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State of Gelation of Randomly Cross-Linked Poly(butadiene) Chains. Nuclear Magnetic Resonance, Swelling, and Elongation

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ABSTRACT: Properties of cross-linked poly(butadiene) chains are studied by varying the chain molecular weight and the sulfur concentration. The modulus of elasticity, the swelling ratio in a state of maximum swelling, and the gel fraction are shown to be functions of a single variable defined by the product of the chain molecular weight and the sulfur concentration. The chain molecular weight was varied from $\bar{M}_n = 7 \times 10^4$ to 30×10^4 g/mol, and the sulfur concentration was varied from $\gamma_c^S = 0.35$ to 5 g/g. A threshold of percolation is determined by the value $\bar{M}_n\gamma_c^S \simeq 500$ g/mol. Only finite clusters are formed when the value $\gamma_c^S\bar{M}_n$ is smaller than 500. The transverse relaxation of protons attached to polymer chains is also shown to depend upon the variable of gelation. NMR properties observed on swollen or stretched systems give an insight into the corresponding deformations of chain segments. The real NMR probe is proved to be one chain segment. NMR shows that the state of maximum swelling can be described as a situation where branched systems are in a c^* concentration.

I. Introduction

It is nowadays attempted to describe properties of polymeric gels within the framework of percolation. Such a description accounts for the collective behavior of chain segments which determine the network structures.[1] The attention has been mainly focused on properties observed near the percolation threshold.[2] Whether the description of polymeric gels is critical or not, it is based on scaling laws which apply to the gel fraction G or to the average mesh size ξ; the scaling property appears through power laws of the variable ϵ defined with respect to the threshold of percolation:

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

with $\beta = 0.4$ or 1 for critical or classical descriptions, and

$$\xi \propto \epsilon^{-\nu}$$

with $\nu = 0.84$ or $^1/_2$ for critical or classical descriptions, respectively. No general framework has been proposed until now to describe properties of gels which are in a state of percolation far from the threshold.[3]

In this work, systems formed by polymeric chains cross-linked at random are studied. Considering the probability p to attach one chain to another, it has been already shown that the threshold of gelation is defined by $p_c = M_b/\bar{M}_w$; M_b and $\bar{M}_w$ are the molar weights of one monomeric unit and one chain, respectively.[4] Also, the critical domain of description of the gelation process observed around p_c is very narrow because it is defined by $|\epsilon| \leq (M_b/\bar{M}_w)^{1/3}$ ($\epsilon = 0$ for $p = p_c$); consequently, properties of cross-linked long chains must be analyzed within a classical framework.[5] The critical description should apply to long chains in semidilute solutions which are cross-linked at a concentration near c^*, the concentration of chain overlap.[5]

This work deals with investigations into structural properties of cross-linked polymer chains. These investigations are based on static responses of gels to external constraints corresponding to uniaxial deformations or swelling effects induced by a good solvent. Investigations are also based on semilocal observations resulting from the magnetic relaxation of protons located on network chain segments. NMR is combined with swelling effects or elongation of vulcanized chains to disclose the mechanisms of deformation of chain segments which determine network structures.

Two main problems are encountered in describing properties of polymeric gels. The first one concerns the determination of a relevant variable appropriate to the characterization of any state of gelation. Such a variable must combine the chain molecular weight and the concentration of cross-linking agent in order to attempt to predict a state of gelation from values given to these experimental parameters. Once the state of gelation is determined, it is necessary to characterize the corresponding statistical structure of the network by using relevant physical quantities. The interpretation of NMR properties relies upon the assumption that there exists a probability distribution function $\mathcal{P}(\vec{r}_{jl}/\zeta)$ of end-to-end vectors of segments joining two consecutive coupling junctions (j) and (l). It is shown in the next section that a NMR parameter χ_c sensitive to the moments of the gel function $\mathcal{P}(\vec{r}_{jl}/\zeta)$ can be defined.[6] Another physical quantity used throughout this study is the swelling ratio Q_m; it is defined as the ratio of the volume of the polymer system in a state of maximum swelling divided by the volume of the dry gel. The purpose of this work was to prove that the modulus of elasticity E, the swelling ratio Q_m, and the NMR parameter χ_c are related to one another; the quantities E, Q_m, and χ_c are actually different functions of the same variable of state of gelation.

The principle of the NMR approach is given in section II. The percolation framework of description of vulcanized chains is introduced in section III. Swelling properties of the polymeric gel are described in section V. The modulus of elasticity is considered in section VI. Investigations based on NMR are analyzed in section VII.

II. Pseudosolid Relaxation of Protons

NMR observations are analyzed by assuming that a polymeric gel is a giant molecule which can be described as an ensemble of network chain segments. The presence of cross-links corresponds to constraints exerted on ends of network chain segments. These constraints prevent monomeric units from rotating completely in space. There exists a permanent nonzero average of dipole–dipole interactions between protons. The residual dipole–dipole interaction is strong enough to govern the transverse

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magnetic relaxation process and to screen the dynamics of monomeric rotations. The relaxation is sensitive only to deviations from isotropic rotations; the relaxation rate is a measure of the rotational asymmetry of monomeric units. A quantitative analysis of this property is given in the following way.[7]

(1) Network Chain Segment. One network chain segment determined by two consecutive coupling junctions (j) and (l) is first considered. Let $\langle \vec{r}_{jl} \rangle$ denote its mean end-to-end vector. Dipole–dipole interactions existing between all protons located on this segment give rise to the residual spin Hamiltonian expressed in the laboratory reference frame as

$$\langle \mathcal{H}_{jl} \rangle = 0.3(3\cos^2\theta\langle \vec{r}_{jl} \rangle - 1)\left(\frac{a\langle \vec{r}_{jl} \rangle}{\langle \vec{r}_{jl}^{\,2} \rangle}\right)^2 \Lambda \sum_{qq'} A_{qq'} B_{qq'} \qquad (1)$$

a is the mean length of one skeletal bond and $\theta(\vec{r}_{jl}\rangle)$ is the angle which the end-to-end vector $\langle \vec{r}_{jl} \rangle$ makes with the steady magnetic field. The sum is extended to all qq' proton pairs located on the chain segment (jl); $A_{qq'}$ is the adiabatic part of the spin operator representing dipole–dipole interactions. Numerical factors $B_{qq'}$ are related to the geometrical structure of monomeric units; they must take all orientations of monomeric units compatible with the end-to-end vector $\langle \vec{r}_{jl} \rangle$ into account. Finally, Λ is a parameter of second order stiffness defined from

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

The z axis is parallel to the steady magnetic field. The parameter Λ describes orientational correlations between three skeletal bonds p, n, and m along one chain segment. It is not the purpose of this work to demonstrate again eq 1. The main feature perceived from this equation is associated with the front factor:

$$(3\cos^2\theta\langle \vec{r}_{jl} \rangle - 1) a \langle \vec{r}_{jl} \rangle^2 / \langle r_{jl}^{\,2} \rangle \qquad (3)$$

The mean-square value $\langle r_{jl}^2 \rangle$ depends upon the statistical framework which is used to describe the polymeric gel (Gaussian approach or effect of excluded volume). The mean vector $\langle \vec{r}_{jl} \rangle$ depends upon the law of deformation which applies to vulcanized chains when an external constraint is exerted on the system. These two quantities are closely related to the statistical structure determined by the giant molecule.

The transverse magnetization assigned to the (jl) chain segment is called $m_{jl}^x(t)$; the magnetization is parallel to the x axis of the rotating frame, and it is expressed as

$$m_{jl}^x(t) = \mathcal{T}r\{e^{i\langle \mathcal{H}_{jl} \rangle t} \mathcal{M}_x e^{-i\langle \mathcal{H}_{jl} \rangle t} \mathcal{M}_x\} \qquad (4)$$

It has been already shown that interactions between protons located on different chain segments can be neglected because of the short range of dipole–dipole interactions and also because diffusional motions of monomeric units with respect to one another are characterized by short correlation times ($\simeq 10^{-8}$ s). The transverse relaxation function is supposed to be determined only by a pure residual interaction of spins.

