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Polybutadiene. Kinetics of Cross-Link Formation Observed from Pseudosolid NMR of Protons

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ABSTRACT: The pseudosolid behavior of the magnetization of protons attached to polybutadiene chains is analyzed to observe the kinetics of cross-link formation. Normalized curves of kinetics are shown to be nearly independent of the concentration of the cross-linking agent (sulfur). The final state of gelation is described by an NMR parameter which is proportional to the concentration of sulfur. The effect of partial average orientation of skeletal bonds is found to be enhanced throughout the whole polymer system whenever the concentration of sulfur is higher than 2×10^{-3} g/g.

I. Introduction

This work deals with NMR observation of the formation of random covalent bridges between high molecular weight polybutadiene chains in a melt. The existence of topological constraints created by the formation of covalent coupling junctions induces an effect of restriction of conformational fluctuations of chain skeletons. The principle of the NMR approach relies upon the detection of this effect of restriction which affects large-amplitude motions of chain segments. More precisely, skeletal bonds are submitted to an average orientational order which exists along any chain segment embedded in a temporary network structure in a melt. This orientational order is enhanced by the formation of cross-links. The effect of enhancement is observed over a large number of skeletal bonds surrounding each cross-link. Consequently, the presence of cross-links can be detected even though their mean concentration is too low to observe them directly. Covalent bridges hinder conformational fluctuations of surrounding chain segments which serve the function of "amplifiers" of properties at one point.

Tensorial interactions which exist between nuclear spins located on chain segments are not averaged to zero because of the average orientational order of skeletal bonds. The residual tensorial interaction of spins which results from the presence of cross-links may govern completely the mechanism of relaxation of the transverse magnetization of protons attached to chain segments. The observation of the formation of cross-links is equivalent to a measurement of the variations of the relaxation rate of the protons of the polybutadiene chains.

The formation of cross-links appears as a progressive invasion of the polymer system by an enhanced orientational order of skeletal bonds. Even though the chemical reaction which governs the formation of cross-links occurs in a uniform way in space and according to a monotonic variation in time, the effect of the restrictions of conformational fluctuations of chain segments which accompanies the cross-linking process is not necessarily uniform.[1] Therefore, it may be of interest to probe statistical properties of chain segments during the gelation. NMR has already proven to be a convenient tool for observation of the kinetics of cross-link formation in high molecular weight polyethylene.[2] The purpose of this work is to characterize the effect of variations of concentration of the cross-linking agent upon the restrictions of conformational fluctuations which affect chain segments during the formation of a permanent network structure.

II. Experimental Section

Polybutadiene samples containing different concentrations of cross-linking agents were kindly supplied by the Manufacture Michelin (France). The chain molecular weight $\bar{M}_n$ was equal to 2.5×10^5 for all samples. The concentration γ_c^s of cross-linking agent (sulfur) was varied from 0.002 to 0.01 g/g of polymer (Table I). All samples were prepared with stearic acid, Santoflex 13, *N*-cyclohexyl-2-benzothiazylsulfenamide (CBS), and zinc oxide (ZnO) in addition to sulfur. The chain microstructure was defined by the following contents of monomeric units: 8% in the vinyl-1,2 conformation, 51% in the trans-1,4 conformation, and 41% in the cis-1,4 conformation. Polymer chains were cross-linked in sealed NMR tubes, with a nitrogen environment at atmospheric pressure in order to avoid any effect of oxidation of polybutadiene. The cross-linking reaction was carried out in the NMR spectrometer by keeping the NMR probe at 423 K. All NMR measurements were performed using a pulse spectrometer (Bruker CXP 60).

III. Enhancement Effect on the Spin–Spin Relaxation

The effect of enhancement of the spin–spin relaxation of protons attached to polybutadiene chains was readily observed by recording the transverse relaxation function $M_x(t,\theta)$ of the polymeric system at different times during the cross-linking reaction. The variable t corresponds to the time evolution of the relaxation function while the variable θ corresponds to the time evolution of the polymeric system. The enhancement effect is illustrated in Figure 1, which corresponds to a sulfur concentration γ_c^s equal to 0.01 g/g of polymer. The cross-linking process was completed after about 30 min at 423 K. It is clearly seen from Figure 1A that the relaxation process is progressively shortened by the presence of cross-links. Also, it is worth noting that the shape of the proton transverse relaxation function $M_x(t,\theta)$ is deformed by comparison with the shape of the function $M_x(t,\theta{=}0)$, observed before the gelation process. In other words, no relaxation function $M_x(t,\theta)$, observed at a time θ during the cross-linking reaction, can be superposed upon the function $M_x(t,\theta{=}0)$ by applying a simple appropriate shift factor s to its time scale; it is found that $M_x(t/s,\theta) \neq M_x(t,\theta{=}0)$, whatever the

