Poly(dimethylsiloxane) Chains Cross-Linked at Random. Percolation and NMR Approaches

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ABSTRACT: The formation of network structures associated with randomly cross-linked polydimethylsiloxane chains is analyzed as a function of time. A cross-linking reaction between the methyl groups and the vinyl groups of vinylmethylsiloxane comonomeric units was induced by heating (150 °C) in the presence of a peroxide; transient states of gelation were observed by quenching samples in ice. The gel fraction, the swelling ratio, and an NMR structural parameter were the physical quantities used to investigate the network structures. The fraction of all vinyl groups that react in a time t is found to be proportional to $t^{1/2}$ in agreement with a mean field percolation treatment of systems of cross-linked chains. The maximum swelling effect was interpreted in terms of the packing of swollen Gaussian domains. The presence of silica aggregates did not perturb the network structures, as observed from their swelling properties.

I. Introduction

This work deals with investigations into the physical properties of polymeric systems formed by cross-linking linear homopolymers; cross-links are randomly located along the chains. Several problems are encountered in the study of vulcanized polymers. The first one concerns the determination of a single variable which can be applied to characterize the state of gelation. This determination requires the use of a framework to describe systems formed by cross-linking chains. The percolation approach is often a satisfactory general way of analyzing properties of polymeric gels.[1−6] Within the percolation framework, characterization of the state of gelation must include both the functionality of percolation units and the concentration of cross-links that are formed. A second problem is the difficulty of measuring accurately the concentration of cross-links during the gelation process. A final problem concerns the characterization of the distribution of the network structure. For long chains that are cross-linked at random, the segmental spacing between cross-links along a single chain is not uniform; it obeys a statistical distribution, and the mesh size of the network is related to this distribution.

In this study, the initial polymer system consists of long dimethylsiloxane−vinylmethylsiloxane copolymers. The gelation process results from the formation of a cross-link between one vinyl group and one methyl group; the cross-linking reaction is induced by heating the polymer in the presence of an initiator (peroxide). The molecular weight of the polymer is not varied. Attention is focused on the evolution of the physical behavior of the polymeric system observed during the gelation process; intermediate states of gelation were obtained by quenching partly cross-linked chain systems in ice, at different times. The initiator concentration was varied to detect possible changes during the cross-linking reaction. Measurements were made of several physical quantities such as the weight fraction of gel, the swelling ratio, and the relaxation rate of the transverse magnetization of protons attached to the polymer. Fumed silica was also mixed with the polymer prior to the gelation process. Silica is frequently used as a filler for polydimethylsiloxane in order to improve its ultimate properties; it was found that silica does not induce any change in the network structures as observed from swelling properties.

Experimental aspects are presented in Section II. The principle of the NMR approach is briefly reviewed in Section III while the framework of mean field percolation used to establish a variable of gelation suitable for the description of the systems studied is outlined in Section IV. Experimental results are analyzed in Section V and yield the time dependence of the kinetics of cross-link formation. Finally, the NMR approach, which is specific to polymeric gels and swelling effects, provides additional details of the network structure and properties (Section VI).

II. Experimental Section

Sample Preparation. In addition to dimethyl monomeric units ($-O-Si(CH_3)_2$), the copolymer contains vinylmethyl monomeric units ($-O-Si(CH_3)(CH=CH_2)$), which are randomly distributed along the chains. The weight average molecular weight, M_w, was 390 000, and the polydispersity index was equal to 2.7. The weight ratio of vinyl groups C_{vi} was equal to 0.78×10^{-3} g/g of polymer; it was kept constant in this study. The copolymer was bought from Rhône-Poulenc (Lyon, France). The initiator of the cross-linking reaction was a peroxide (2,5-dimethyl-2,5-bis(*tert*-butylperoxyhexane) (Aldrich). The peroxide was first mixed with hydrophobic silica (R106, bought from Degussa); then the mixture was added to the copolymer. The initiator weight ratio C_p was varied from 2.25×10^3 to 4.5×10^{-3} g/g of polymer while the weight ratio of silica ϕ_{si} was varied from 0 to 0.4 g/g of polymer.

The polymer initiator/silica 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[7]. One ($-CH_2-CH_2-CH_2-$) link is thus created between two chain segments. The kinetics of formation of cross-links was observed by quenching polymer films (about 1 mm in thickness) 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. Measurements were performed every 1 min during the first 10 min and every 2 min in the period from 10 to 40 min. It is assumed that side reactions of the vinyl free radicals with other vinyl groups or other radicals cannot occur. The polymeric systems studied are listed in Table 1.