(2) Average Proton Transverse Relaxation. The transverse relaxation function $M_x(t)$ observed on vulcanized chains is the average of $m_{jl}^x(t)$ carried out by using the gel function $\mathcal{G}(\vec{r}_{jl}/\zeta)$:

$$M_x(t) = \int \mathcal{G}(\vec{r}_{jl}/\zeta) m_{jl}^x(t) \, \mathrm{d}\langle \vec{r}_{jl} \rangle \qquad (5)$$

with the normalization condition

$$1 = \int \mathcal{G}(\vec{r}_{jl}/\zeta) \, \mathrm{d}\langle \vec{r}_{jl} \rangle \qquad (6)$$

It has been already shown that it is convenient to calculate two integrals to characterize the spin-system response:

$$\phi_1 = \int_0^\infty M_x(t)/\sqrt{t} \, \mathrm{d}t \qquad (7)$$

$$\phi_3 = \int_0^\infty (\mathrm{d}M_x/\mathrm{d}t)/\sqrt{t} \, \mathrm{d}t \qquad (8)$$

Then, considering that $M_x(t)$ is equal to unity for $t = 0$

$$\phi_1 = 45 m_1 \langle r_{jl}^{\,2} \rangle^2 / (\zeta a \sqrt{\Lambda \Delta_G}) \qquad (9)$$

$$\phi_3 = 5 m_3 \sqrt{\Lambda \Delta_G} \zeta a / \langle r_{jl}^{\,2} \rangle^2 \qquad (10)$$

with

$$m_n = (4\pi)^{-1} \int \mathcal{G}(\rho) \rho^{n-2} \, \mathrm{d}\rho \qquad (11)$$

$$\rho = \langle r_{jl} \rangle / \zeta$$

In other words, ϕ_1 and ϕ_3 integrals permit one to disclose properties of the gel distribution function; this is characterized from its intrinsic moments.[8] The parameter Δ_G is equivalent to the spin–spin interaction which would be observed along a single chain segment, in the glassy state. The ratio ϕ_3/ϕ_1 is equal to

$$\chi_c = 1.1 \Lambda \Delta_G (\zeta a / \langle r_{jl}^{\,2} \rangle)^2 m_3/m_1 \qquad (12)$$

The ratio m_3/m_1 is constant whenever the nature of the distribution function is invariant while ζ may be varied. According to eqs 9 and 10, the product $\pi_c = \phi_3/\phi_1$ is proportional to $m_3 m_1$; all NMR parameters are eliminated; the quantity π_c may reveal possible changes of the nature of the distribution function $\mathcal{G}(\langle r_{jl} \rangle/\zeta)$. It will be shown in section VIII that specific spin echoes can be formed to prove the presence of a pure residual interaction of spins.

The NMR probe is one chain segment. The polymeric gel obeys a statistical description which is reflected by the quantity $\langle r_{jl}^2 \rangle$ while the law of deformation of chain segments is revealed by the quantity ζ.

III. Percolation Framework

(1) Variable of Gelation. It has been recently proposed to introduce one variable of gelation ϵ, in the following way.[9] The formation of a system of randomly cross-linked chains is described by analogy with a process of percolation; then, the reduced variable of percolation is defined as

$$\epsilon = (p - p_c)/p_c \qquad (13)$$

p is the probability that one covalent bridge is formed between two polymer chains; p_c is the value of p corresponding to the threshold of percolation. The probability p must be expressed as a function of the concentration of sulfur.

(2) Units of Percolation. Any chain is considered as one unit of percolation which contains a number f_c of U functions; f_c is equal to the number of monomeric units which can react with a cross-linking reagent. The functionality f_c of one U unit of percolation is proportional to the number N of monomeric units in one chain: $f_c = z^* N$ ($z^* \le 1$). The corresponding number $\mathcal{N}_u^i$ of U functions per gram of polymer is

$$\mathcal{N}_u^i = \mathcal{A}z^*/M_b \qquad (14)$$

$\mathcal{A}$ is the Avogadro number and $M_b/\mathcal{A}$ is the mass of one monomeric unit. Cross-links are pictured as difunctional V units of percolation. The ideal state of maximum gelation should correspond to cross-links formed between all monomeric units which can react with one another. Let γ_c^s denote the mass of sulfur per unit mass of polymer; then, the corresponding number of V functions is

$$\mathcal{N}_v^i = 2\gamma_c \qquad (15)$$

with

$$\gamma_c = \gamma_c^s\mathcal{A}/\bar{x}_s M_s \qquad (16)$$

$\bar{x}_s$ is the average number of sulfur atoms participating in one cross-link and M_s is the mass of one sulfur atom, expressed in moles.

Then, any state of gelation is characterized by the fraction ϕ_u of U functions and the fraction ϕ_v of V functions which participate in the formation of the infinite cluster and clusters with a finite size. The fractions ϕ_u and ϕ_v obey the following relation:

$$\phi_u\mathcal{N}_u^i = \phi_v\mathcal{N}_v^i \qquad (17)$$

Then, according to the description of gelation processes proposed by Flory, the probability p of percolation is defined as

$$p = \phi_u\phi_v \qquad (18)$$

or

$$p = 2\phi_v^{\,2}\gamma_c^s M_b/\bar{x}_s M_s z^* \qquad (19)$$

When all cross-links corresponding to the initial concentration γ_c^s are formed, the fraction ϕ_v is set equal to unity. To express the variable ϵ of gelation, the threshold of percolation p_c is defined as

$$p_c = w(1,2)M_b/z^*\bar{M}_w \qquad (20)$$

the parameter $w(1,2)$ may depend upon the chain microstructure of polybutadiene. Then

$$\epsilon = 2\gamma_c^s\bar{M}_w/w(1,2)\bar{x}_s M_s - 1 \qquad (21)$$

or

$$\epsilon = 2\bar{M}_w/M_\kappa w(1,2) - 1 \qquad (22)$$

where M_κ is the mean molar weight of the segment separating two consecutive cross-links along one chain; M_κ is defined by

$$M_\kappa = \bar{x}_s M_s/\gamma_c^s \qquad (23)$$

The variable ϵ is equal to zero for

$$\gamma_c^s\bar{M}_w = \bar{x}_s M_s w(1,2)/2 \qquad (24)$$

The value of the threshold $\gamma_c^s\bar{M}_w$ is a function of the mean content of atoms in one sulfur bridge.

The purpose of this study was to characterize the dependence of the three physical quantities E, Q_m, and χ_c upon the variable of gelation ϵ, by varying both the chain molecular weight $\bar{M}_w$ and the concentration γ_c^s of cross-linking agent.

IV. Experimental Section

All cross-linked chain samples were prepared and supplied by the Manufacture Michelin (France). The chain molecular weight M_w of polybutadiene, determined by osmometry, was varied from 0.77×10^5 to 3.54×10^5 g/mol. The concentration γ_c^s of cross-linking agent (sulfur) was varied from 0.0035 to 0.01 g/g of polymer. All samples were prepared with stearic acid, santoflex 13, N-cyclohexyl-2-benzothiazylsulfenamide (CBS), and zinc oxide (ZnO) in addition to sulfur. The role of santoflex 13 is to avoid thermoxidation. Several chain microstructures were studied; they were differing by the contents of the monomeric units in the vinyl-1,2, cis-1,4, or trans-1,4 conformations.

Table I
Characterization of Vulcanized Polybutadiene Chains

microstructure	M_n	M_w	γ_c^s	Q_m	E (MPa)
8% 1,2-vinyl, 54% 1,4-trans, 38% 1,4-cis	70 000	77 000	1	10.5	0.26
			1.4	6.4	0.37
8% 1,2-vinyl, 52% 1,4-trans, 40% 1,4-cis	120 000	130 000	1	6.7	0.53
8% 1,2-vinyl, 51% 1,4-trans, 41% 1,4-trans,	160 000	171 000	0.35	166	0.13
			0.4	45.5	0.24
			0.45	23.8	0.28
			0.5	16.1	0.37
			1	5	0.64
			5	2.7	1.57
			10	2.3	1.64
8% 1,2-vinyl, 52% 1,4-trans, 40% 1,4-cis	170 000	180 000	1	5.3	0.57
			1.4	4.6	0.82
40% 1,2-vinyl, 36% 1,4-trans, 24% 1,4-cis	180 000	190 000	0.5	9.4	0.38
			1	5.7	0.71
			1.5	4.8	0.95
			2.5	4.2	1.3
19.6% 1,2-vinyl, 46.3% 1,4-trans, 34.1% 1,4-cis	300 000	354 000	0.5	6.7	
			1	4.4	

The state of maximum swelling on the cross-linked networks was induced by the osmotic pressure of cyclohexane, which is a good solvent of polybutadiene. According to a few chains can be extracted from the vulcanized network (those which are not cross-linked with the others) the system was washed during two days before measuring by gravimetry the ratio of equilibrium swelling Q_m. This one is expressed by

$$Q_m = 1 + \rho_P/\rho_S(m_{Q_m} - m_0)/m_0$$

where m_0 is the gel weight after extraction, and m_{Q_m} the weight of the swelling gel; ρ_P and ρ_S are the polybutadiene and cyclohexane densities (respectively 0.9 and 0.78).

NMR experiments were performed using a pulse spectrometer MSL 100 Bruker operating at 60 MHz. All relaxation functions were measured by using Carr-Purcell spin-echo sequences. It has been shown that relaxation functions measured by this kind of sequences are equivalent to those obtained by the usual experimental procedure, proposed by Hahn.

Most of the proton transverse relaxation functions have been recorded at room temperature. The thermal effect can be observed by increasing the temperature of the samples with the help of a thermic regulation.