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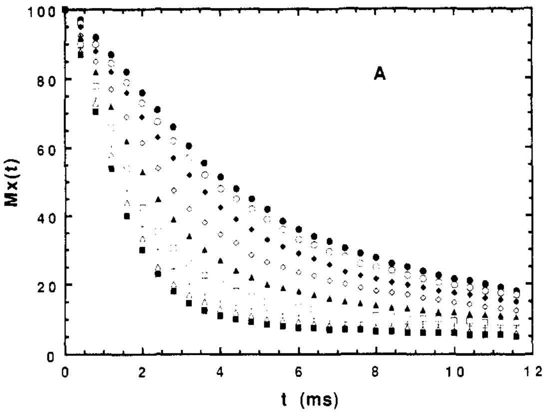
Table I
Concentrations of Cross-Linking Reagents in Studied Polybutadiene Samples

	C_I	C_{II}	C_{III}	C_{IV}	C_V	C_{VI}
ZnO, g/g	0.04	0.04	0.04	0.04	0.04	0.04
stearic acid, g/g	0.025	0.025	0.025	0.025	0.025	0.025
Santoflex 13, g/g	0.015	0.015	0.015	0.015	0.015	0.015
sulfur, g/g	0.002	0.0035	0.004	0.0045	0.005	0.01
CBS, g/g	0.002	0.0035	0.004	0.0045	0.005	0.01



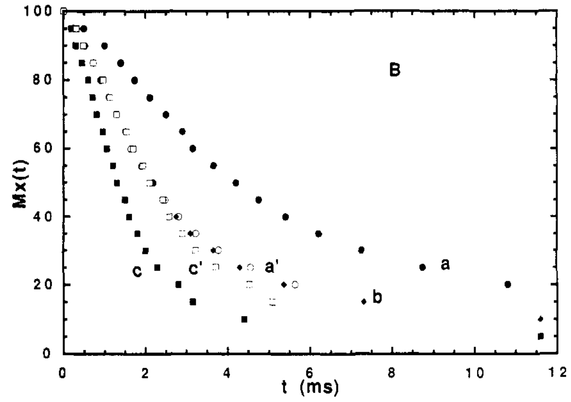


Figure 1. (A) Shortening effect of the transverse relaxation function during the cross-linking reaction at 150 °C. Sulfur concentration: $\gamma_c^s = 0.01$ g/g. Times of observation θ (min): 4 (●); 16 (○); 20 (◆); 22.7 (◇); 24 (▲); 25.3 (□); 26.7 (+); 28 (△); 32 (■). (B) Relaxation functions reported in Figure 1A which do not obey a superposition property after applying a shift factor at the time scale: (a) 4 min (●); (b) 24 min (◆); (c) 32 min (■). a′ (○) and c′ (□) curves are derived from a and b.

value for s. For example, relaxation functions observed at times θ = 4 (curve a), 24 (curve b), and 32 min (curve c) are reported in Figure 1B. It is also shown in this figure that the three relaxation functions do not have the property of superposition; curves a′ and c′ are derived from curves a and c, respectively. No value of the shift factor s can be determined to obtain an exact superposition of a′, b, and c′ curves. In the state where all cross-links are formed a fast decay of the magnetization is first observed until its amplitude is reduced to about 0.2; then, there is a long tail. All relaxation functions were obtained by forming spin-echoes resulting from the usual experimental procedure, proposed by Hahn.[3]

IV. Relaxation Mechanisms

It is now well-known that the transverse magnetic relaxation of protons observed in high molecular weight melts occurs by two main mechanisms. One of them is due to the existence of nonisotropic rotations of monomeric units, which gives rise to a residual interaction of spins; this partial interaction induces a pseudosolid behavior of the magnetization.[4] The other mechanism is a classical contribution associated with the dynamics of skeletal bonds; it depends upon spectral densities of thermal energy $J(n\omega_0\tau_c)$ where ω_0 is the Larmor frequency and τ_c is the correlation time of molecular motions.