Gel Measurements. The gel fraction G is defined as the ratio of the weight of cross-linked polymer in a polymer/silica

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Table 1. Description of the Studied Systems and Experimental Values of the Kinetics Factor, *K*, and the Time of Gelation Threshold t_0, Defined in Sections IV.2 and V.2, Respectively

C_{vi} (g/g of polymer)	C_p (g/g of polymer)	Φ_{si} (g/g of polymer)	t_0 (min)	K (min^{-1})	Kt_0
780×10^{-6}	4.5×10^{-3}	0.4	2.6	0.41	1.1
780×10^{-6}	3.4×10^{-3}	0.4	4.7	0.32	1.55
780×10^{-6}	2.25×10^{-3}	0.4	7.6	0.20	1.55
780×10^{-6}	4.5×10^{-3}	0.2	3	0.38	1.1
780×10^{-6}	4.5×10^{-3}	0	3.5	0.33	1.1

mixture obtained after extracting free chains to the initial weight of polymer in the mixture. Let M_G denote the weight of silica and cross-linked polymer measured after extracting free chains; M_M^i, is the total initial weight of the mixture (including the weight of silica).

The gel fraction is given by

$$G = \frac{M_G}{M_M^i}(1 + \phi_{si}) - \phi_{si}$$

for samples that contain silica. Silica aggregates were not detected in sol fractions. Methylcyclohexane, which is a good solvent for poly(dimethylsiloxane), was used to extract the free chains. The solvent was replaced after 24 h in order to achieve complete sol phase extraction.

Swelling Measurements. The maximum swelling of the cross-linked networks was induced by exposure to methylcyclohexane. Free chains were extracted from the vulcanized networks after washing for three days before the swelling ratio Q_m was measured; Q_m is given by

$$Q_m = 1 + \frac{\rho_p}{\rho_s}\left(\frac{M_{Q_m} - M_G}{M_G}\right)(1 + \phi_{si})$$

where M_{Q_m} is the weight of the swollen gel, including silica; ρ_p and ρ_s are the densities of poly(dimethylsiloxane) and methylcyclohexane i.e. 0.98×10^3 and 0.78×10^3 kg/m^3, respectively. The swelling ratio Q_m was determined with an uncertainty of 5%.

NMR Measurements. NMR experiments were performed using a Bruker pulse spectrometer CXP, operating at 45 MHz. All relaxation spectra were determined by using Carr–Purcell spin-echo sequences.[8] It has been shown that relaxation spectra measured with such sequences are equivalent to those obtained from the usual experimental procedure, proposed by Hahn.[9] The proton transverse relaxation spectra were recorded at room temperature.

The swelling effect was observed from NMR, using carbon tetrachloride as a swelling solvent. Swollen networks were kept in NMR tubes sealed under nitrogen atmosphere.

Fourier Transform Infrared Spectroscopy Measurements. Infrared spectra were taken of samples that did not contain silica. The thicknesses of the samples were about 0.1 mm. The absorption peak of the Si–CH=CH$_2$ group appears at a wavelength $\lambda = 1600$ cm^{-1}. The fraction of vinyl groups is estimated by dividing the height of this peak by the height of the peak characteristic of the Si–(CH$_3$)$_2$ groups, which is detected at 1260 cm^{-1}.

III. Principle of the NMR Approach

In this section, an NMR technique for the observation of segmental fluctuations in polymeric systems is briefly reviewed.

III.1. Gel Distribution Function. The method of observation of the properties of the network chain segments by NMR makes use of the transverse magnetic relaxation of protons attached to the segments. It is based on the reduction of dipole–dipole interactions induced by restricted fluctuations which occur along one segment. The method has been described elsewhere; it is summarized in this section.[9]

Starting from one chain segment, defined by two nodes and the number N of skeletal bonds that it contains, the strength of the averaged magnetic interactions along this segment is a function both of the mean distance between the two nodes and of the number N; the mean distance will herafter be called r. The magnetization associated with a single segment can be expanded in the basis of eigenfunctions of the Zeeman energy of the spins

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

where $\omega_{nn'}$ is a broadening frequency induced by the dipole–dipole interactions and $P_{nn'}$ is a quantum weighting factor; θ_r is the angle that the mean end-to-end vector **r** makes with the steady magnetic field direction. The sum is over all eigenstates of the Zeeman energy. The mean skeletal bond length is designated by b, and the parameter Λ accounts for angular correlations of three neighboring skeletal bonds, located along a single segment; it is called the second-order stiffness of the chain.[9] The statistical nature of the description enters through the quantity denoting the mean square end-to-end distance between segment ends: $\sigma(N)^2$. Equation 1 applies to weakly stretched segments. It is clearly seen from this equation that the ratio $\{rb/\sigma(N)^2\}^2$ plays the role of a time scaling factor; the statistical structure of polymeric gels is predicted to govern the transverse magnetic relaxation of nuclei attached to network chain segments.

A distribution function, $\mathsf{G}(\mathbf{r}/\sigma(N))$, can be associated with the statistical structure of a polymeric gel; it is introduced to describe the irreversible behavior of the transverse magnetization observed over the whole polymeric sample. This magnetization is

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

the normalized ρ vector is defined as $\rho = \mathbf{r}/\sigma(N)$); $\mathsf{G}(\rho)$ is the probability distribution function of the mean end-to-end vectors of the network chain segments and $\mathsf{L}(N)$ is the normalized distribution of the number of skeletal bonds in each segment. In vulcanized polymers, there is a distribution of chain segment lengths between two consecutive cross-links along one chain.