Pseudosolid echoes have been described elsewhere. They are formed from the following appropriate pulse sequence:

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

The swelling effect studied by NMR was made by using deuteriated cyclohexane; swollen networks were placed in sealed NMR tubes with a nitrogen environment.

Measurements of the modulus of elasticity E were performed by analyzing the variation of the stress with a strain corresponding to a low uniaxial elongation. The networks were cut into long rectangular strips: the sections of the strips were measured. The two ends of the strips were fixed at chops. The upper chop was fixed, and the lower one was connected to a scale in which some weights could be placed. The initial distance of the two chops being known, the strain corresponds to the displacement of the

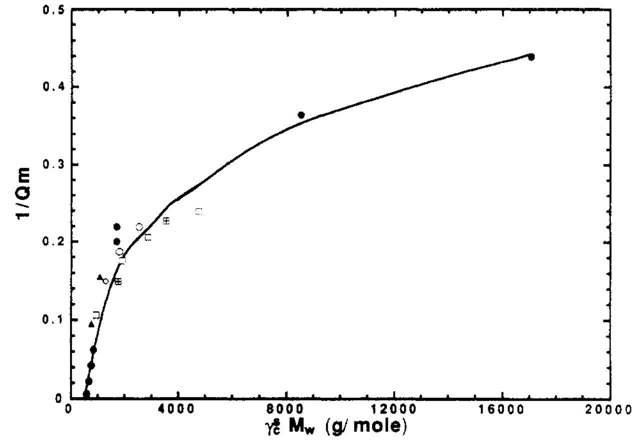

Figure 1. Variations of the inverse of the swelling ratio Q_m reported as a function of the variable $\gamma_c^s\bar{M}_w$: 0.77 × 10^5 g/mol (▲), 1.3 × 10^5 g/mol (◊), 1.7 × 10^5 g/mol (●), 1.8 × 10^5 g/mol (○), 1.9 × 10^5 g/mol (□), 3.54 × 10^5 g/mol (⊡).

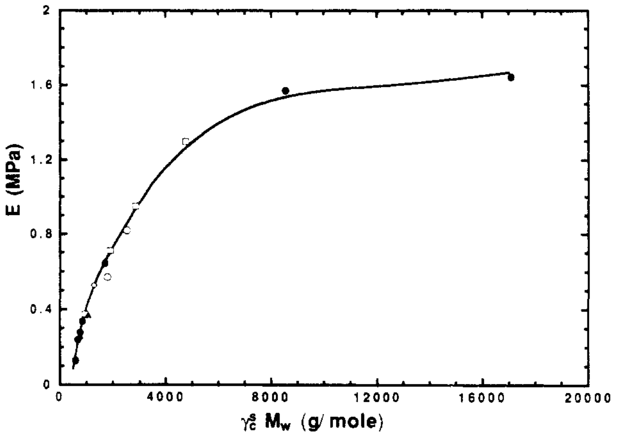

Figure 2. Variations of the modulus of elasticity E reported as a function of the variable $\gamma_c^s\bar{M}_w$: 0.77 × 10^5 g/mol (▲), 1.3 × 10^5 g/mol (◊), 1.7 × 10^5 g/mol (●), 1.8 × 10^5 g/mol (○), 1.9 × 10^5 g/mol (□).

lower chop when weights are placed in the scale. The stress corresponds to the ratio of the weight on the section of the network.

The strained networks studied from NMR were also cut into rectangular strips. The two extremities of each strip were firmly stuck with a cyanoacrylate instant adhesive on two pieces of glass. The upper one was connected to a Teflon rod, and the lower one was fixed. 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 between two chops and then firmly stuck between two rectangular pieces of glass. The angle θ_g between the pieces of glass and the axes of extension was measured. The axis of the rectangular pieces of glass was perpendicular to the tube axis. So the angle θ_g corresponnds to the incline angle $\theta_i = \pi/2 - \theta_g$ between the uniaxial extension and the plane of the steady magnetic field. The angle θ_R between the axis of extension and the magnetic field was then varied by rotating the sample tube in the plane of the field.

V. State of Maximum Swelling

The effect of swelling is induced by the osmotic pressure of a good solvent exerted on chain segments. The swelling process results usually from two mechanisms: the disengagement of chain segments from one another and then the swelling of each segment. However, the presence of trapped entanglements may hinder the process of full disengagement of segments; then, polymer chains overlap partially even in a state of maximum swelling. The state of maximum swelling is characterized by the swelling ratio Q_m. In any case, this quantity must be a function of the variable of gelation ϵ whatever the complex mechanism which gives rise to the swelling effect. According to most recent theoretical descriptions of gel properties, any network structure can be pictured as an ensemble of cells determined by correlation domains. The mean square size ξ^2 of every cell is a function of the variable ϵ even though this function has not been given any quantitative expression over the whole range of variations of ϵ.

Values of the inverse of the swelling ratio observed for different chain microstructures, several chain molecular weights and different concentrations of sulfur are reported as a function of the variable $\gamma_c^s\bar{M}_w$ in Figure 1. Although experimental results are slightly scattered around $\gamma_c^s\bar{M}_w$ = 3000 g/mol, a single curve can be drawn. The limiting value of $\gamma_c^s\bar{M}_w$ which corresponds to an infinite swelling ratio ($1/Q_m = 0$) can be estimated from Figure 1: $\gamma_c^s\bar{M}_w$ = 500 g/mol. This estimate is considered as a rough determination of the threshold of gelation of poly(butadiene) chains in the presence of sulfur. No specific property can be assigned to a given chain microstructure; it is not necessary to introduce a factor $w(1,2)$ which would depend upon the chain microstructure. Figure 1 clearly shows that the swelling ratio is unchanged when both $\bar{M}_w$ and γ_c^s are varied, provided the value of the product $\gamma_c^s\bar{M}_w$ is kept constant. For example, the value of Q_m^{-1} is equal to about 0.15 when the chain molecular weight is equal to 0.77 × 10^5, or 1.3 × 10^5, or 1.7 × 10^5 g/mol while corresponding values of γ_c^s are equal to 1.4, 1, or 1 g/g. A more detailed discussion about the swelling effect is given in section VIII, by considering NMR observations.

VI. Modulus of Elasticity

The modulus of elasticity E is also a function specific to gel systems which must depend upon the gelation variable ϵ. Variations of E are illustrated in Figure 2; the modulus of elasticity is unchanged when the value of the product $\gamma_c^s\bar{M}_w$ is kept constant, even though γ_c^s and $\bar{M}_w$ are varied. The quantity E is found to vary according to the following empirical law

$$E^2 \propto (\gamma_c^s\bar{M}_w - 500)$$

within the range $500 \leq \gamma_c^s\bar{M}_w \leq 8000$ g/mol; the threshold of gelation, determined from Figure 3, is found to be equal to about 500 g/mol. The modulus of elasticity is usually predicted to be proportional to ϵ^3, near the threshold of percolation. It must be noted that no prediction has been made until now about the dependence of E upon ϵ, over a broad range of variations of this parameter. The above empirical law may serve as a basis to describe the property of gel elasticity, at small deformations. Although Q_m and E are still unknown functions of the gelation variable ϵ, Q_m^{-1} can be represented as a function of E (Figure 4); the relationship which exists between Q_m^{-1} and E is not monotonous; a plateau is found to occur when E varies from 0.6 × 10^6 to 1.2 × 10^6 Pa. The plateau shows that the number and the size of meshes which form the polymeric gel do not vary whereas the structure contains more anchoring points.

VII. Gel Fraction

Finally, the gel fraction G is another function of the

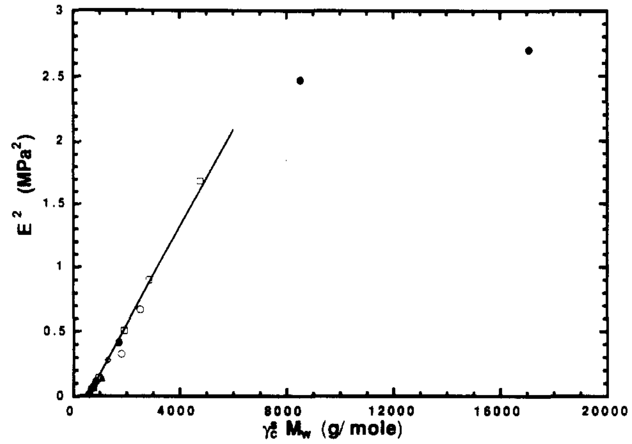

Figure 3. Partial linear variation of the square of the modulus of elasticity E as a function of the variable $\gamma_c^s\bar{M}_w$: 0.77 × 10⁵ g/mol (▲), 1.3 × 10⁵ g/mol (◇), 1.7 × 10⁵ g/mol (●), 1.8 × 10⁵ g/mol (○), 1.9 × 10⁵ g/mol (□).

