentation with a reduction of entropy equal to

$$\Delta s = k \log \left(\frac{1 - \exp(h(1 - d_0/d)mg/kT)}{h(1 - d_0/d)mg/kT} \right)$$

h is the height of the solution, and d and d_0 are the densities of one particle and the solvent, respectively. The mass of one particle is m, and g is the acceleration induced by the gravity. Correspondingly, the mean position of one particle goes from $\bar{z}_0 = h/2$ to $\bar{z} = kT/mg(1 - d_0/d)$ for large values of h. Particles are confined in a small part of space. Note that the relevant variable is $(1 - d_0/d)$; it resembles the variable $\lambda^2 - 1$ observed from NMR.

VII. Conclusion

The study of physical systems formed from long polymer chains cross-linked at random can be conveniently divided into two parts.

The first one concerns the search for one variable which permits us to define the state of gelation of the system. In this work, it is shown that the relevant variable used to characterize vulcanized polybutadiene chains is determined by the product of the number of skeletal bonds in one chain by the concentration of cross-linking agent. Both the modulus of elasticity and the gel volume in a state of maximum swelling are found to be a function of this variable.

The second part of the study of vulcanized chains deals with the identification of statistical units which govern macroscopic properties of network structures. For example, the maximum volume of the gel in a state of maximum swelling is controlled by the size of these swollen units, but these units are intertwined and the maximum swelling depends also upon the degree of interdispersion of these units from one another. In this work, statistical units are not identified exactly. Characteristic elementary network chain segments are introduced. Small uniaxial extensions of gels are used to induce small deformations of these segments. Permanent constraints which originate the property of elasticity induce also a pseudo-solid behavior of the transverse magnetization of nuclei linked to network chain segments. A careful analysis of this behavior permits us to disclose the law of deformation of these segments. For small extensions, the deformation appears as an effect which adds to the extension of segments observed in the absence of any stretching of the polymeric gel. This additional orientational effect of monomeric units has an axial symmetry around the direction of the external force. For a given segment, the strength of this effect is proportional to its contour length. In accordance with the variation of entropy which accompanies the deformation of each segment, this law accounts for the $\lambda^2 - 1/\lambda$ dependence observed for NMR properties and the $\lambda - 1/\lambda^2$ dependence observed for the retractive force of the gel but it does not describe a property of affinity.

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