III.2. Moments of the Gel Distribution Function. The transverse magnetic relaxation can be treated by considering two tractable integrals

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

and

$$\Phi_3 = \int_0^\infty t^{-1/2} (dM_x^R(t)/dt)\, dt \quad (4)$$

It has been shown that[9]

$$\Phi_1 \approx \Lambda^{-1/2} \Delta_G^{-1/2} \sigma(N)/b[m_1/m_2] \quad (5)$$

and

$$\Phi_3 \approx \Lambda^{1/2} \Delta_G^{1/2} b/\sigma(N)[m_3/m_2] \quad (6)$$

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

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

Each moment m_β is intrinsic because it is defined in terms of a reduced variable; it reflects the shape of the distribution function $G\,(\mathbf{r}/\sigma(N))$. The quantum averages $\Delta_G^{\pm 1/2}$ are defined as follows:

$$\Delta_G^{\pm 1/2} = = \sum_{nn'} P_{nn'}\,(\omega_{nn'})^{\pm 1/2} \tag{8}$$

They depend on spin operators which define nuclear dipole−dipole interactions.[9]

III.3. The NMR Structural Parameter. The ratio defined by

$$\chi_c = \Phi_3/\Phi_1 \tag{9}$$

is called the NMR structural parameter; from eqs 5 and 6, it is equal to

$$\chi_c = \Delta_G^* \Lambda / \langle \sigma(N)^2 \rangle \tag{10}$$

For simplicity, the dipole−dipole interaction Δ_G^* includes numerical factors; Δ_G^* is considered as an intrinsic nuclear magnetic quantity specific to the polymer that is observed.[9] Equation 10 shows that the inverse of the NMR structural parameter χ_c must be a simple function of the mean number of bonds in the network chain segments.[10] This NMR parameter is used in the next few sections to probe the mean segmental mesh size in polymer networks.

III.4. NMR Width of the Distribution. The product defined by

$$\pi_c = \Phi_3 \Phi_1 \tag{11}$$

is called the NMR distribution width; it is expressed as

$$\pi_c \approx m_1 m_3 / m_2^{\,2} \tag{12}$$

The NMR distribution width can in principle be used to reveal variations in the statistics that describe polymeric gels (Gaussian or excluded volume statistics).

IV. State of Gelation

In this work, a description of the properties of long randomly cross-linked chains is given within the framework of bond percolation, considered in the mean field approximation;[2] then, it is also assumed that the state of gelation of the polymeric system can be described using only one percolation variable, which will be defined in Section IV.2.[6] The percolation units are polymer chains; percolation arises from the formation of chemical cross-links between vinyl and methyl groups.

IV.1. Percolation Threshold. The mean functionality of the polymer chains, with respect to vinyl groups, is called f_{vi}; it is equal to the average number of vinyl groups per chain; for simplicity, it is assumed that

$$f_{vi} = C_{vi}\, M_w / M_{vi} \tag{13}$$

where C_{vi} is the concentration (w/w) of vinyl groups and M_w is the weight average molecular weight of the polymer; M_{vi} is the molar weight of one vinyl group ($M_{vi} = 27$) and $f_{vi} \approx 10$. It is then possible to define the threshold of gelation with respect to the vinyl functionality:

$$p_c = 1/(f_{vi} - 1) \tag{14}$$

The above simple definition of p_c will be used to define the variable of gelation.

IV.2. Variable of Gelation. Let $\alpha(t)$ denote the fraction of vinyl groups that have reacted with methyl groups, at a time t. The initial weight of polymer is called M_p^i; the initial number of vinyl groups is then

$$N_{vi}^{\,i} = C_{vi}\, M_{\,p}^{\,i} A / M_{vi} \tag{15}$$

(A is Avogadro's number). The initial number of methyl groups is

$$N_{me}^{\,i} = 2 M_{\,p}^{\,i} A / M_m \tag{16}$$

where M_m is the molar weight of one monomeric unit; $\beta(t)$ is the fraction of methyl groups that have reacted at time t. The mean functionality associated with methyl groups is given by the ratio $2M_w/M_m$ (in this estimate the presence of a small fraction of vinyl groups in one chain is neglected); this means that the functionality is about equal to 10^4. The probability of linking percolation units through the vinyl functionality is then calculated according to the Flory model; it is simply expressed as

$$p = \alpha(t)\beta(t)(2M_w/M_m - 1) \tag{17}$$

The necessary condition

$$\alpha(t) N_{vi}^{\,i} = \beta(t) N_{me}^{\,i} \tag{18}$$

applies at any time. On taking this condition into consideration, the probability, p, is written as

$$p = \alpha(t)^2 C_{vi} M_m (2M_w/M_m - 1)/2M_{vi} \tag{19}$$

The variable of gelation is here expressed as the deviation from the percolation threshold

$$\epsilon = \frac{p}{p_c} - 1 \tag{20}$$

Hence,

$$\epsilon(t) = \alpha(t)^2 C_{vi} (2M_w/M_m - 1)(C_{vi} M_w / M_{vi} - 1) M_m / 2M_{vi} - 1 \tag{21}$$

or

$$\epsilon(t) \approx \alpha(t)^2 C_{vi}^{\,2} M_w^{\,2} / M_{vi}^{\,2} - 1 \tag{22}$$

