Evidence for a Linear NMR−Elasticity Interrelationship in Polymeric Gels

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ABSTRACT: A linear relationship between the elastic modulus of polymer networks and the transverse relaxation rate of protons attached to the unconstrained polymer is established by considering poly(dimethylsiloxane) (PDMS) chains, cross-linked at random according to two different ways. Networks of type A were composed of long poly(vinylmethyl−dimethylsiloxane) copolymers. With randomly distributed vinyl functions (molar fraction of vinyl functions: 2×10^{-3} per monomeric unit), links were formed between vinyl and methyl groups, at 150 °C; then, networks were quenched at 0 °C, during the gelation process. Networks of type B were composed of vinyl-terminated PDMS chains and poly(methylhydrosiloxane−dimethylsiloxane) copolymers, with additional hydride-terminated PDMS chains (molar fraction of hydride functions: 10^{-2} per monomeric unit). For these systems, measurements of the storage modulus or of NMR were performed, in situ, during the gelation. This study extends the NMR−swelling interrelationship to the property of elasticity.

I. Introduction

In a permanent polymeric network observed above the glass transition temperature, cross-link junctions prevent the strands from completely reorientating; the freedom of internal bond rotations in network chain segments is impeded by the hindrance associated with cross-links. This results in a rotational anisotropy of skeletal bond vectors which in turn leads to a nonzero average of nuclear spin interactions expressed as tensorial functions of space variables of nuclei. The formation of a network gives rise to a residual energy of dipole−dipole interactions between protons attached to segments which depend on the architecture of the polymeric gel.[1] Similarly, the deuterium magnetic resonance is sensitive to anisotropic random motions through the residual energy of quadrupolar interaction, which is a tensorial function of space variables analogous to the dipole−dipole interaction.[2] Induced orientation in mechanically deformed elastomers has received a lot of attention in recent years mostly due to the molecular level insight provided by deuterium NMR investigations.[3−5] The splitting of the resonance doublet has been correlated to network characteristics obtained from swelling measurements or from the elasticity. NMR experiments have been performed essentially on well-characterized end-linked elastomers observing the orientational anisotropy of labeled network chain segments or the induced alignment of labeled probe chains in uniaxially-strained unlabeled host networks. The induced alignment has been recently ascribed to the screening of the short-range excluded volume interaction, which is repulsive; the screening is due to an effective anisotropic attractive potential induced by density fluctuations of permanently deformed chains.[6,7]

In permanent gels, the proton transverse relaxation is governed by residual magnetic interactions which induce a solid-like behavior; it is thus sensitive in a specific way to the presence of cross-links. Characteristic spin-echoes can be performed to give experimental evidence for the nonzero average of dipole−dipole interactions. It has been shown that proton relaxation curves can be given a standard analysis which permits one to overcome difficulties inherent in the description of nonexponential relaxation functions usually observed on polymeric systems.[8] This NMR approach has been quantitatively illustrated from gels synthesized from end-linked calibrated poly(propylene oxide) precursors; the chain molecular weight was varied from 425 to 4000.[9] This analysis will be briefly reviewed in section III; it is based on an integral treatment of relaxation curves, and it gives access to the first and to the third moments of the probability distribution function of end-to-end vectors of network chain segments which will hereafter be called $G(r/\sigma)$. The mean distance between two consecutive nodes designated by r and σ is a simple function of the number of bonds, N, which determines the mean segmental spacing between consecutive nodes. The distribution function is usually Gaussian in dry gels while it obeys the excluded volume statistics in swollen end-linked chain systems. More precisely, a so-called NMR structural parameter, χ_c, can be numerically calculated; it has been shown that χ_c is proportional to $\sigma^{-2}\alpha N^{-2\nu}$; the exponent ν is equal to $^1/_2$ (dry gels). The exponent obtained for swollen end-linked chain systems is $^3/_5$; furthermore, there is a direct relationship between χ_c and the volume of these swollen gels which proves that NMR is sensitive to the swelling of elementary segments which in turn are involved in the macroscopic swelling effect. The NMR structural parameter is analogous to a relaxation rate; it provides a standard measure of the segmental spacing between two nodes.[10]

The NMR approach is extended here to systems formed by long polymer chains cross-linked at random; the number of bridges per chain is small (≤ 5). More precisely, this work aims at giving evidence for a simple interrelationship between the modulus of elasticity, E, and the NMR parameter, χ_c, determined from unconstrained polymeric gels. It will be shown that, in contrast to ^{2}H-resonance investigations, the ^{1}H-relaxation observation of the property of elasticity does not require any sample elongation. For low cross-link densities, the mean segmental spacing between two consecutive bridges has a pure statistical definition and is not a suitable parameter for describing the network structures. A percolation framework is available that provides a semiquantitative description of the effect of

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gelation. According to the mean field percolation theory, the relevant gelation parameter is the mean number of cross-links per chain; network structures are composed of so-called active segments that give rise to the properties of elasticity and of swelling. The mean size of these segments is predicted to be a function of the deviation from the gelation threshold.