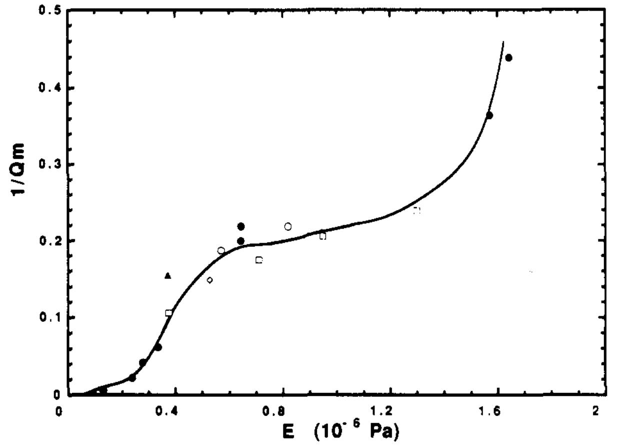

Figure 4. Variations of the inverse of the swelling ratio Q_m reported as a function of the modulus of elasticity E: 0.77 × 10⁵ g/mol (▲), 1.3 × 10⁵ g/mol (◇), 1.7 × 10⁵ g/mol (●), 1.8 × 10⁵ g/mol (○), 1.9 × 10⁵ g/mol (□).

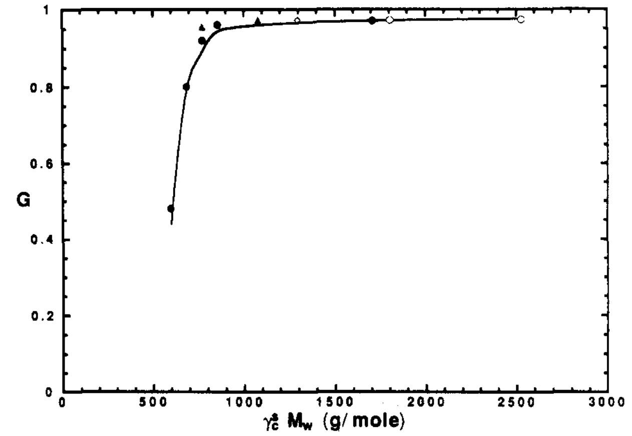

Figure 5. Variations of the gel fraction G as a function of the variable $\gamma_c^s\bar{M}_w$, for several molecular weights: 0.77 × 10⁵ g/mol (▲), 1.3 × 10⁵ g/mol (◇), 1.7 × 10⁵ g/mol (●), 1.8 × 10⁵ g/mol (○).

variable ϵ which can be used to characterize the state of gelation of cross-linked chains. Experimental values of G are reported as a function of the variable $\gamma_c^s\bar{M}_w$ in Figure 5. The threshold of gelation is found to be about equal to about 500 g/mol. The function $G(\epsilon)$ is equal to unity whenever all chains are attached to one another. This value of G is reached although the polymer system is not in a state of maximum gelation. Consequently, G is not suitable to the description of the whole process of gelation.

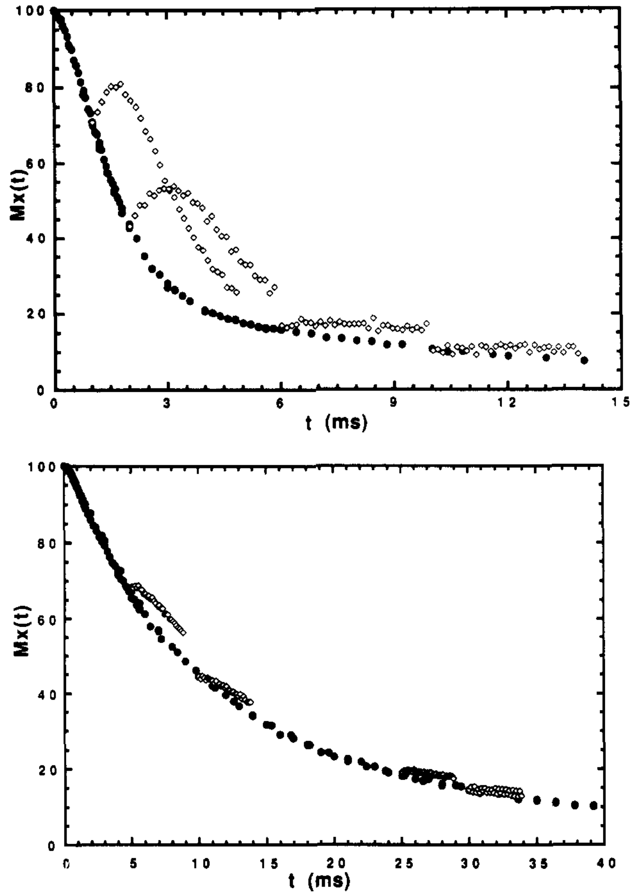

Figure 6. (A, top) Pseudosolid spin–echoes observed at 150 °C in cross-linked chains; illustration of the property of intersection (molecular weight: M_w = 0.77 × 10⁵ g/mol, sulfur concentration γ_c^s = 0.01 g/g). (B, bottom) Distorted pseudosolid spin–echoes observed at 150 °C in a melt (molecular weight: M_w = 0.77 × 10⁵ g/mol).

VIII. NMR Approach to the Swelling Effect

The NMR approach relies upon the observation of the residual interaction of spins which results from non isotropic rotations of monomeric units. The effect of anisotropy arises from the presence of cross-links which prevent chain segments from moving in all directions in space. In this section NMR measurements are performed on swollen vulcanized chains.

(1) Pure Residual Spin–Spin Interaction. Pseudosolid spin echoes can be formed when the transverse magnetic relaxation of protons is governed by a residual interaction of spins. Let $\mathscr{E}(t,\tau)$ the function which describes one echo which starts from the relaxation function $M_x(t)$ at $t = \tau$. In the absence of any dynamic contribution to the relaxation mechanism, spin–echo functions must obey well-defined properties; for example when one echo function starts at a time $t = \tau$, the initial tangent at $t = \tau$ must satisfy the relation

$$\left.\frac{\partial\mathscr{E}(t,\tau)}{\partial t}\right|_{t=\tau} = -\left.\frac{\mathrm{d}M_x(t)}{\mathrm{d}t}\right|_{t=\tau} \tag{25}$$

This property is illustrated in Figure 6A. Also, the intersection of two echo functions $\mathscr{E}(t,\tau_1)$ and $\mathscr{E}(t,\tau_2)$ must occur at $t = \tau_1 + \tau_2$, as it is shown in Figure 6A; echo functions were recorded at 150 °C at the end of the cross-linking reaction of polymer chains ($\bar{M}_w$ = 0.77 10⁵ g/mol and γ_c^s = 0.01 g/g). These echo functions are contrasted to those recorded at 150 °C before the beginning of the cross-linking reaction (Figure 6B); the mobility of polymer chains in the temporary network structure is high enough to give rise to a partial average of the residual interaction of spins. Spin–echo functions are completely distorted and amplitudes are small. In Figure 6B, the dynamics of chain segments is mixed up with the residual energy to induce the relaxation process of the proton transverse magnetization. In Figure 6A, the pure residual interaction of spins is sensitive only to the asymmetry of monomeric motions. All NMR observations described throughout this study correspond to a pure residual spin–spin interaction.

(2) State of Maximum Swelling. Vulcanized systems are observed in a state of maximum swelling to induce the disengagement of network chain segments from one another and to characterize them. According to eq 12, the NMR parameter χ_c is proportional to the ratio $(\zeta a/\langle r_{jl}^2\rangle)^2$. Variations of χ_c are represented as a function of the variable $\gamma_c^s\bar{M}_w$ in Figure 7A. Like Q_m, E, and G, the parameter χ_c is unchanged when the product of γ_c^s by $\bar{M}_w$ is kept constant, whatever the values of these two variables. The threshold of gelation, estimated from Figure 7A, is equal to about 500 g/mol. A deeper insight into the statistical structure of the polymeric system is obtained by introducing the following three hypotheses:

(i) It is supposed that the width ζ of the gel distribution function $\mathcal{G}(\langle r_{jl}\rangle/\zeta)$ and mean square fluctuations $\langle r_{jl}^2\rangle$ within the segment (j,l) are closely related to each other: $\zeta^2 = \langle r_{jl}^2\rangle$. A different hypothesis is made in section X about elongation effects. Consequently, ϕ_1 and ϕ_3 defined by eqs 9 and 10 are proportional to ζ and ζ^{-1}, respectively.