This definition confers a symmetric role on methyl and vinyl groups. The threshold of gelation occurs at a time t_0 such that $\epsilon(t_0)$ is equal to zero. Then

$$\epsilon(t) = \kappa(\alpha(t)^2 - \alpha(t_0)^2) \tag{23}$$

with

$$\kappa = C_{vi}^{\,2} M_w^{\,2} / M_{vi}^{\,2} \tag{24}$$

Variations in the concentration of peroxide are expected to act on the kinetics of formation of cross-links without modifying the time dependence of $\epsilon(t)$. In this description, the probability of linking one vinyl group to another methyl group within the same chain has been

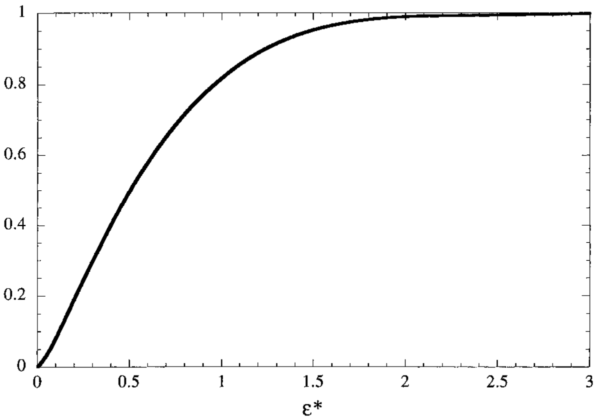

Figure 1. Theoretical variation of the gel fraction as a function of the gelation variable ϵ^*.

neglected. The variable $\epsilon(t)$ will be considered in the next few sections to characterize the state of gelation.

V. Analysis of Gel Fraction Variations

In this section, the variation of the gel fraction with time is analyzed in order to derive the time dependence of the gelation variable.

V.1. Gel Fraction and Gelation Variable. Considering the framework of percolation, the analysis starts from the probability distribution function of clusters of size s; let $P\,(s,\epsilon)$ denote this function, which depends on the deviation from the percolation threshold and which is generally expressed as

$$P\,(s,\epsilon) = s^{-\tau}P(\epsilon s^{\sigma}) \tag{25}$$

where $P(\epsilon s^{\sigma})$ is a scaling function. In the classical approach, the values of the exponents τ and σ are equal to $^5/_2$ and $^1/_2$, respectively; P is usually approximated by a simple exponential function of s.[11]

$$P(\epsilon s^{\sigma}) = As^{-5/2}\exp(-b^2\epsilon^2 s) \tag{26}$$

where A is a constant and b^2 may be a slowly varying function of the functionality of the percolating units. In this work, the concentration of vinyl groups is kept constant; consequently, b^2 is also constant. The gel fraction obeys the following relationship, which defines the first moment of the cluster size distribution function $P\,(s,\epsilon)$

$$1 - G = A\sum_{s=1}^{\infty} s^{-3/2}\exp(-b^2\epsilon^2 s) \tag{27}$$

with $G = 0$ for $\epsilon = 0$ ($A = 2.6$). This equation leads to the theoretical curve of G as a function of $\epsilon^* = b\epsilon$, shown in Figure 1; this curve is then compared with the experimental variation of G plotted as a function of time below.

V.2. Time Dependence of the Gelation Variable. The variations of the gel fraction shown in Figure 2 correspond to different values of the initial weight ratio of the initiator (C_p = 2.25, 3.4 and 4.5 10^{-3} g/g of polymer); the weight ratio of silica was kept constant. The gel fraction increases sharply and reaches a plateau; the plateau value is close to 1; for this value of G, all chains are linked to one another. Comparing Figures 1 and 2, it is asumed that each value of the gel fraction corresponds to one single value of time and also to one single value of the gelation variable ϵ^*. Then, ϵ^* is plotted as a function of t, for each polymeric system studied; ϵ^* was found to depend linearly on t (Figure 3). The extrapolation of each straight line, through experimental points, yields the time t_0, which is taken to be the time of gelation threshold ($\epsilon^* = 0$); ϵ^* varies according to the empirical equation

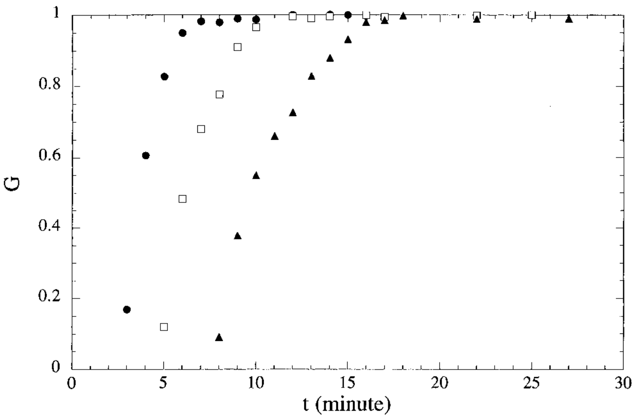

Figure 2. Time dependence of the gel fraction observed for several values of the peroxide weight ratio: $C_p = 4.5 \times 10^{-3}$ (●), 3.4×10^{-3} (□), and 2.25×10^{-3} (▲) g/g of polymer. The silica weight ratio Φ_{si} was equal to 0.4 g/g of polymer.