In most cases, the transverse relaxation function can be expressed as a product of two functions

$$M_x(t) = M_x^e(t)\ \Phi_e(t) \tag{1}$$

in which $\Phi_e(t)$ is a relaxation function usually characterized by a time scale of about 100 ms or more wherease $M_x^e(t)$ represents a fast decay with a characteristic time of about 2 or 3 ms. The function $\Phi_e(t)$ reflects the dynamics of the skeletal bonds while $M_x^e(t)$ is associated with the degree of asymmetry of these motions. The residual dipole–dipole interaction of spins located on one monomeric unit p which belongs to one chain segment (i,j), determinated by two coupling junctions i and j, is expressed as

$$\mathcal{H}_D^{ij}(p) = (3\cos^2\theta_{ij} - 1)\frac{\langle r_{ij}\rangle^2 \Lambda a^2}{\langle r_{ij}{}^2\rangle_0{}^2}\mathcal{H}_D^0 \tag{2}$$

with

$$\mathcal{H}_D^0 = \frac{3}{5}\sum_{k\neq k'} A_{kk'}(3\cos^2[\theta(\vec{b}_{kk'})] - 1) \tag{3}$$

$\mathcal{H}_D^0$ is the dipole–dipole interaction which should be observed along one chain in the glassy state. The front factor in eq 2 expresses the reduction of the dipole–dipole interaction induced by large-amplitude motions of chain segments. The variable $\langle\vec{r}_{ij}\rangle$ is the nonzero average end-to-end vector of the chain segment (i,j) and θ_{ij} is one of its angular coordinates with respect to the steady magnetic field B_0; $A_{kk'}$ is the spin operator for nuclei k and k' which are joined by the vector $(\vec{b}_{kk'})$. The angular coordinate $\theta[\vec{b}_{kk'}]$ is defined in a local reference frame associated with the monomeric unit p; Λ is the parameter of second-order stiffness which takes angular correlations between three skeletal bonds, located on one chain segment, into considerations.[5] The study of cross-link formation does not require an explicit expression of $\mathcal{H}_D^{ij}(p)$; it is only necessary to emphasize that the residual interaction depends upon the average square distance $\langle r_{ij}\rangle^2$ and the mean-square end-to-end distance $\langle r_{ij}{}^2\rangle_0$. It is now well-known from neutron-scattering experiments that chain segments obey Gaussian statistics in a melt or in a polymeric gel; consequently, the quantity $\sigma_{ij}{}^2 = \langle r_{ij}{}^2\rangle_0$ is equal to $\lambda_c N_{ij} a$ (λ_c is the Kuhn step length, a is the average skeletal bond length, and N_{ij} is the number of skeletal bonds in the segment (i,j)). Thus, the residual dipole–dipole interaction of spins is proportional to $\Lambda\langle r_{ij}\rangle^2/N_{ij}{}^2a^2 = \Lambda\langle r_{ij}\rangle^2 a^2/(\sigma_{ij}{}^2)^2$.

It is worth emphasizing that a residual interaction of spins is associated with the temporary network structure which characterizes any high molecular weight polymer melt. The increase of the residual interaction of spins resulting from a cross-linking reaction is not only induced by the decrease of the number N_{ij} of skeletal bonds between two consecutive cross-links along one chain segment but also results from the restriction of conformational fluctuations of a given segment due to the presence of other cross-links. This last effect may be reflected by Λ.

V. Pseudosolid Behavior

Typical pseudosolid behavior of the transverse magnetization is observed whenever its dynamics is fully

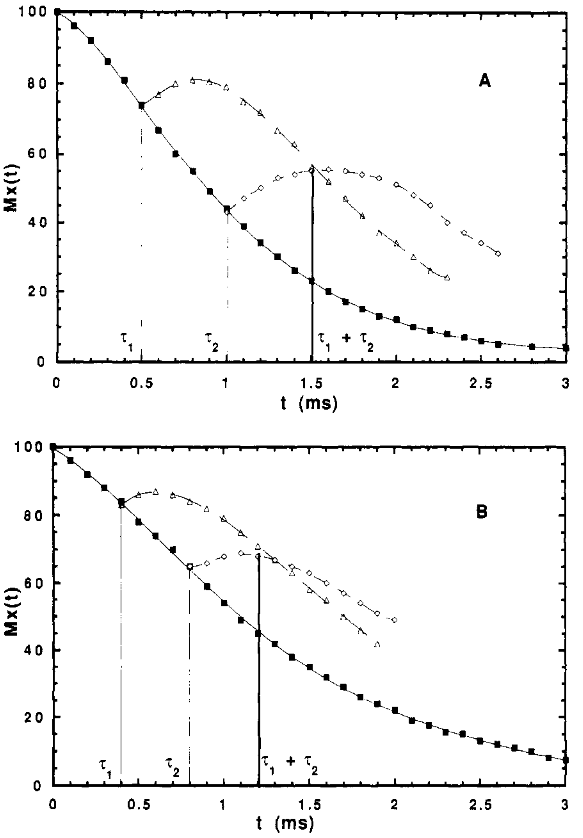


Figure 2. (A) Pseudosolid spin echoes observed at 25 °C, after the end of the cross-linking reaction. They illustrate the property of intersection (sulfur concentration: $\gamma_c^s = 0.01$ g/g). (B) Distorted pseudosolid spin echoes observed before the beginning of the cross-linking reaction.