The purpose of this work was to compare network properties involved in the effect of elasticity of long cross-linked chains with those detected from NMR. It has been already shown that the NMR structural parameter, χ_c, is a linear function of the modulus of elasticity, E, measured on unconstrained vulcanized polybutadiene by varying both the sulfur concentration and the chain molecular weight.[11] This experimental evidence must be strengthened further by studies of other systems of randomly cross-linked chains. Two series of networks, hereafter called A and B, were studied. Networks in series A were produced by cross-linking long poly(vinylmethyl−dimethyl)siloxane copolymers; the molar fraction of randomly distributed vinyl functions was equal to 2×10^{-3} per monomeric unit. Bridges consisted of three methylene groups, connecting two skeletal silicon atoms. Networks in series B were produced by end-linking vinyl-terminated poly(dimethylsiloxane) (PDMS) chains with polyfunctional poly(methylhydrosiloxane−dimethyl)siloxane copolymers; hydride-terminated PDMS chains were added to reaction mixtures in order to vary the length of bridges resulting from the vinyl−hydride reaction. In these systems, the molar fraction of hydride functions was about equal to 10^{-2} per monomeric unit.

Experimental aspects about this work are presented in the next section. The NMR background is briefly reviewed in section III. Experimental results are shown in sections IV and V; they are analyzed and discussed in section VI.

II. Experimental Section

Sample Preparation. For networks in series A, the reaction mixture consists of copolymers in which vinylmethyl monomeric units ($-OSi(CH_3)(CH{=}CH_2)$) are randomly incorporated into PDMS chains. The weight average molecular weight, M_w, was 3.9 10^5 and the polydispersity index was equal to 2.7. The vinyl group weight fraction was equal to 0.78×10^{-3} g/g; it was kept constant in this study. The copolymer was bought from Rhône-Poulenc (Lyon, France). The cross-linking was initiated by a peroxide (2,5-dimethyl-2,5-bis(*tert*-butyldioxy)hexane) from Aldrich. The peroxide weight ratio, C_p, was varied from 0.225 to 0.45 g/g. The polymer mixture was heated at 150 °C under pressure (100 bars). The peroxide yields two free radicals when heated; each of them can react with one vinyl group, which becomes a free radical and reacts with a neighboring methyl group.[12] A propylene link is thus created between two chain segments. Elastomers were molded to obtain thin films (diameter, 19 mm; thickness, 1 mm). The kinetics of formation of cross-links was observed by quenching polymer films in ice in order to stop the chemical reaction and to keep the polymer network in the state reached at a given time t; this observation time was varied from 0 to 40 min. The thickness was supposed to be small enough to ensure a short kinetics of quenching. The heat diffusion in the cross-linked systems was observed from NMR; the thermal equilibrium at 0 °C was reached within less than 1 min when samples were cooled from 150 °C.

For networks in series B, the weight average molecular weight of vinyl-terminated PDMS precursors was $M_w = 1.7 \times 10^4$; for the poly(methylhydro−dimethylsiloxane) copolymer, the polydispersity index was 1.5 and M_w was equal to 2.2×10^4 ($M_n = 8.7 \times 10^3$) while for hydride-terminated PDMS chains, M_w was equal to 10^3. The weight fraction of hydride functions in the copolymer was 1700 ppm. The ratio of the number of hydride functions to the number of vinyl functions was called $\tau_{H/Vi}$ while the ratio of the number of hydride functions in polyfunctional units to the total number of hydride functions was called σ_H; values of $\tau_{H/Vi}$ were equal to 1, 1.3, and 1.6 and values of σ_H were equal to 1, 0.72, and 0.45. Vinyl-terminated chains were end-linked via platinum-catalyzed hydrosilation; prior to the gelation process, copolymers were divided into two parts: one with only vinyl functions and the other one with hydride functions and a Karstedt Pt complex added to achieve a concentration of 1 part platinum per 10^4 parts vinyl. Networks were obtained by mixing the two parts at room temperature. Polymers were bought from Rhône-Poulenc (France).

Gel Fraction Measurements. The gel fraction G was defined as the ratio of the weight of polymer, M_G, obtained after extracting free chains, to the initial weight of polymer, M_p^i. Methylcyclohexane, which is a good solvent for poly(dimethylsiloxane), was used to extract free chains. The solvent was renewed after 24 h in order to achieve the sol phase extraction.

Elastic Modulus. The modulus of elasticity was measured using a TA-XT2 Texture analyzer (Rhéo Society, France); measurements were performed on nonextracted gels, at room temperature. Elastomers in series B were molded to obtained $120 \times 120 \times 3$ mm films; the thickness was measured within an accuracy equal to ±0.01 mm. The rate of deformation was 0.1 mm/s.