(ii) Let us consider a given network structure formed by chain segments. It is also supposed that network chain segments contain a number of monomeric units which is not constant throughout the polymeric gel. There exists a broad distribution of chain segment lengths between two consecutive cross-links formed along one chain. The normalized distribution function of the number n of monomeric units which separate two cross-links is represented by $\varphi(n)$; this is called a segmental distribution function. The average number $\bar{n}$ is defined by

$$\bar{n} = \sum_n n\varphi(n) \tag{26}$$

an estimate of $\bar{n}$ is given by eq 23:

$$\bar{n} \simeq \bar{x}_s M_s/\gamma_c^s M_b \tag{27}$$

The estimate of $\bar{n}$ is obtained by neglecting all correlations between cross-links during their formation process.

(iii) Notwithstanding the huge polydispersity of chain segments, the c^* theorem proposed by De Gennes is supposed to apply to the description of a system of swollen vulcanized chains. According to this theorem, the polymer concentration Q_m^{-1} in the state of maximum swelling must be proportional to the concentration corresponding to the situation where all swollen segments are disengaged from one another and are in contact with one another.[10] Then, the definition of the swelling ratio is

$$Q_m \propto \sum_n n^{3\alpha}\varphi(n)/\bar{n} \tag{28}$$

α is an exponent which characterizes the swelling state of a network chain segment in vulcanized systems. The segmental distribution function $\varphi(n)$ is characterized by several intrinsic moments:

$$\mu_\beta = \sum_n (n/N_c)^\beta \varphi(n/N_c) \tag{29}$$

$$\bar{n}^\beta = \mu_\beta N_c^{\ \beta} \tag{30}$$

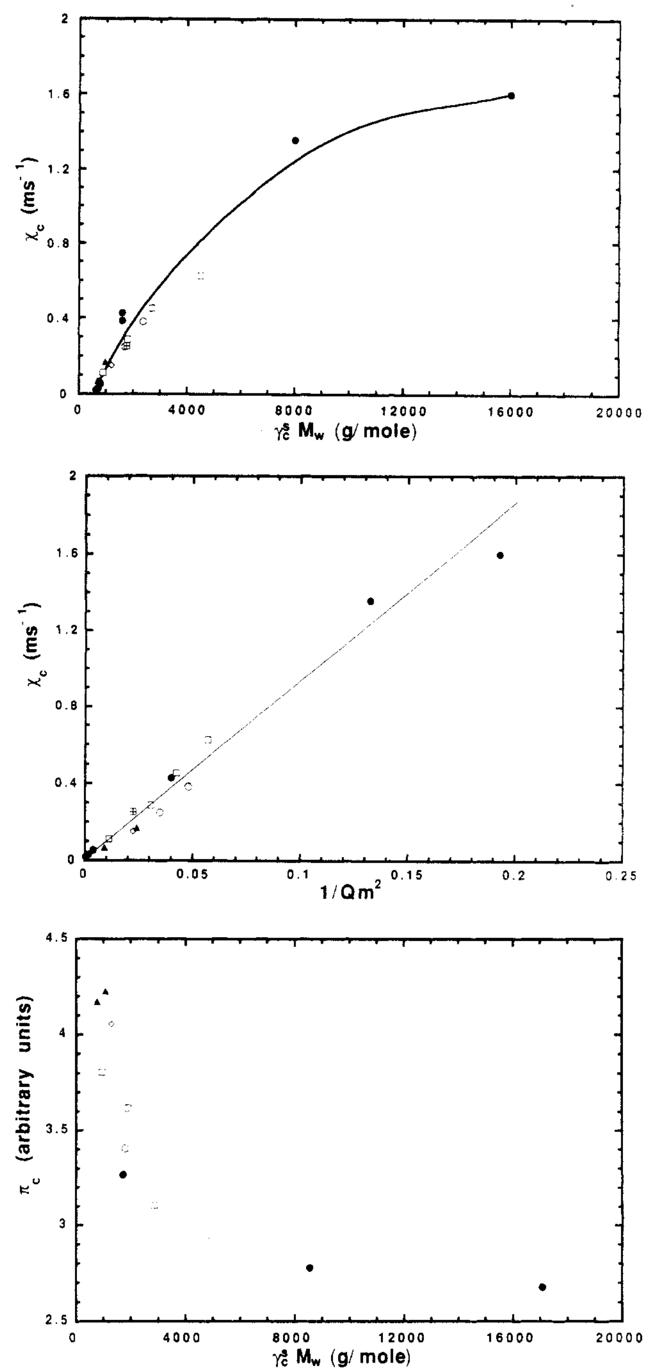

Figure 7. (A, top) Variations of the parameter χ_c, determined in the state of maximum swelling as a function of $\gamma_c^s M_w$: 0.77×10^5 g/mol (▲), 1.3×10^5 g/mol (◊), 1.7×10^5 g/mol (●), 1.8×10^5 g/mol (○), 1.9×10^5 g/mol (□), 3.54×10^5 g/mol (⊞). (B, middle) Linear variation of the parameter χ_c determined in the state of maximum swelling as a function of the square of the inverse of the swelling ratio Q_m: 0.77×10^5 g/mol (▲), 1.3×105 g/mol (◊), 1.7×10^5 g/mol (●), 1.8×10^5 g/mol (○), 1.9×10^5 g/mol (□), 3.54×10^5 g/mol (⊞). (C, bottom) Decrease of the parameter π_c determined in the state of maximum swelling as a function of the variable $\gamma_c^s M_w$: 0.77×10^5 g/mol (▲), 1.3×10^5 g/mol (◊), 1.7×10^5 g/mol (●), 1.8×10^5 g/mol (○), 1.9×10^5 g/mol (□).

N_c is the width of the normalized distribution function of lengths of chain segments between cross-links. Therefore

$$Q_m \propto \mu_{3\alpha}(N_c)^{3\alpha-1}/\mu_1 \tag{31}$$

$$\bar{n} = \mu_1 N_c \tag{32}$$

Similarly, integral parameters defined by eqs 9 and 10 must be averaged over the distribution of all network chain segments:

$$\bar{\phi}_1 \propto \sum_n \varphi(n)\,\zeta(n) \qquad (33)$$

$$\bar{\phi}_3 \propto \sum_n \varphi(n)/\zeta(n) \qquad (34)$$

In the presence of a good solvent, $\zeta(n)$ is proportional to n^α; finally, the χ_c parameter is defined as

$$\chi_c \propto \bar{n}^{-\alpha}/\bar{n}^{\alpha} \qquad (35)$$

or

$$\chi_c \propto (\mu_{-\alpha}/\mu_\alpha) N_c^{-2\alpha} \qquad (36)$$

The parameter χ_c is represented as a function of Q_m^{-2} in Figure 7B; it is clearly seen in this figure that the quantity χ_c can be considered as a linear function of Q_m^{-2} over the range $580 \leq \gamma_c^s \bar{M}_w \leq 8000$ g/mol; this result is described empirically according to the relation

$$(N_c^{3\alpha-1})^{-2} \propto n_c^{-\alpha-1}/N_c^{\alpha-1} \qquad (37)$$

This empirical relation leads to

$$N_c^{6\alpha-2} = N_c^{2\alpha}$$

$$\alpha = {}^1/_2$$

if it is assumed that the distribution function is simply expressed as $\varphi(n/N_c)$ as is usual; the parameter N_c measures the width of the distribution. The value $\alpha = {}^1/_2$ may indicate that the system of swollen vulcanized chains behaves like an ensemble of branched polymers. According to eq 36, the increase of χ_c observed as a function of $\gamma_c^s \bar{M}_w$ reflects the reduction of the mesh size of the network structure.

The quantity $\pi_c = \phi_3\phi_1$ is proportional to the product $m_3 m_1$ of the moments of the gel distribution function $\mathcal{G}(\langle r_{jl}\rangle/\zeta)$; π_c can be considered as a measure of the width of the gel function. Variations of π_c were observed as a function of the product $\gamma_c^s \bar{M}_w$; vulcanized chains were in a state of maximum swelling. It is seen from Figure 7C that the NMR parameter π_c is reduced when the variable of gelation is increased. It must be noted that intrinsic m_1 and m_3 moments of the gel function are defined from the reduced variable $\vec{\rho} = \vec{r}_{jl}/\zeta$; consequently, the parameter π_c concerns only the mathematical structure of the gel function and not its physical width ξ. Similarly, the distribution function of lengths of chain segments which separate two consecutive cross-links is involved in the parameter π_c from the product of intrinsic moments: $\mu_{-\alpha}$ and μ_α. The reduction of π_c observed as a function of $\gamma_c^s \bar{M}_w$ reflects also a reduction of intrinsic widths of the gel function and the segmental distribution function. The network structure becomes less and less loose by increasing the value of the product $\gamma_c^s \bar{M}_w$.

Even though the products of intrinsic moments m_3 and m_1, on the one hand, and $\mu_{-\alpha}$ and μ_α on the other hand, are not found to be constant when the product $\gamma_c^s \bar{M}_w$ is varied, the ratio m_3/m_1 or $\mu_{-\alpha}/\mu_\alpha$ are not expected to vary strongly. Consequently, it is considered that χ_c yields a reasonable estimate of the variation of N_c as a function of $\gamma_c^s \bar{M}_w$.