governed by a residual interaction of spins. The presence of this interaction is clearly revealed by the formation of pseudosolid spin echoes.[6] These are obtained by applying a specific pulse sequence to the spin system; this sequence has already been described elsewhere. Pseudosolid spin echoes have specific properties. For example, the intersection of two echoes formed at $t = \tau_1$ and $t = \tau_2$ must occur at $t = \tau_1 + \tau_2$. This is illustrated by spin echoes observed at room temperature in the polybutadiene sample with the concentration of cross-links ($\gamma_c^s = 0.01$ g/g; Figure 2A).

This behavior is in contrast to that of the magnetization corresponding to a polybutadiene sample observed before the beginning of the cross-linking reaction. It is clearly seen in Figure 2B that the intersection of two echoes formed at $t = \tau_1$ and $t = \tau_2$ is not found to occur at $t = \tau_1 + \tau_2$. This result calls for the following comment. When the relaxation rate of entanglements T_R^{-1} is higher than the residual interaction of spins associated with the temporary network structure of a melt, a partial motional averaging of this interaction is induced. Under these circumstances, pseudosolid echoes are badly shaped and do not obey any characteristic property.

The effect of the cross-linking reaction upon the orientational order of skeletal bonds is illustrated in Figure 3A–C. Pseudosolid echoes progressively formed in a polybutadiene sample characterized by a sulfur concentration $\gamma_c^s = 0.002$ g/g are observed at 423 K at the beginning of the cross-linking reaction (Figure 3A). The relaxation rate of disentanglement is still high enough to induce a partial motional averaging effect of the residual interaction of spins in the presence of a low concentration of cross-links; correspondingly, pseudosolid spin echoes are flat. In the presence of a growing concentration of cross-links, these echoes are less and less flat and distorted; they are illustrated in Figure 3B, recorded 52 min after the beginning of the cross-linking reaction. The maximum amplitude of each echo $\tilde{E}(t,\tau)$ compared with the amplitude of the relaxation function $M_x(t)$ at the same time increases during the gelation process. Finally, the cross-linking reaction is complete 96 min after the beginning of the observations. The pseudosolid spin echoes are well-defined (Figure 3C).