NMR Measurements. NMR experiments were performed using a Bruker pulse spectrometer CXP, operating at 45 MHz. All relaxation functions were determined by using Carr−Purcell spin−echo sequences.[13] It was shown that relaxation functions measured from such sequences were equivalent to those obtained from the usual experimental procedure, proposed by Hahn. The proton transverse relaxation functions were recorded at room temperature.

III. NMR Background

The direct dependence of NMR on the mean segmental spacing between cross-links, in calibrated gels, calls for a short description of the physical basis which underlies the definition of the NMR structural parameter, χ_c. The method has been already described elsewhere; it is reviewed in this section.[8] It is essentially based on the effect of reduction of dipole−dipole interactions induced by restricted fluctuations which occur along one segment. The nonzero average of magnetic interactions results from the existence of anchoring points which prevent isotropic configurational fluctuations of chain segments.

Starting from one chain segment, defined by two nodes and the number N of skeletal bonds that it contains, the strength of averaged magnetic interactions, along this segment, is a function of both the mean distance between the two nodes and the number N; the mean end-to-end vector will hereafter will be called $\mathbf{r}$. The magnetization associated with one segment is written as an expansion, in the basis of eigenfunctions ($|n\rangle$) of the Zeeman energy of spins

$$m_x(t,\mathbf{r},N) = \sum_{nn'} P_{nn'} \cos[0.3\Lambda\omega_{nn'}t\,(3\cos^2\theta_r - 1)r^2b^2/\{\sigma^2(N)\}^2] \quad (1)$$

$\omega_{nn'}$ is a broadening frequency induced by the dipole−dipole interaction and $P_{nn'}$ is a quantum weighting factor. The mean square end-to-end distance between segment ends is $\sigma(N)^2$, and Λ accounts for the chain stiffness. The mean skeletal bond length is b. Equation 1 applies to weakly stretched segments; the statistical framework of description appears through the expression of $\sigma(N)^2$. It is seen from eq 1 that the ratio $\{\rho b/\sigma(N)^2\}^2$ plays the role of a time scaling factor.

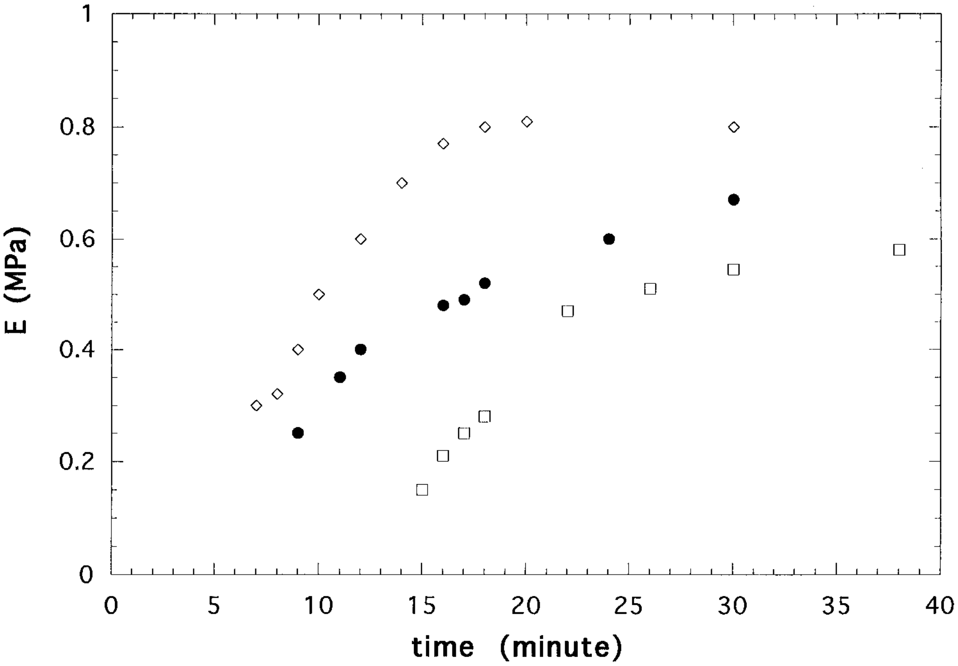

Figure 1. Elastic modulus as a function of the time allowed for cross-linking at 150 °C, for networks in series A. The peroxide weight fraction (g/g) was as follows: 0.225 (□), 0.34 (●) and 0.45 (◇).