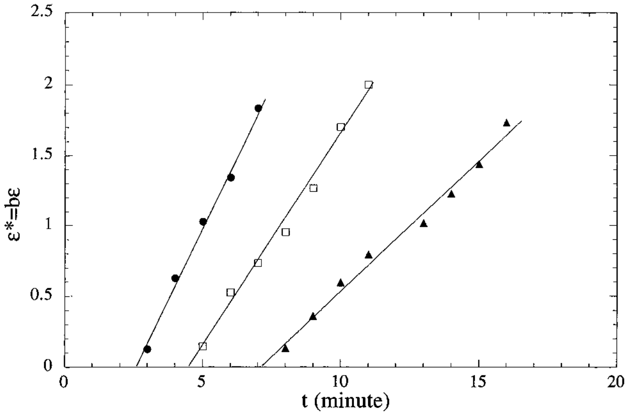

Figure 3. Time dependence of the gelation variable ϵ^* obtained for several values of the peroxide weight ratio: $C_p = 4.5 \times 10^{-3}$ (●), 3.4×10^{-3} (□), and 2.25×10^{-3} (▲) g/g of polymer. The silica weight ratio Φ_{si} was equal to 0.4 g/g of polymer.

$$\epsilon^* = K(t - t_0) \tag{28}$$

which determines the value of t_0; the values of K and t_0 are listed in Table 1. They increase when the weight ratio of peroxide, C_p, is increased; it must be noted that the parameter K is proportional to C_p ($K = 92.8C_p$) while the product Kt_0 is nearly constant: $Kt_0 \approx 1.3 \pm 0.2$ (Table 1).

V.3. Kinetics of Link Formation. On comparing eq 23 with the empirical eq 28, it is seen that the kinetics of link formation must vary according to the following equation for the fraction $\alpha(t)$ of reacted vinyl functions at a time t:

$$\alpha(t) = \sqrt{K/\kappa b}\sqrt{t} \tag{29}$$

This time dependence may reflect a possible diffusion process of the initiator involved in the mechanism of link formation. This result was corroborated by measurements of the change in amplitude of IR absorption of vinyl groups during the gelation process, in the pure polymer; silica was not added to the polymer because

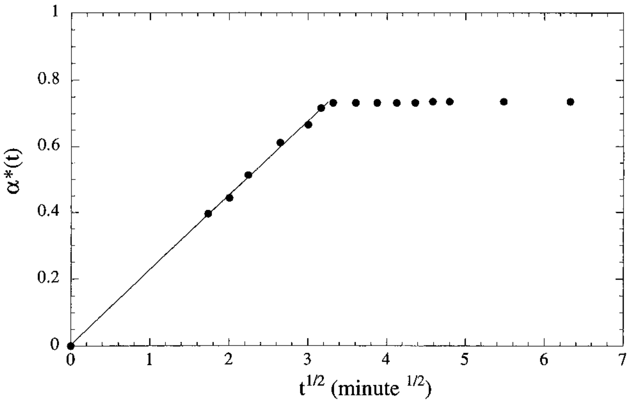

Figure 4. Time dependence of the fraction of vinyl groups α*(*t*) that have reacted. Measurements were performed by FTIR spectroscopy. The peroxide weight ratio C_p was equal to 4.5×10^{-3} g/g of polymer and $\Phi_{si} = 0$ g/g of polymer.

of the requirement to have thin films. The fraction α*(*t*) was derived from the decrease in amplitude of FTIR absorption at 150 °C; α*(*t*) is plotted as a function of time in Figure 4. Measurements were performed at 300 K; the weight ratio of initiator was $C_p = 4.5 \times 10^{-3}$ g/g of polymer. The dependence on the square root of time is found to characterize the kinetics of link formation, in the absence of silica, as well. The presence of inorganic aggregates does not perturb the mechanism of gelation. The maximum value of the fraction of vinyl groups that have reacted is only 75%. Furthermore, Figure 4 shows that the expression for the gelation variable given by eqs 19 and 23 applies to the description of the formation of the network structure; it is worth noting that the percolation approach is in good agreement with experimental results and the nearly constant value of the product Kt_0 must be associated with the definition of the time t_0 of the gelation threshold given by eq 23: $\kappa\alpha(t_0)^2 \approx \kappa t_0$.