(3) States of Intermediate Swelling. States of intermediate swelling are obtained by adding small amounts of solvent to the system of vulcanized chains. Several samples corresponding to a chain molecular weight $\bar{M}_w = 1.7 \times 10^5$ g/mol and a sulfur concentration $\gamma_c^s = 0.004$ g/g were prepared with different amounts of solvent to obtain several states of progressive swelling characterized by a swelling ratio Q. Sample tubes were sealed. A strong decrease of χ_c is observed as a function of Q (Figure 8A). The value of χ_c falls from 0.6 to 0.04 over the range $1 \leq Q \leq 5$; then, the value of χ_c is nearly constant until the swelling ratio reaches the maximum value Q_m. A similar behavior was observed by changing the sulfur concentration ($\gamma_c^s = 0.005$ or 0.01 g/g). Experimental results are also reported in Figure 8A. The strong decrease of the NMR parameter χ_c is usually ascribed to the disengagement process of network chain segments. For a given system, the segmental distribution function is considered as invariant during the progressive swelling, whereas the width ζ of the gel function must be increased. There is less and less screening of excluded volume effects. Consequently, the parameter χ_c is expected to be a decreasing function when small amounts of solvent are progressively added to polymeric gels. Variations of the parameter π_c reported in Figure 8B, for the same vulcanized chains, exhibit an increase which reflects an intrinsic broadening of gel functions induced by the presence of solvent.

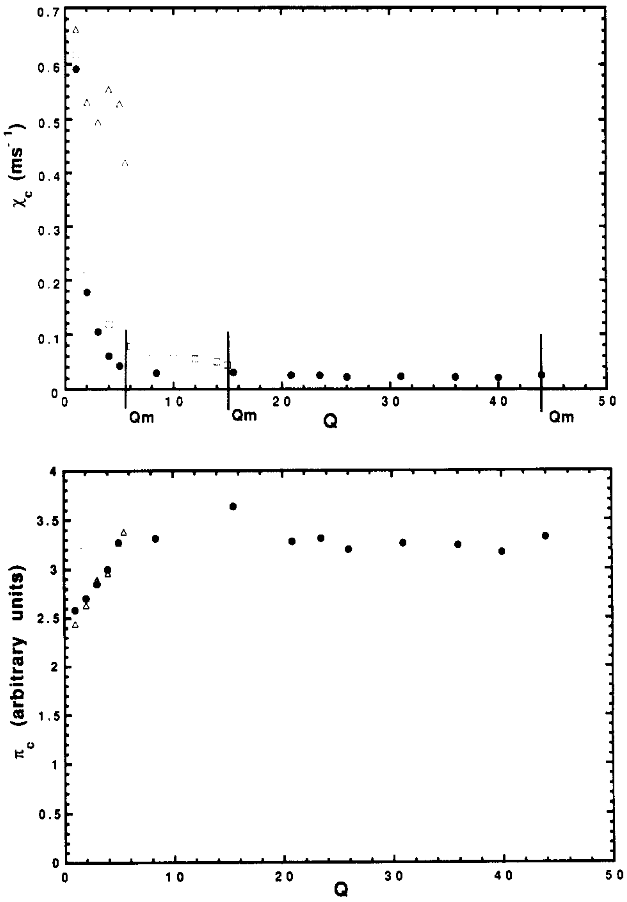

Figure 8. (A, top) Decrease of the parameter χ_c determined in states of intermediate swelling as a function of the swelling ratio Q. The molecular weight is 1.7×10^5 g/mol. $\gamma_c^s = 0.01$ g/g (△), 0.005 g/g (□), 0.004 g/g (●). (B, bottom) Variation of the parameter π_c determined in states of intermediate swelling as a function of the swelling ratio Q. The molecular weight is 1.7×10^5 g/mol. $\gamma_c^s = 0.01$ g/g (△), 0.004 g/g (●).

As a conclusion of this section, it is clearly shown that the transverse relaxation of protons attached to vulcanized chains is very sensitive to the deformation of network chain segments, whatever the state of swelling induced by the addition of solvent.

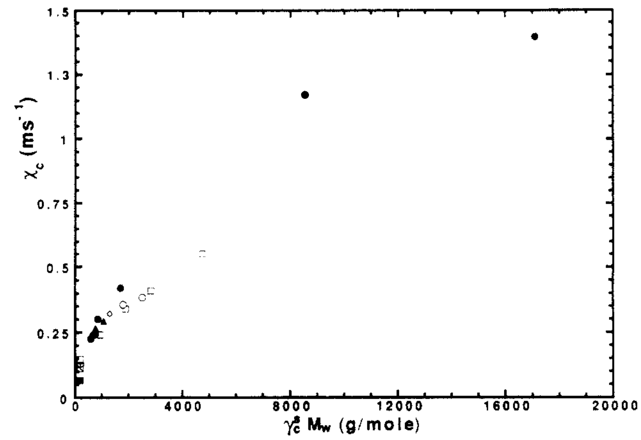

Figure 9. Variations of the parameter χ_c determined in bulk at 150 °C as a function of the variable $\gamma_c^s M_w$: 0.77 × 10^5 g/mol (▲), 1.3 × 10^5 g/mol (◇), 1.7 × 10^5 g/mol (●), 1.8 × 10^5 g/mol (○), 1.9 × 10^5 g/mol (□). Values of χ_c determined in melts ($\gamma_c^s = 0$) at 150 °C are also reported: 0.77 × 10^5 g/mol (■), 1.3 × 10^5 g/mol (▧), 1.7 × 10^5 and 1.8 × 10^5 g/mol (⊕), and 1.9 × 10^5 g/mole (⊡).

IX. NMR in the Reaction Bath

The NMR parameter χ_c was also measured in the reaction bath, i.e., without extracting any free chain after the cross-linking reaction; χ_c is reported as a function of the variable $\gamma_c^s \bar{M}_w$, in Figure 9.

This figure shows that the state of gelation ($\gamma_c^s \bar{M}_w \geq 500$ g/g) and the state of branching ($\gamma_c^s \bar{M}_w > 500$ g/g) are clearly detected from NMR measurements performet at 150 °C.

X. NMR Approach to Elongation

In this section, the segmental NMR probe defined by eqs 1 and 4 is used to characterize deformations of network structures, induced by stretching vulcanized chains. The interpretation of NMR properties necessitates the statement of precisely two assumptions. The first one concerns the gel distribution function of mean end-to-end vectors of network chain segments throughout the polymeric system. The second assumption deals with the statistical nature of fluctuations undergone by chain segments which determine a given network structure.

(1) Gel Distribution Function. According to the description proposed by Flory to interpret the property of elasticity of vulcanized chains, it is considered that the deformation of mean end-to-end vectors of chain segments is in affinity with the macroscopic deformation applied to the polymeric sample. For a uniaxial elongation characterized by a stretching ratio $\lambda > 1$, any end-to-end vector $\langle \vec{r}_{jl} \rangle$ is supposed to be transformed into the mean end-to-end vector $\langle \vec{u}_{jl} \rangle$, defined by

$$\langle \vec{u}_{jl} \rangle = \mathbf{C}(\lambda) \langle \vec{r}_{jl} \rangle \tag{38}$$

with the transformation matrix

$$\mathbf{C}(\lambda) = \begin{pmatrix} \lambda & & \\ & \lambda^{-1/2} & \\ & & \lambda \end{pmatrix} \tag{39}$$

the direction of stretching is parallel to the z axis; the matrix of transformation applies to x, y, and z components, respectively. The sample volume is supposed to be invariant upon stretching, provided the amplitude of deformation is small. Also, in addition to the law of deformation, it is assumed that fluctuations of network chain segments in a stretched polymeric gel still obey Gaussian statistics. Then, the gel distribution function is expressed as

$$\mathbf{G}(\langle \vec{u}_{jl} \rangle, \lambda) = (2\pi\zeta^2/3)^{-3/2} \exp(-3\langle \vec{u}_{jl} \rangle \mathbf{C}^{-2} \langle \vec{u}_{jl} \rangle / 2\zeta^2) \tag{40}$$

ζ is the width which characterizes the distribution function in the absence of any deformation.

(2) Proton Transverse Relaxation. For the sake of simplicity, the effect of stretching upon NMR properties is illustrated from the relaxation function $M_x^{\mathrm{p}}(t)$ associated with one proton pair attached to a network chain segment; then, eq 4 is expressed as

$$m_{jl}^x(t) = \cos\,(i\delta t \Lambda a \langle \vec{u}_{jl} \rangle \mathbf{D} a \langle \vec{u}_{jl} \rangle / \zeta^4) \tag{41}$$

with

$$\mathbf{D} = \begin{pmatrix} -1 & & \\ & -1 & \\ & & 2 \end{pmatrix} \tag{42}$$

δ is the dipole–dipole interaction strength within one pair.