The probability distribution function of mean end-to-end vectors of network chain segments, $G(\mathbf{r}/\sigma(N))$, is associated with the statistical network structure; the transverse magnetization observed over the whole polymer gel is an average carried out over all network chain segments. The irreversible behavior of the magnetization is represented by

$$M_x^{\mathrm{R}}(t) = \sum_N L(N) \int \mathrm{d}\rho \; m_x(t,\rho,N) G(\rho) \tag{2}$$

where $L(N)$ is the normalized distribution of the number of skeletal bonds in segments; it accounts for the random formation of cross-links along one chain. The normalized ρ vector is defined as $\rho = \mathbf{r}/\sigma(N)$. The rate of fluctuations of end-to-end vectors is supposed to be low compared with the strength of dipole–dipole interactions detected from NMR. The statistical structure of polymeric gels is predicted to govern the transverse magnetic relaxation of nuclei attached to network chain segments. The transverse magnetic relaxation can be treated by considering two integrals easily carried out; on the one hand

$$\Phi_1 = \int_0^{\infty} t^{-1/2} \, M_x^{\mathrm{R}}(t) \, \mathrm{d}t \tag{3}$$

and, on the other hand

$$\Phi_3 = \int_0^{\infty} t^{-1/2} \, (\mathrm{d}M_x^{\mathrm{R}}(t)/\mathrm{d}t) \, \mathrm{d}t \tag{4}$$

Then, it can be shown, from eqs 1 and 2, that the calculation of Φ_1 and Φ_3 integrals amounts to estimating intrinsic moments of $G(\rho)$

$$\Phi_1 \approx \Lambda^{-1/2} \Delta_{\mathrm{G}}^{-1/2} \sigma(N)/b[m_1/m_2] \tag{5}$$

and

$$\Phi_3 \approx \Lambda^{1/2} \, \Delta_{\mathrm{G}}^{1/2} \, b/\sigma(N)[m_3/m_2] \tag{6}$$

with the following definitions of m_β ($\beta = 1$, 2, and 3)

$$m_\beta = \int_0 (\rho)^\beta G(\rho) \, \mathrm{d}\rho \tag{7}$$

The quantum averages $\Delta_{\mathrm{G}}^{\pm 1/2}$ are defined as

$$\Delta_{\mathrm{G}}^{\pm 1/2} = \sum_{nn'} P_{nn'} (\omega_{nn'})^{\pm 1/2} \tag{8}$$

The ratio defined by

$$\chi_{\mathrm{c}} = \Phi_3/\Phi_1 \tag{9}$$

is called the NMR structural parameter; it is expressed as

$$\chi_{\mathrm{c}} = \frac{\Delta_{\mathrm{G}}^{*} \, \Lambda m_3}{\sigma^2(N) m_1} \tag{10}$$

Numerical factors are included in the definition of Δ_{G}^{*}, which is considered as a intrinsic nuclear magnetic quantity specific to the polymer that is observed. The ratio Φ_3/Φ_1 is independent of the numerical procedure applied to the analysis of relaxation curves. The structural NMR parameter, χ_{c}, is related in a simple way to the distribution function, $G(\rho)$, of anchoring points. Equation 10 shows that the inverse of the NMR structural parameter χ_{c} must be simply proportional to the number of bonds which form one calibrated network chain segment, if fluctuations are Gaussian.[9] For exponential $M_x(t)$ functions, χ_{c} is exactly the relaxation rate.

IV. Quenched Cross-Linked Systems

Networks in series A were first studied; copolymers were randomly bridged by links formed between methyl and vinyl groups; the mean number of vinyl functions per chain is 4. Cross-linked systems were quenched at 0 °C, during the progress of the cross-linking reaction, to obtain different states of gelation. The modulus of elasticity, E, associated with these transient states was then measured at room temperature. The variations of E observed as a function of the time allowed for cross-linking at 150 °C are shown in Figure 1, for the three

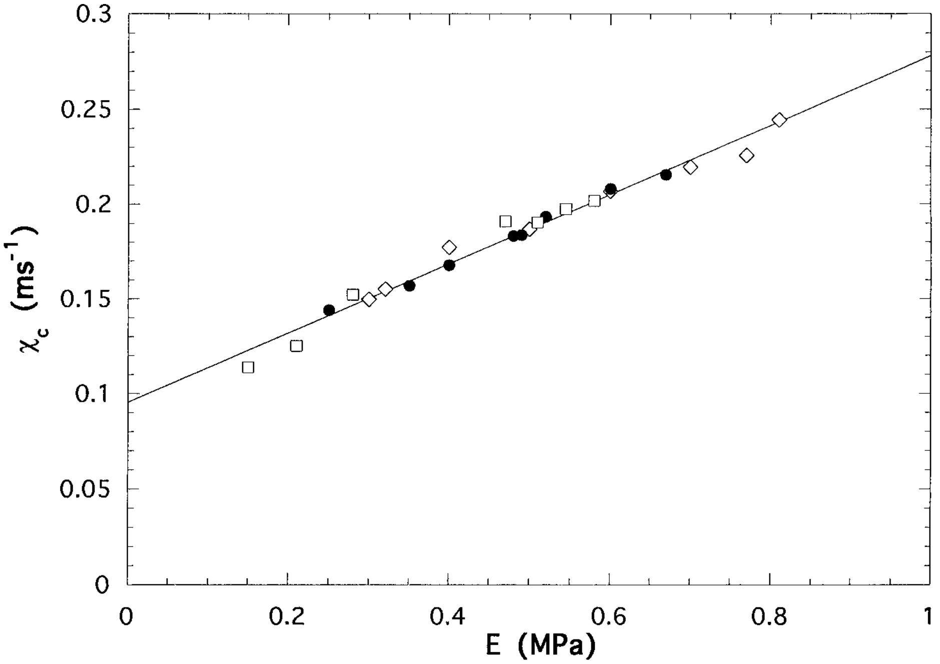

Figure 2. NMR structural parameter χ_c as a function of the elastic modulus, *E*, for networks of type A. Times of measurements correspond to those in Figure 1 (key to points as in Figure 1).