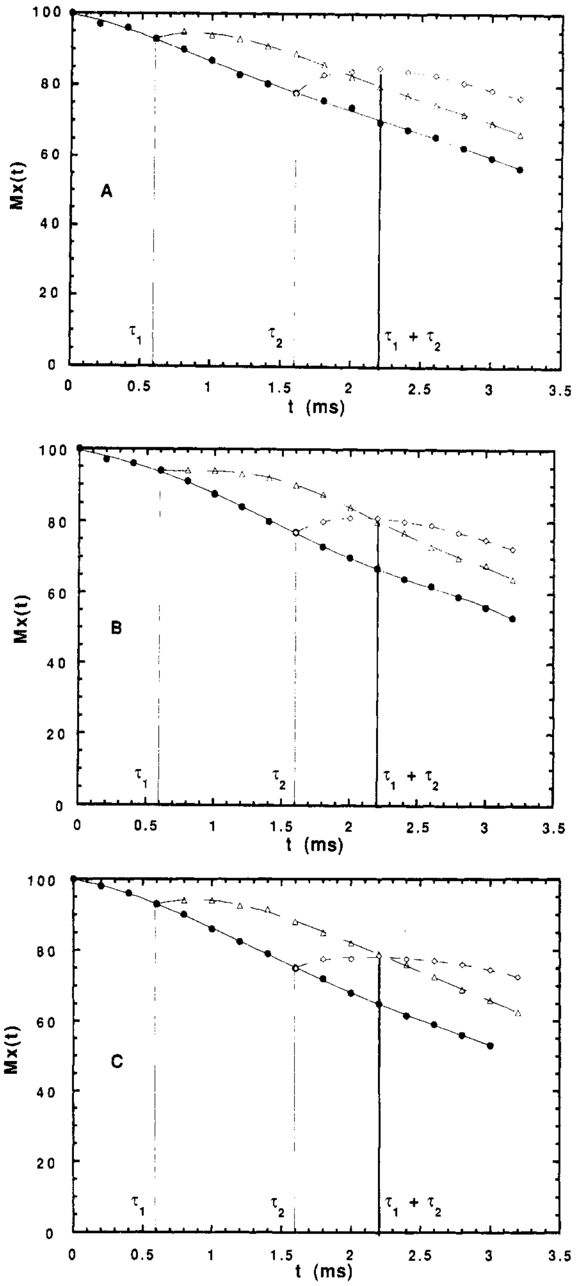


Figure 3. Evolution of pseudosolid spin echoes observed at 150 °C during the cross-linking reaction (sulfur concentration: $\gamma_c^s = 0.002$ g/g). Times of observations are (A) $\theta = 4$ min, (B) $\theta = 52$ min, and (C) $\theta = 96$ min.

The effect of the formation of one cross-link between two chains is, first, to slow down their diffusional motion because it takes more time to get a net displacement of the four arms of the starlike polymer which is obtained than to get a displacement of two separate chains. The formation of one link does not involve the slowing down of the two chains only. It affects also local motions of surrounding chains. More precisely, it may be suggested that each cross-link induces an effect of hindrance within one characteristic cell $\mathcal{C}_c$ which contains q_c monomeric units. Let ω_b denote the average volume of one monomeric unit. The volume of one $\mathcal{C}_c$ cell is then equal to $q_c\omega_b$, and the range of the nuclear magnetic interaction of one cross-link with its neighboring units is determined roughly by the radius $R_\gamma = (q_c\omega_b)^{1/3}$. The parameter q_c defines the number of skeletal bonds which undergo an enhancement of their orientational order because they are in the vicinity of one cross-link.

VI. Principle of the NMR Approach

NMR observation of the progressive effect of cross-linking of chains relies upon the following analysis. The total concentration of cross-links which can be formed is called γ_c,

$$\gamma_c = \gamma_c^s \mathcal{A}/M_s\bar{x}_s$$

where $\bar{x}_s$ is the mean number of sulfur atoms involved in one covalent bridge. The fraction of cross-links established, at a time θ, is represented by $f(\theta)$ $(0 \leq f(\theta) \leq 1)$.

VI.1. Two Relaxation Functions. Domains defined around cross-links do not overlap one another when the concentration of covalent bridges is such that

$$q_c < n_c$$

with

$$n_c = \mathcal{A}/\gamma_c M_b$$

or

$$n_c = \bar{x}_s M_s/\gamma_c^s M_b$$

n_c is the mean number of monomeric units per cross-link and M_b is the average molecular weight of one monomeric unit. In this case, the relaxation function observed over the whole polymer sample should be divided into two parts:

$$M_x^T(t) = \frac{q_c}{n_c} f(\theta)\, M_x^c(t) + \left(1 - \frac{q_c}{n_c} f(\theta)\right) M_x^L(t) \qquad (4)$$

$M_x^T(t)$ corresponds to 1 g of polymer. The relaxation function $M_x^c(t)$ is associated with one monomeric unit submitted to an enhanced orientational order while $M_x^L(t)$ is associated with one monomeric unit p which does not experience any constraint induced by the presence of cross-links. Correspondingly, the relaxation function $M_x^L(t)$ is governed by the residual interaction of spins $\mathcal{H}_D^e(p)$:

$$\mathcal{H}_D^e(p) = \frac{(3\cos^2\theta_e - 1)\langle\vec{r}_e\rangle^2 \wedge a^2}{\langle\vec{r}_e^{\,2}\rangle_0^{\,2}} \mathcal{H}_D^0 \qquad (5)$$

$\langle\vec{r}_e\rangle$ is the mean end-to-end vector which exists between two consecutive entanglements along one chain, in the absence of any cross-links. The relaxation function $M_x^c(t)$ is governed by the residual interaction $\mathcal{H}_D^c(p)$:

$$\mathcal{H}_D^c(p) = \frac{(3\cos^2\theta_c - 1)\langle\vec{r}_c\rangle^2 \wedge a^2}{\langle\vec{r}_c^{\,2}\rangle_0^{\,2}} \mathcal{H}_D^0 \qquad (6)$$

$\langle\vec{r}_c\rangle$ is the mean end-to-end vector which exists between two consecutive cross-links along one chain.

The relaxation function $M_x^c(t)$ is expressed as

$$M_x^c(t) = \frac{T_r\{\exp(i\mathcal{H}_D^c t)\mathcal{M}_x \exp(-i\mathcal{H}_D^c t)\mathcal{M}_x\}}{T_r\{\mathcal{M}_x^{\,2}\}} \qquad (7)$$

in which $\mathcal{M}_x$ is the transverse spin operator. A similar expression applies to $M_x^L(t)$.