VI. Investigations into Network Structure Properties

In this section, network structure properties of polymeric systems that were quenched in ice at different times during the progress of the gelation process are investigated in two ways. In the dry state, the NMR structural parameter was determined as a function of time. In the swollen state, both the swelling ratio and the NMR structural parameter were determined and related to each other.

VI.1. NMR Structural Parameter. Pseudo-solid spin-echoes were performed to prove that the relaxation mechanism of the transverse magnetization of protons linked to chain segments is induced by a pure residual dipole−dipole interaction of spins; these echoes are shown in Figure 5. They show that the residual dipole−dipole interaction is strong enough to govern the transverse magnetic relaxation process and to screen the observation of the dynamics of monomeric rotations.[9] The relaxation is sensitive only to deviations from isotropic rotations and the relaxation rate is a measure of the rotational asymmetry of the monomeric units.

Values of the NMR structural parameter χ_c were measured during the progress of the gelation process after quenching samples to 0 °C; they are plotted as a function of ϵ^* in Figure 6A. Measurements were performed on samples containing different values of the weight ratio of the initiator; the experimental points lie on a single curve. The plateau value of χ_c was found to be independent of the initiator weight ratio. The NMR width parameter π_c of the G ($\rho/\sigma(N)$) distribution was studied as a function of time (Figure 6B); it was found to be constant. This result shows that the statistical nature of the description does not vary during the process of gelation.

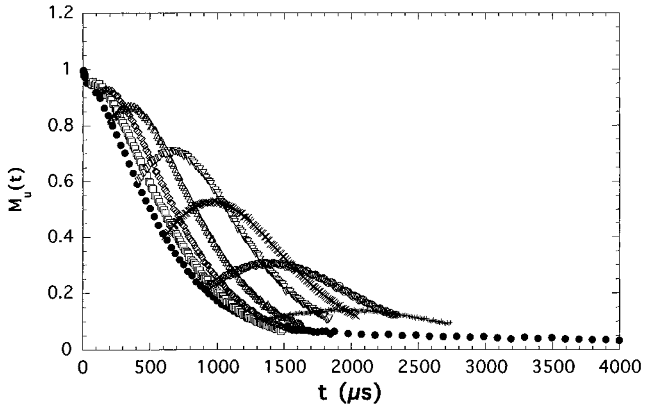

Figure 5. Transverse relaxation curve of protons. Curves A, B, C, D, E, F and *G* are pseudo-solid spin echoes (the peroxide weight ratio C_p was equal to 4.5×10^{-3} g/g of polymer and Φ_{si} = 0 g/g of polymer).

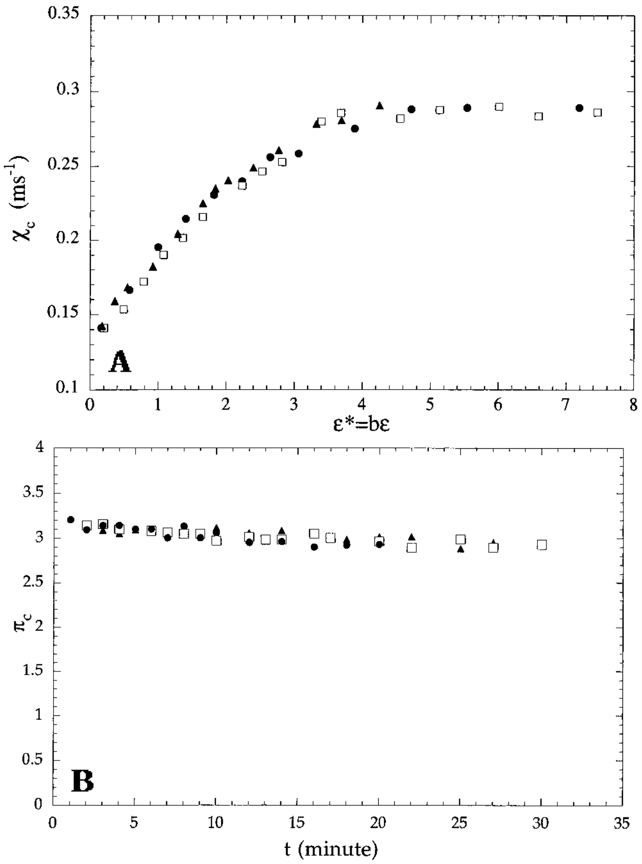

Figure 6. (A) Variations of the NMR structural parameter χ_c vs ϵ^*. (B) Time dependence of the NMR width parameter π_c. (Peroxide weight ratio: C_p = 4.5 (●), 3.4 (□) and 2.25 × 10^{-3} (▲) g/g of polymer; the silica weight ratio Φ_{si} was equal to 0.4 g/g of polymer).