weight fractions of peroxide used to cross-link copolymers ($C_p = 0.225$, 0.34, and 0.45 g/g). Correspondingly, the NMR structural parameter was calculated from transverse relaxation curves of protons recorded from unconstrained samples at room temperature. The linear dependence of χ_c on the elastic modulus, *E*, is shown in Figure 2. The best numerical fit leads to the empirical equation

$$\chi_c = 0.095 + 0.18E \qquad (11)$$

The value of χ_c, determined when the elastic modulus is equal to zero, corresponds to the presence of a temporary network in the melt. It is worth noting that the time at which all chains started to be linked to one another was measured when the gel fraction reached a plateau value nearly equal to unity; these times were 20, 14, and 10 min for the corresponding weight fractions of peroxide equal to 0.225, 0.34 and 0.45 g/g. The fraction of unreacted vinyl functions was controlled using Fourier transform infrared spectroscopy (FTIR); for the system obtained from the weight fraction of peroxide equal to 0.45, this fraction was equal to 0.25 at the end of the cross-linking reaction.

V. In Situ Observation of the Gelation Kinetics

The attention was then focused on properties of polymeric networks in series B; polyfunctional units are not small molecules but chains composed of methylhydrosiloxane and dimethylsiloxane monomeric units. The mean number of monomeric units, in one chain, is about 120 while the mean number of hydride functions is about 15; these are distributed in space, along one given chain. Links were formed between hydride and vinyl groups, but bridges between vinyl-terminated PDMS chains cannot be considered as punctual, even approximately. These networks were first observed in situ during the gelation process.

The storage modulus $G'(\nu)$, was measured during the cross-linking reaction, at room temperature, at 1 Hz; typical variations are reported as a function of time in Figure 3, for $\tau_{H/Vi} = 1$ or 1.3 and $\sigma_H = 1$. Correspondingly, the NMR structural parameter was calculated from relaxation curves recorded during the gelation process; typical variations of χ_c are shown in Figure 4, for $\tau_{H/Vi} = 1$ or 1.3 and $\sigma_H = 0.72$. The NMR structural parameter, χ_c, is reported as a function of $G'(\nu)$ in Figure 5; experimental points lie on a straight line. It is represented by the empirical equation

$$\chi_c = 0.044 + 1.48G'(\nu) \qquad (12)$$

A linear dependence of χ_c on the storage modulus was observed whatever the values of $\tau_{H/Vi}$, the ratio defined by the number of hydride functions to the number of vinyl functions, or the values of σ_H, the ratio defined by the number of hydride functions in multifunctional chains to the total number of hydride functions.

Then, networks were observed after completion of the gelation process. A linear dependence of χ_c on the elastic modulus was determined from the straight line drawn in Figure 6; it is represented by the empirical equation

$$\chi_c = 0.064 + 0.41E \qquad (13)$$

The storage modulus, $G'(\nu)$, was also measured at a frequency equal to 1 Hz and 300 K, after completion of the gelation process; *E* was found to be proportional to $G'(\nu)$, according to the empirical equation

$$E = 3.4\, G'(\nu) \qquad (14)$$

Consequently, there is also a linear dependence of χ_c on $G'(\nu)$. The ratio of the slope determined in eq 15 over the slope defined in eq 16 is equal to 3.6 while the slope in eq 16 is 3.4; there is a reasonable agreement between these two values. Fractions of unreacted hydride functions were also controlled from FTIR spectroscopy; typical values of these fractions corresponding to Figure 3 are 0.95 and 0.9, respectively, after completion of the gelation process.

VI. Discussion

The main feature about experimental results concerns the linear relationship between χ_c determined from unconstrained gels and *E*; this can be represented by