Such an analysis was applied to the study of cross-linked polyethylene chains. The relaxation function was found to be a linear expression of two basic functions; one of these ($M_x^L(t)$) was observed in the absence of cross-links while the other one ($M_x^c(t)$) was observed at the end of the cross-linking reaction.[2] The gel fraction $f(\theta)$ measured by NMR was found to be in agreement with the gel fraction G measured directly by weighing washed samples. However, this analysis cannot be extended to cross-linked polybutadiene chains. In no case could experimental relaxation functions observed in these systems be described as a linear expression of two basic functions.

VI.2. Role of Entanglements. The main difference between NMR properties observed in polyethylene and polybutadiene arises from the effect of polydispersity. In the case of polyethylene, the weight-average molecular weight was 2.2×10^5 and the index of polydispersity was 15; short chains (1.5×10^4) play the role of a solvent, and entanglements form a network structure which is observed as temporary by NMR. Magnetic properties in one $\mathcal{C}_c$ cell are contrasted to the remaining part of the polymer in all of the cells. In the case of polybutadiene, the index of polydispersity is very low and the molecular weight is high enough to allow the network structure formed by entanglements to be permanent. The presence of cross-links enhances this effect of permanent network structure. Consequently, it is supposed that a progressive evolution of nuclear magnetic properties occurs throughout the polymer system considered as a whole during the cross-linking reaction. The analysis relies upon the assumption that one cell $\mathcal{C}_e$ can be associated with each segment defined by two consecutive entanglements along one chain. Each segment is characterized by its mean contour length $L_e = aN_e$. The value of the molecular weight M_e corresponding to the mean spacing between entanglements is known for polybutadiene: $M_e \approx 2 \times 10^3$.[7] Therefore, the mean volume of each $\mathcal{C}_e$ cell is written as

$$V_e \approx N_e^{3/2} C_\infty^{3/2} a^3$$

The characteristic ratio C_∞ of long polybutadiene chains is about 6. Therefore, the average number of monomeric units in the volume V_e is $n_e = 7 \times 10^3$; this volume is considered as a space domain where long-range dynamic fluctuations which occur along one chain are screened. The mean number of entanglements in one $\mathcal{C}_e$ cell is equal to 35. It will be shown in section VII that NMR begins to be sensitive to the presence of covalent bridges when the concentration of sulfur is about 10^{-3} g/g. This corresponds to a number of monomeric units n_c equal to 6×10^3. It is considered in this work that the presence of cross-links affects the orientational order of all skeletal bonds in a uniform way throughout the polymer system when there is about one cross-link per $\mathcal{C}_e$ cell. In other words, contrary to the case of polyethylene, the system of cross-linked polybutadiene chains cannot be divided into two types of domains characterized by two different basic relaxation functions.

VI.3. Gel Distribution Function. It is considered that in the absence of any cross-links there is a distribution function of mean end-to-end vectors $G(\langle\vec{r}_e\rangle/\sigma_e)$ corresponding to the temporary network structure defined by entanglements; σ_e^2 is the mean-square end-to-end distance between two entanglements. This function has been applied to the description of NMR properties observed in a polybutadiene melt or in poly(dimethylsiloxane). It is now supposed that in the presence of cross-links there is a modified distribution function. The width of this Gaussian function is no longer defined by σ_e; it depends upon the concentration of cross-links which are formed at a given time θ during the gelation process. Let $\sigma_c(\theta) = \sigma_c(f(\theta)\gamma_c)$ denote the root-mean-square end-to-end distance between any two coupling junctions in the polymer system; then $\sigma_c(\theta) = \sigma_e$ for $\theta = 0$.

VI.4. Moments of the Gel Distribution Function. Relaxation functions observed during the process of cross-linking are analyzed in the following way. It is first considered that each segment (i,j) can be characterized by one transverse magnetic relaxation function of protons $m_{ij}^{x}(t,\theta)$. This is governed by the residual interaction defined along the segment (i,j). Then, the transverse magnetization observed over the whole gel system is written as

$$M_x(t,\theta) = \int m_{ij}^{x}(t,\theta)\, g\{\langle\vec{r}_c\rangle/\sigma_c(\theta)\}\, \mathrm{d}\langle\vec{r}_c\rangle \qquad (8)$$