Let χ_c^0 denote the initial value of the NMR structural parameter; it characterizes the polymer system before the polymer network formation, and it is due to the presence of entanglements. The experimental curve, displayed in Figure 6A, is analyzed on the one hand according to eq 10 and on the other hand by considering that the NMR width parameter π_c is constant. It is

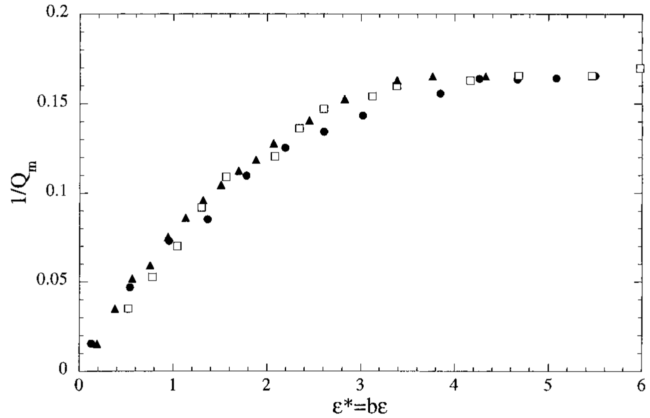

Figure 7. Variation of the inverse of the swelling ratio $1/Q_m$ with ϵ^*, obtained for several values of the peroxide weight ratio: $C_p = 4.5 \times 10^{-3}$ (●), 3.4×10^{-3} (□), and 2.25×10^{-3} (▲) g/g of polymer. The silica weight ratio Φ_{si} was equal to 0.4 g/g of polymer.

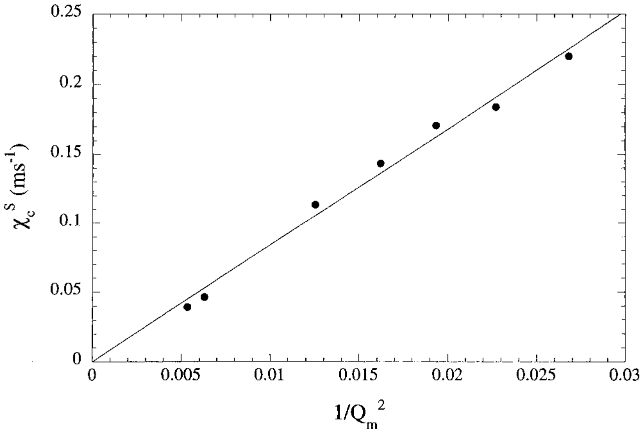

Figure 8. Variations of the NMR parameter χ_c with the inverse square of the swelling ratio $1/Q_m^2$. The peroxide weight ratio was $C_p = 4.5 \times 10^{-3}$ g/g of polymer and the silica weight ratio Φ_{si} was equal to 0.4 g/g of polymer.

assumed that there exists a mean segmental spacing N_D which determines the mesh size of the network structure in the dry state; the statistical framework is Gaussian. Consequently, the experimental curve drawn in Figure 6A illustrates the dependence of the inverse of the mean number N_D on the variable ϵ^*, at different times.

VI.2. Swelling Properties. For each sample, the swelling ratio Q_m was measured in the state of maximum swelling. The inverse of Q_m is shown as a function of ϵ^* in Figure 7; several values of the weight ratio of peroxide were considered. The plateau value reached at the end of the gel formation does not depend on the initial concentration of the initiator; this result confirms the similar property observed from the χ_c parameter in Figure 6A.

Figure 8 shows that the NMR parameter, called χ_c^s, varies linearly with the inverse square of the swelling ratio ($C_p = 4.5 \times 10^{-3}$ g/g of polymer and $\phi_{si} = 0.4$ g/g of polymer). This result is interpreted in the following way. One can consider the polymeric network structure as an ensemble of cells determined by a mean number of bonds N_Q. The swelling process results from the disengagement of chain segments, from one another; however, the presence of trapped loops may hinder the process of full disengagement of segments and consequently, chain segments may overlap partially even in a state of maximum swelling. It is supposed that

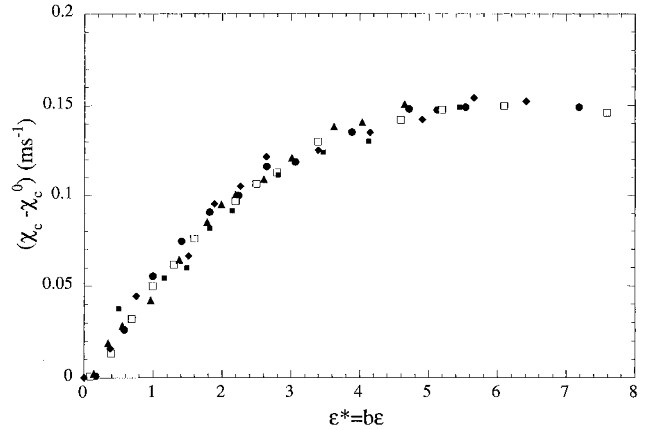

Figure 9. Time dependence of the difference of the NMR structural parameter χ_c. The results were obtained for several values of the silica weight ratio: $\Phi_{si} = 0.4$ (●), 0.2 (◆) and (▼) 0 g/g of polymer.The peroxide weight ratio C_p was equal to 4.5×10^{-3} g/g of polymer.