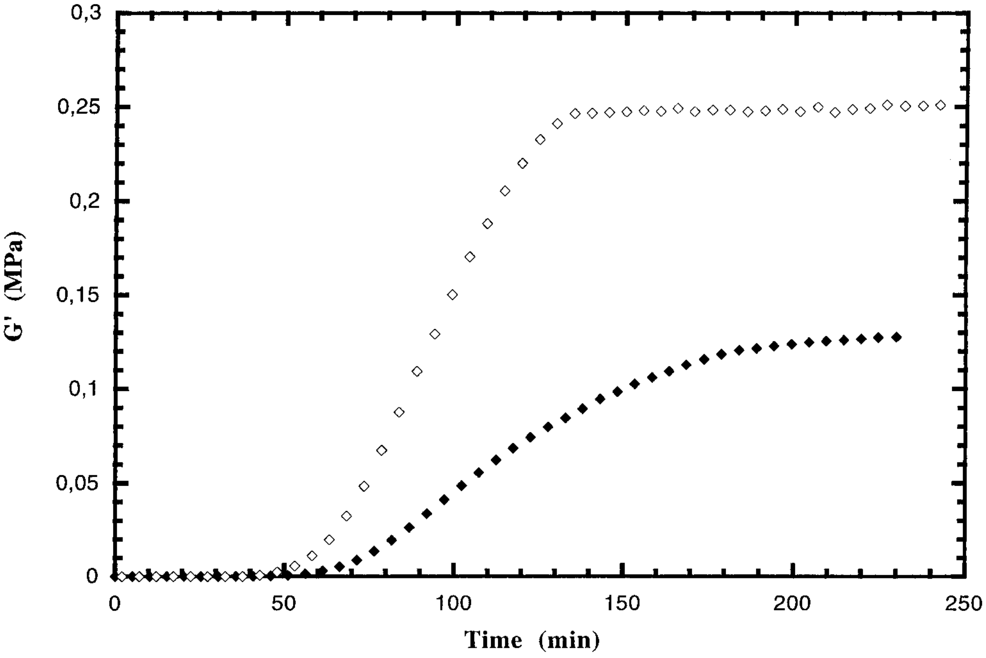

Figure 3. Storage modulus measured in situ as a function of time during the cross-linking, for networks in series B: $\sigma_H = 1$; $\tau_{H/Vi} = 1$ (◆) and 1.3 (◇).

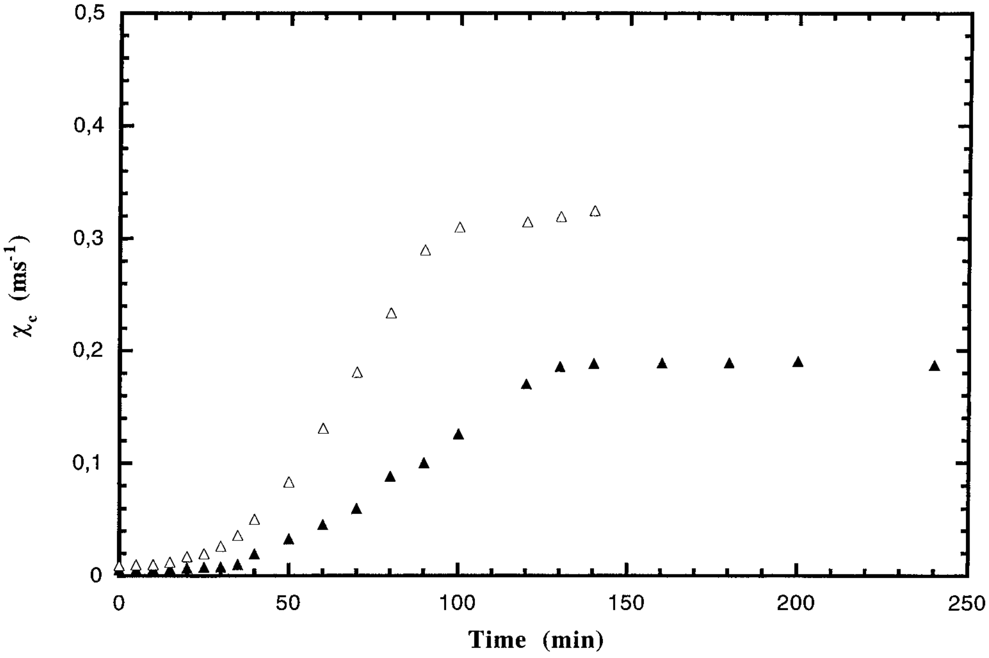

Figure 4. NMR structural parameter measured in situ as a function of time during the cross-linking, for networks in series B: $\sigma_H = 0.72$, $\tau_{H/Vi} = 1$ (▲) and 1.3 (△).

the empirical equation

$$\chi_c = \chi_c^0 + p_c E \tag{15}$$

where χ_c^0 is extrapolated to the zero value of E. It may be worth noting that such a linear dependence has been already reported for long polybutadiene chains, cross-linked at random by sulfur; χ_c^0 is equal to 0.15 ms^{-1} and $p_c = 0.30$ ms^{-1}/MPa. For these networks, it has been shown both experimentally and theoretically that the relevant gelation–percolation variable is a function of the mean number of cross-links per chain; E is a nonlinear function of the difference ($\gamma_c^s M_w - 500$) in which γ_c^s is the sulfur weight fraction ($0.002 \le \gamma_c^s \le 0.01$ g/g) and M_w is the weight average molecular weight of the polymer ($77 \times 10^3 \le M_w \le 180 \times 10^3$).[11] For these systems, the experimental estimate of the gelation theshold is 500;[6] it corresponds to the minimum number of cross-links per chain required to form a network; for this value of the $\gamma_c^s M_w$ product, the modulus of elasticity is equal to zero.