The probability distribution function $G\{\langle\vec{r}_c\rangle/\sigma_c(\theta)\}$ can be characterized by its moments by calculating the quantities

$$\phi_1^{T} = \int t^{-1/2} M_x^{T}(t)\, \mathrm{d}t \qquad (9)$$

and

$$\phi_3^{T} = \int t^{-1/2} \frac{\mathrm{d}M_x^{T}(t)}{\mathrm{d}t}\, \mathrm{d}t \qquad (9')$$

with $M_x(0) = 1$. More weight is given to the initial part of the relaxation function than to its tail. The quantities ϕ_1^T and ϕ_3^T are functions of the time variable θ of the evolution of the polymer system. It has been already shown elsewhere that

$$\phi_1^{T} \propto \frac{\sigma_c}{a\sqrt{\Delta}} \frac{1}{\sqrt{\Lambda}} \frac{m_1}{m_2} \qquad (10)$$

and

$$\phi_3^{T} \propto \frac{a\sqrt{\Delta}}{\sigma_c} \sqrt{\Lambda} \frac{m_3}{m_2} \qquad (10')$$

with the general definition

$$M_n = \int_0^{\infty} \left(\frac{\langle r_c\rangle}{\sigma_c}\right)^n G\left(\frac{\langle r_c\rangle}{\sigma_c}\right) \frac{\mathrm{d}\langle r_c\rangle}{\sigma_c} \qquad (11)$$

and the normalization condition

$$\int G\left(\frac{\langle r_c\rangle}{\sigma_c}\right) \frac{\mathrm{d}\langle r_c\rangle}{\sigma_c} = 1 \qquad (11')$$

Δ represents the strength of dipole–dipole interactions, in the absence of any motion of chain segments.[8] It is of interest to calculate the ratio $\chi_c = \phi_3/\phi_1$

$$\chi_c \propto \frac{a^2\Delta}{\sigma_c^{\,2}} \Lambda \frac{m_3}{m_1}$$

and the product $\pi_c = \phi_3\phi_1$

$$\pi_c \propto m_3 m_1/m_2^{\,2}$$

The product $\phi_3^T\phi_1^T$ permits us to observe possible changes of the mathematical structure of the distribution function G resulting from the presence of cross-links. In the case where the product is found to be constant, the ratio ϕ_3^T/ϕ_1^T is directly related to the mean-square value of the average end-to-end vector $\langle\vec{r}_c\rangle$ associated with the network structure defined by entanglements and cross-links.[7]

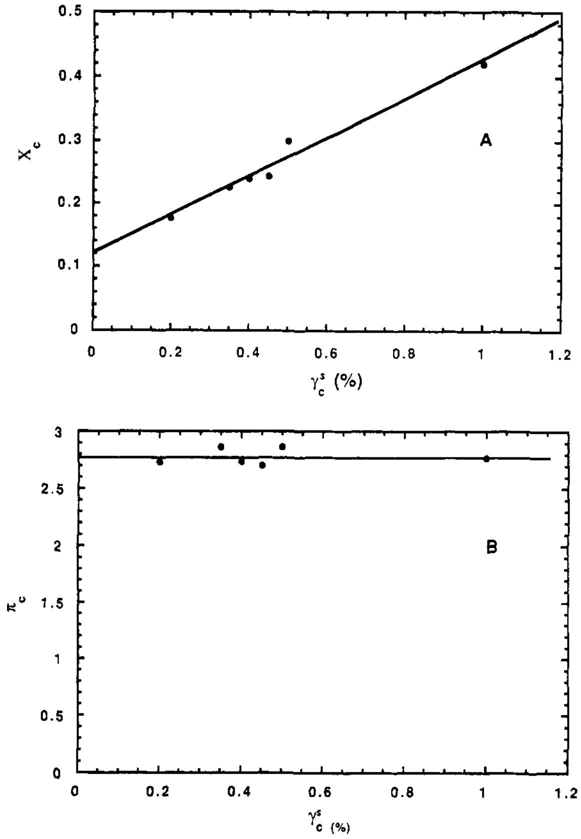


Figure 4. (A) Linear variation of the parameter χ_c determined in the final state of gelation as a function of sulfur concentration. (B) Parameter π_c determined in the final state of gelation which is independent of sulfur concentration.

Before analyzing NMR experimental results, it is worth characterizing final states of cross-linked chains which are reached when the formation of all covalent bridges is completed.