swollen domains obey both a packing condition and Gaussian statistics; the swelling ratio is then expressed as $Q_m \approx N_Q^{1/2}$. Correspondingly, the NMR structural parameter is written as $\chi_c^s \approx N_Q^{-1}$ or $\chi_c^s \approx Q_m^{-2}$, in accordance with experimental results. The dependence of χ_c^s on Q_m^{-2} implies that excluded volume effects are screened; this reveals the presence of short segments crossing swollen domains which are, nevertheless, characterized by a mesh size, associated with the mean segmental spacing N_Q. This relationship between N_Q and Q_m applies also to polybutadiene chains cross-linked with sulfur.[12]

VII. Role of Silica

The main purpose of this section was to show that variations of the weight ratio of silica aggregates do not induce any change in the gelation mechanism, except for numerical factors; the weight ratio of initiator was kept constant (4.5×10^{-3} g/g of polymer) while the weight ratio of silica was varied from 0 to 0.40 g/g of polymer. The observation of the gel fraction, G, during the progress of the gelation, again yielded a linear dependence of the gelation variable ϵ^* with time; straight lines were drawn through the experimental points of G vs time t, and the corresponding values of the slope K are listed in Table 1. The addition of silica slightly increases the value of the slope. Figure 9 shows the variations of the difference ($\chi_c - \chi_c^0$) vs the variable ϵ^*, for different cross-linked polymers in which the weight ratio of the initiator and of the silica were varied. The initial value of the NMR structural parameter, χ_c^0, depends on the silica weight ratio. The experimental points lie on a single curve.

Variations of the inverse of the swelling ratio, observed for different values of the weight ratio of silica and of the initiator, are presented vs ϵ^* in Figure 10. The plateau value, reached at the end of the gel formation, does not depend on initial concentrations.

It is concluded that network structure properties are hardly modified by the presence of silica; this is probably due to the chemical treatment of the surface of the aggregates which prevents chain adsorption.

VIII. Conclusion

In this work, attention was focused on polymer networks that result from the presence of bridges randomly distributed along high molecular weight

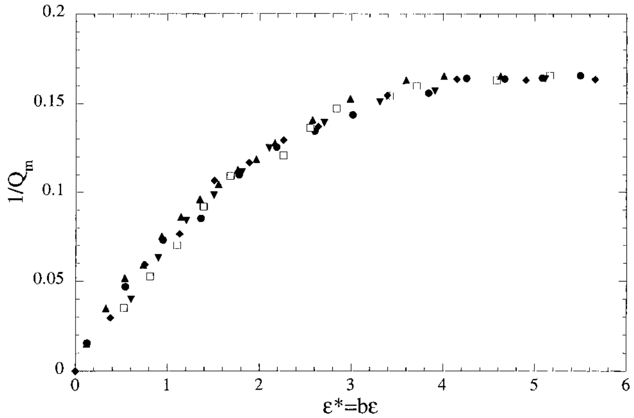

Figure 10. Variations of the inverse of the swelling ratio $1/Q_m$ vs ϵ^*. The results were obtained for several values of the weight ratio of silica and of the peroxide $\Phi_{si} = 0.4$ (●), 0.2 (◆) and (▼) 0 g/g of polymer and $C_p = 4.5 \times 10^{-3}$g/g; $C_p = 3.4 \times 10^{-3}$ (□) and 2.25 (▲) 10^{-3} g/g of polymer and $\Phi_{si} = 0.4$ g/g of polymer.

polymer chains. The concentration of cross-links was low, but polymeric systems were in states of gelation far enough from the percolation threshold to apply a mean field percolation theory to the analysis of the experimental results; this approach leads to the determination of a variable defining the state of gelation at each step of the polymer network formation. This variable is defined by the deviation from the time of threshold of gelation. Within this framework of analysis, the value of the gelation variable can be derived from the gel fraction measured at any time during the cross-linking process; the time dependence of the gelation variable is then related to the fraction of cross-links formed. This analysis is in good agreement with direct observations made by FTIR spectroscopy performed during the polymeric gel formation to monitor the concentration of cross-links. This work shows that the mean field description of the gelation process can be used to estimate the cross-link density in a polymer gel when the formation of links is not easily detected directly.

The statistical structure associated with each state of gelation can be conveniently characterized by observing fully swollen polymeric gels, using NMR. There is a well-defined relationship between the swelling ratio of a gel and the magnetic relaxation rate of protons. This relationship implies that, in the state of maximum swelling, systems formed by long chains cross-linked at random are composed of nearly uniform domains which are swollen; these domains obey a packing condition—in other words they are supposed to be in juxtaposition. The Gaussian statistics that characterizes these domains reveals a screening effect of the excluded volume property. This result contrasts with that obtained from gels formed from end-linked calibrated polymer precursors; for such systems the swelling effect obeys the *c**-theorem proposed by De Gennes.[13] This theorem states that domains obey both a packing condition and excluded volume statistics; NMR observations made on these systems are in agreement with this theorem.[10]

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