The analysis of the linear dependence is made in the following way.

(i) It is now well established that the proton transverse relaxation observed on high molten polymers exhibits a gel-like behavior; the relaxation process is sensitive to the effect of entanglement. Temporary networks which characterize molten high polymers are detected as permanent networks when the rate of dissociation of entanglements is smaller than the residual dipole–dipole interaction of protons; consequently, the NMR structural parameter is related to the mean segmental spacing between entanglements.[14] Ac-

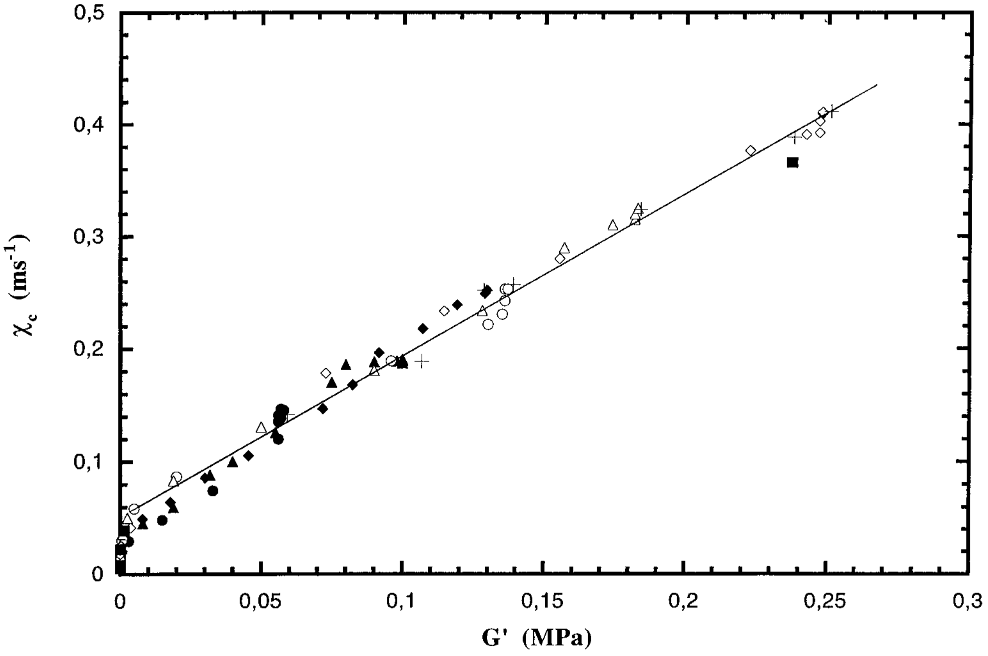

Figure 5. NMR structural parameter as a function of the storage modulus, for networks in series B: $\tau_{H/Vi} = 1$ and $\sigma_H = 0.45$ (●), 0.72 (▲), 1 (◆); $\tau_{H/Vi} = 1.3$ and $\sigma_H = 0.45$ (○), 0.72 (△), 1 (◇); $\tau_{H/Vi} = 1.6$ and $\sigma_H = 1$ (□); after completion of the gelation process (+).

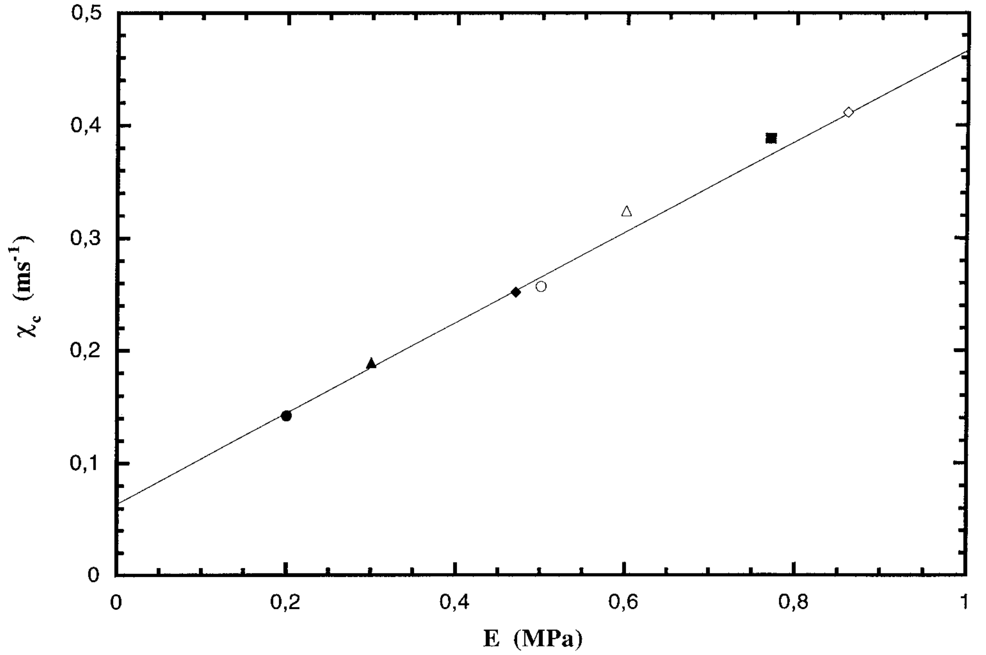

Figure 6. NMR structural parameter as a function of the elastic modulus, for networks in series B, after completion of the gelation process (key to points as in Figure 5).