The average of $m_{jl}^x(t)$ must be carried out by using eq 40; it is supposed that the polymeric gel can rotate around a vertical axis, perpendicular to the steady magnetic field direction:

$$M_x^{\mathrm{p}}(t,\lambda,\theta) = \mathrm{Re}\{1 + it^*(\lambda^2 - 1/\lambda)(3\cos^2\theta - 1) + t^{*2}[\lambda(3\cos^2\theta + 1) + (3\sin^2\theta - 1)/\lambda^2] - 2it^{*3}\}^{-1/2} \tag{43}$$

with $t^* = \delta t$ and θ is the angle which the direction of stretching makes with the magnetic field direction.

Equation 43 calls for the following comments:

(i) The most striking result concerns the independence of the cubic term upon the stretching ratio λ. This property is illustrated experimentally in section X.3. Relaxation curves must tend to be coincident to one another when they are observed at long times. They must draw a spinkle-shaped pattern.

(ii) The effect of stretching gives rise to a linear term with a factor equal to $(\lambda^2 - 1/\lambda)(3\cos^2\theta - 1)$. This term induces a quasi-linear behavior of the relaxation function near the time origin. The slope of the initial tangent to the relaxation function is shown to be proportional to $\lambda^2 - 1/\lambda$ in section X.3.

(3) Experimental Relaxation Functions. Typical transverse relaxation functions of protons attached to stretched network structures are reported in Figure 10A. They were recorded at room temperature; numerical values given to the stretching ratio were λ = 1, 1.8, 2.6, 3, and 3.4. The chain molecular weight was $\bar{M}_w = 1.6 \times 10^5$ g/mol while the sulfur concentration was $\gamma_c^s = 0.005$ g/g. The slope q_m of initial tangents is represented as a function of the stretching function $\lambda^2 - 1/\lambda$ in Figure 10.B.

The spinkle-shaped pattern of relaxation curves is illustrated in Figure 11; relaxation curves were recorded at room temperature. The sulfur concentration is $\gamma_c^s = 0.05$ g/g, while the chain molecular weight is $\bar{M}_w = 1.9 \times 10^5$ g/mol. More generally, the $\lambda^2 - 1/\lambda$ dependence of relaxation functions was also observed from the χ_c NMR parameter. This property is illustrated in Figure 12 ($\bar{M}_w = 1.7 \times 10^5$ g/mol and $\gamma_c^s = 0.005$ g/g):

$$\chi_c = s_m(\lambda^2 - 1/\lambda) \tag{44}$$

Then, the slope s_m is shown to be a function of the gelation variable, in Figure 13.

(4) Angular Effects. Finally, the crucial role played by the factor of the linear term in eq 43 was detected by rotating a stretched network structure around a vertical

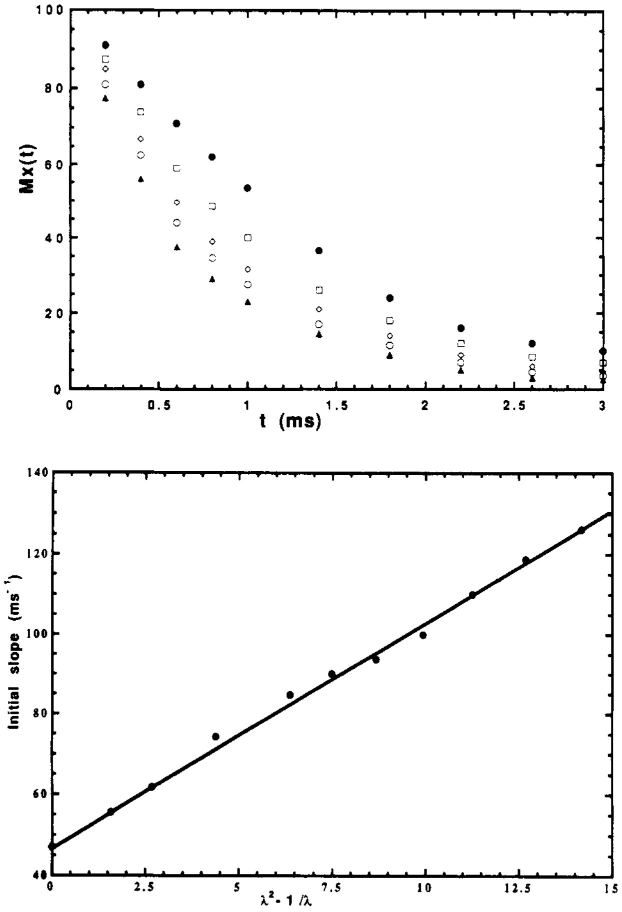

Figure 10. (A, top) Proton transverse relaxation functions recorded at room temperature. Chain molecular weight 1.6 × 10^5 g/mol; sulfur concentration 0.005 g/g. Numerical values of the stretching ratio λ: 1 (●), 1.8 (□), 2.6 (◇), 3 (○), and 3.4 (▲). (B, bottom) Linear variation of the initial slope of the relaxation functions measured in stretched state as a function of the variable stretching $\lambda^2 - 1/\lambda$. M_w = 1.7 × 10^5 g/mol and γ_c^s = 0.005 g/g.

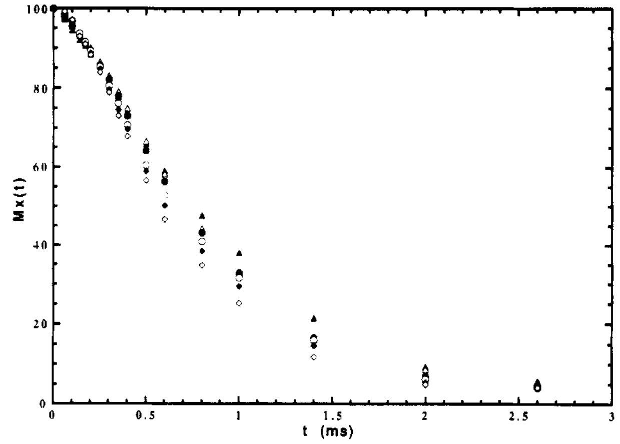

Figure 11. Proton transverse relaxation functions recorded at room temperature. Chain molecular weight 1.9 × 10^5 g/mol; sulfur concentration 0.005 g/g. Numerical values of the stretching ratio λ: 1.2 (▲), 1.6 (△), 1.8 (●), 2.2 (○), 2.3 (◆), and 2.6 (◇).

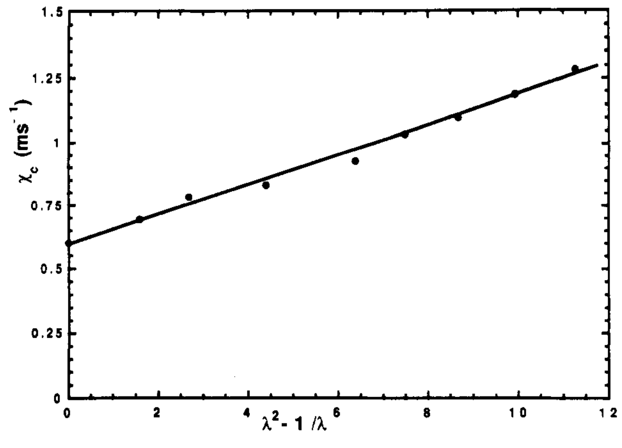

Figure 12. Linear variation of the parameter χ_c determined in stretched state as a function of the variable stretching $\lambda^2 - 1/\lambda$. M_w = 1.7 × 10^5 g/mol and γ_c^s = 0.005 g/g.

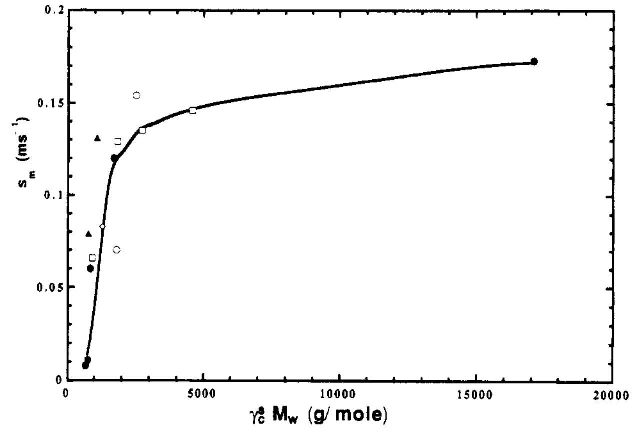

Figure 13. Representation of the slope s_m as a function of the variable $\gamma_c^s M_w$: 0.77 × 10^5 g/mol (▲), 1.3 × 10^5 g/mol (◇), 1.7 × 10^5 g/mole (●), 1.8 × 10^5 g/mole (○), and 1.9 × 10^5 g/mol (□).

axis; the angle θ_i between the direction of stretching and the horizontal plane was given several values: 0°, 14°, 34°, 42°, 53°, and 61° ($\bar{M}_w = 1.7 \times 10^5$ g/mol and $\gamma_c^s = 0.005$ g/g). The stretching ratio was equal to 3. Experimental variations of χ_c, corresponding to different values of θ_i, are reported as a function of θ in Figure 14A,B. These typical angular variations of the NMR parameter χ_c can be compared with theoretical curves drawn by using relations between spherical harmonics to replace $3 \cos^2 \theta - 1$ with the expression

$$(3 \cos^2 \theta - 1)(3 \sin^2 \theta_i - 1) - 3 \sin^2 \theta \cos^2 \theta_i$$

Theoretical curves are shown in Figure 14C; they are in accordance with experimental ones. The most striking result concerns the value of the NMR parameter χ_c observed when the direction of stretching makes a magic angle with the magnetic field. This parameter is nearly equal to the value observed in the absence of any stretching. The spin–spin relaxation is enhanced by the sample elongation. This effect originates from the presence of the linear term in eq 43. Angular effects observed for θ_i = 0 are in accordance with measurements performed on deuterated cross-linked chains.[11]

(5) NMR–Elasticity Interrelationship. Fluctuations of chain segments are responsible for the property of elasticity observed at small deformations. These fluctuations are also responsible for the spin–spin relaxation of protons. Both the NMR parameter χ_c and the modulus of elasticity E depend upon the gelation variable $\epsilon \simeq \gamma_c^s \bar{M}_w - 500$. Consequently, the parameter χ_c must be a function of E. The relationship which exists between χ_c and E is illustrated in Figure 15. To get a better sensitivity, χ_c was determined at 150 °C; several chain molecular weights were considered while the sulfur concentration was kept constant. The parameter χ_c exhibits a linear dependence upon E over the range $0.1 \leq E \leq 1.3$ MPa. Assuming that the modulus of elasticity is roughly

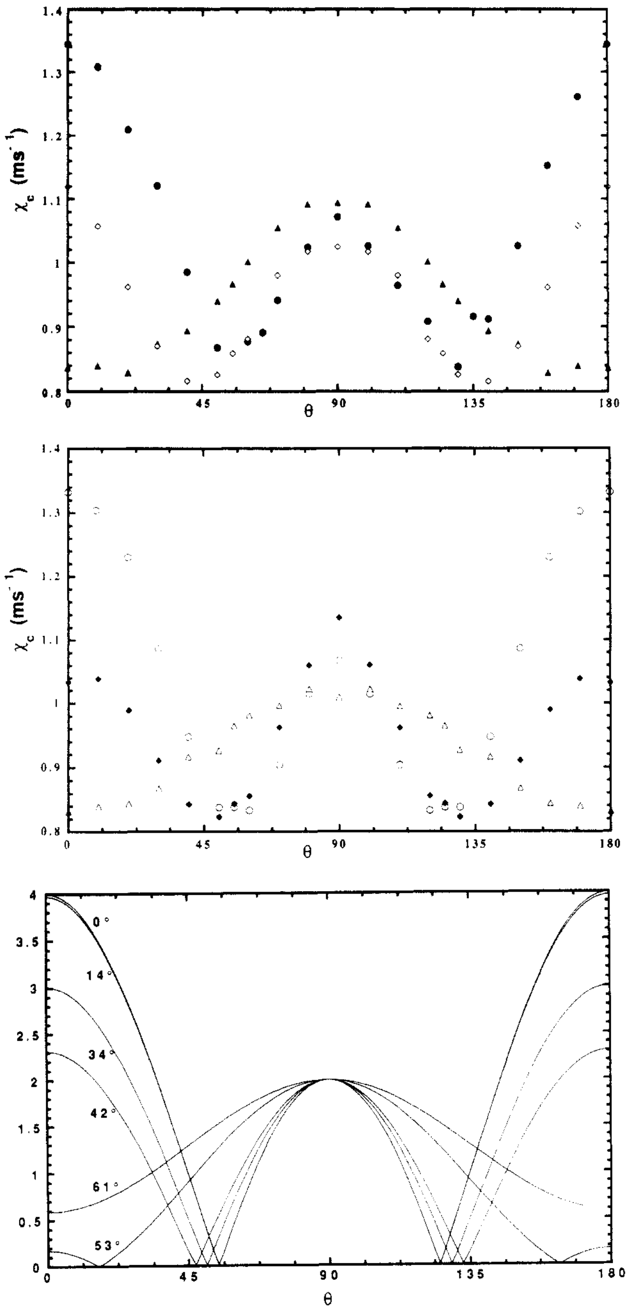

Figure 14. (A, top) Effect of sample rotation with respect to the steady magnetic field for several inclination angles θ_i between the axis of extension and the plane of the field. $\bar{M}_w$ = 1.7 × 10^5 g/mol and γ_c^s = 0.005 g/g. The parameter χ_c was determined in the stretched state λ = 3. θ = 0° (●), 34° (◊), 53° (▲). (B, middle) Effect of sample rotation for several inclination angles θ_i. θ = 14° (○), 42° (♦), 61° (△). (C, bottom) Simulation of the angular variable of the spin–spin interaction energy as a function of the rotation angle θ_R for several inclination angles θ_i (0°, 14°, 34°, 42°, 53°, and 61°).

expressed as

$$E \propto \nu_e k T \tilde{\zeta}^2/\langle \Delta\zeta^2\rangle \qquad (45)$$

ν_e is the number of active segments per unit volume; ν_e^{-1} is proportional to the mean molar weight which separates two consecutive coupling junctions along one chain. According to eq 27 $\nu_e^{-1} \propto \bar{n}Mb$, and according to eq 12 the NMR parameter χ_c is also proportional to $(\bar{n})^{-1}$.

XI. Conclusion

The main problem encountered in describing physical properties of vulcanized chains concerns the search for a relevant variable which permits one to define the state of gelation of vulcanized chains not only near the threshold of percolation but also in the case of polymeric systems formed from long chains and/or high concentrations of cross-links.

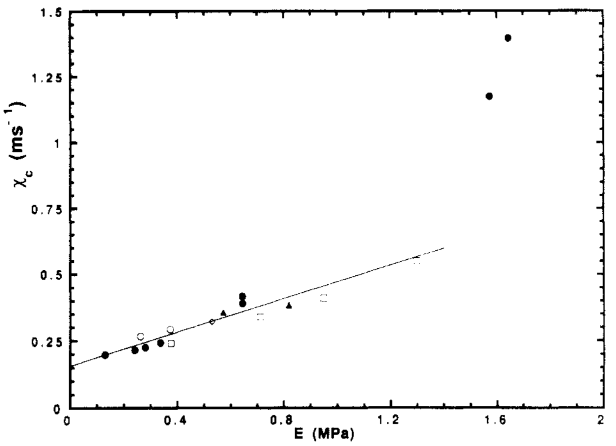

Figure 15. Partial linear dependance of the NMR parameter χ_c determined in bulk at 150 °C upon the modulus of elasticity E measured at room temperature: 0.77 × 10^5 g/mol (▲), 1.3 × 10^5 g/mol (◊), 1.7 × 10^5 g/mol (●), 1.8 × 10^5 g/mol (○), 1.9 × 10^5 g/mol (□).

The main feature about investigations reported in this work concerns the determination of one variable defined by the product of the chain molecular weight and the sulfur concentration. Usual physical quantities such as the modulus of elasticity, the gel fraction and the swelling ratio, in the state of maximum swelling, are functions of this variable. Once a state of gelation is defined, it is necessary to characterize the corresponding statistical structure of the network. Such a characterization results from NMR measurements performed on swollen or stretched polymeric systems. The dependence of the transverse magnetic relaxation of protons attached to polymer chains upon the variable of state gelation shows that the relevant space scale of NMR observations is semilocal. The NMR probe is a chain segment defined by two consecutive coupling junctions along one chain. Proton relaxation properties observed on stretched networks are very sensitive to orientational effects with respect to the magnetic field direction, in accordance with observations made from deuteriated systems.[11] Effects of elongation on NMR are interpreted by assuming on the one hand that fluctuations are still Gaussian and on the other hand that deformations of chain segments are in affinity with the macroscopic deformation of the network structure. The state of maximum swelling is described as a ensemble of polydisperse branched systems in a c^* concentration.

This work is considered as a necessary step which permits us to disclose experimentally the dependence of characteristic gel quantities upon the variable of gelation. The purpose of the next step will be to give a theoretical basis to experimental curves. The variable defined in this work does not apply to the case of high concentrations of cross-links where the chain molecular weight has no longer any effect.

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