cording to eq 10, χ_c can be viewed as a parameter proportional to the modulus of temporary elasticity G_N^0 in molten high polymers[15]

$$\chi_c \approx \Delta\sigma_G^* \, G_N^0/RT \tag{16}$$

the physical quantity G_N^0 has a pure dynamical determination obtained from viscoelastic measurements.[16]

(ii) According to the mean field percolation theory, there exist active network segments associated with a given state of gelation of randomly cross-linked chains.[17] Whatever their exact definition, these segments give rise to the properties of elasticity and of swelling. The modulus of elasticity *E* reflects a zero-frequency property which depends only on the deviation from the gelation threshold. In contrast to the mean entanglement spacing, the length of active segments is infinite at the threshold of gelation and *E* is equal to zero.

(iii) This study deals with polymeric systems in which the concentration of cross-links is lower than the entanglement concentration. Equation 15 shows that the formation of cross-links results in an additional contribution to the effect of entanglement. An experimental estimate of this contribution is given by the ratio χ_c^0/p_c; values of this ratio are 0.5 MPa for networks in series A, 0.16 MPa for networks in the series B, and 0.5 MPa for vulcanized polybutadiene. These values are close to those of the modulus of temporary elasticity obtained from viscoelastic measurements carried out on the pure polymers.[16]

(iv) The proton transverse relaxation has been already used to provide insights into these networks structures swollen by a good solvent.[11,18] NMR measurements have been carried out on randomly cross-linked chains in the state of maximum swelling. For networks in series A and B and for vulcanized polybutadiene, previously reported results have shown that the NMR structural parameter χ_c is proportional to $1/Q_m^2$ where Q_m is defined as the ratio of the volume of the swollen gel to the volume of the dry gel. The direct proportionality of χ_c to $1/Q_m^2$ indicates a single contribution to the determination of the NMR parameter. It shows that active chain segments involved in the property of swelling are those which are detected from NMR. Hence, the interpretation is based on the assumption that swollen segments obey a packing condition (property of juxtaposition); the mean square end-to-end distance of a segment is proportional to the number N_s of bonds that it contains, and the swelling ratio Q_m is proportional to $N_s^{1/2}$. Equation 10 leads to the observed dependence of χ_c on Q_m whatever the exact definition of N_s which is infinite at the gelation threshold.

VII. Conclusion

The observation of the proton transverse relaxation has proved to be a suitable method for providing insights into temporary network structures which characterize molten high polymers. Relaxation investigations apply to polymeric gels formed from short end-linked polymer precursors. There is a quantitative relationship established between the relaxation rate measured on unconstrained elastomers and the precursor molecular weight. Variations of the glass transition temperature of polymeric gels with the precursor molecular weight require to perform NMR measurements at a constant temperature interval above the glass transition. In this work, we were concerned with much less uniform network structures generated by the random distribution of a small mean number of cross-links per chain in entangled polymers. The exact nature of active segments which participate in the properties of elasticity and of swelling is still undefined. However, in these elastomers, the proton relaxation is again directly related to the existence of network structures; furthermore, it presents two striking features. On the one hand, the relaxation rate measured on unconstrained elastomers is a linear function of the modulus of elasticity. On the other hand, the magnetic relaxation results from two contributions. One is attributed to the effect of elasticity induced by the cross-linking; the other one reflects the effect of entanglement. It may be worth noting that the discrimination between the property of elasticity and the NMR approach arises from the frequency ranges of observation. The very nature of measurements performed to obtain the modulus of elasticity requires the existence of a network to avoid any flow of the polymer; the frequency of observation goes to zero. In high polymers, the proton relaxation is sensitive to fluctuations provided their rate is higher than about 10^2 Hz (equivalent to the strength of residual dipole−dipole interactions); otherwise fluctuations with a lower rate must be considered as frozen. This condition explains why the temporary elasticity can be observed from NMR whenever the dissociation rate of entanglements is lower than 10^2 Hz; there is an additional contribution due to the permanent elasticity when chains are cross-linked.

This study corroborates the existence of a direct relationship between NMR and macroscopic properties of elastomers. The elastic modulus corresponds to the linear response of an elastomer to an uniaxial strain; as a general physical property, this linear response must depend on fluctuations which occur in the unconstrained gel.[19] Hence, it is considered that fluctuations that occur along active network segments are involved both in the property of elasticity and in the relaxation process of protons observed in the absence of any strain.

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