VII. Final State of Gelation

It has been recently shown that the state of gelation of vulcanized polybutadiene chains can be determined by using the reduced variable $\epsilon = \gamma_c^s\bar{M}_n - W(1,2)$; $\bar{M}_n$ is the number-average molecular weight of polymer chains, and γ_c^s is the initial concentration of sulfur. The threshold $W(1,2)$ depends upon the chain microstructure; it has been found to be equal to 800 g^{-1} for the polybutadiene chains used in this study.[9] On the one hand, it has also been shown that the polymer volume fraction measured in the state of maximum swelling by a good solvent is represented by a single curve whatever the concentration of sulfur or the molecular weight $\bar{M}_n$. On the other hand, the modulus of elasticity E is also a single function of $\gamma_c^s\bar{M}_n$ provided the value of this product is higher than 800 g^{-1}. In this work, the value of $\gamma_c^s\bar{M}_n$ varies from 500 to 2500 g^{-1}; no infinite clusters are formed in samples characterized by a sulfur concentration of 2×10^{-3}, while the five other samples behave like permanent gels.

The final state of gelation was characterized by the NMR parameter χ_c; variations of χ_c were found to be a linear function of sulfur concentration (Figure 4A). For $\gamma_c^s = 0$, the ratio $\chi_c(0)$ corresponds to simply entangled chains. Results reported in Figure 4 show that the effects of cross-linking upon the NMR behavior are additive. Enhancement of the orientational order of skeletal bonds results from a density of topological constraints which is proportional to the concentration of cross-links. There is no mutual influence of cross-links upon one another to increase the orientational order. In addition to Figure 4A, Figue 4B shows that the product π_c is kept constant; this independence with respect to the concentration of cross-links shows that the mathematical structure of the statistical law of distribution of end-to-end vectors between coupling junctions is invariant except for the width of this distribution. The quantity $\chi_c(\gamma_c^s)$ is expressed as

$$\chi_c(\gamma_c^s) = \chi_c(0) + \mu\gamma_c^s \qquad (12)$$

The numerical value of the slope μ is determined experimentally: $\mu = 0.307$.

According to eqs 10, 10′, and 12, the quantity $1/\sigma_c^2$ is also a linear function of γ_c^s

$$1/\sigma_c^2 = 1/\sigma_e^2 + \mu^*\gamma_c^s \qquad (13)$$

with

$$\mu^* = \mu m_1/(\kappa m_3 a^2 \Delta\Lambda) \qquad (13')$$

κ accounts for numerical constants in eqs 10 and 10′. Also, the average number of entanglements per gram of polymer is written as a function of the number N_e of monomeric units located between two consecutive entanglements along one chain

$$\gamma_e = \mathcal{A}/N_e M_e$$

or

$$1/\sigma_e^2 = \gamma_e M_b/\mathcal{A}C_\infty a^2$$

with

$$\sigma_e^2 = \mathcal{A}C_\infty a^2 N_e$$

Therefore, the empirical law (13) represents the addition of densities of coupling junctions whatever their exact nature; the total density γ_J of junctions obeys the relation

$$\frac{\nu_J M_b}{\mathcal{A}C_\infty a^2} = \frac{\nu_e M_b}{\mathcal{A}C_\infty a^2} + \mu^*\gamma_c^s \qquad (14)$$

where

$$\gamma_J = \gamma_e + \mu^{**}\gamma_c \qquad (15)$$

with

$$\mu^{**} = \mu m_1 M_s x_s C_\infty/\kappa m_3 M_b \Delta\Lambda$$

The estimate of the average number of cross-links formed at the highest sulfur concentration is about 5 per $\mathcal{C}e$ cell; this number is small compared with the estimate of the number of entanglements in one $\mathcal{C}_e$ cell. This is probably the reason why a simple linear dependence of χ_c upon the sulfur concentration is observed in Figure 4A. The presence of cross-links induces a weak perturbation of NMR properties. Deviations from the linear behavior represented by eq 15 should disappear when the sulfur concentration becomes much higher than 0.01 g/g.

VIII. Kinetics of Cross-Link Formation

The NMR parameter $\chi_c(\theta)$ is represented as a time function in Figure 5. Several concentrations of cross-linking agent are considered. The search for a possible effect of the sulfur concentration upon the kinetics of cross-link formation is developed in the following way. All experimental curves are first given the same amplitude of variations in Figure 6; γ_c^s curves are transformed into γ_c^N curves. Then, a shift factor a_γ is applied to the time scale of each curve, except for the curve corresponding to the highest sulfur concentration $\gamma_c^N(\max)$; this curve is left unchanged. For each sulfur concentration, a new function $\chi_c^R(\theta)$ is defined according to the equation

$$\chi_c^R(\theta) = \chi_c^N(a_\gamma\theta)$$

with

$$a_\gamma = \gamma_c^s/\gamma_c^s(\max)$$

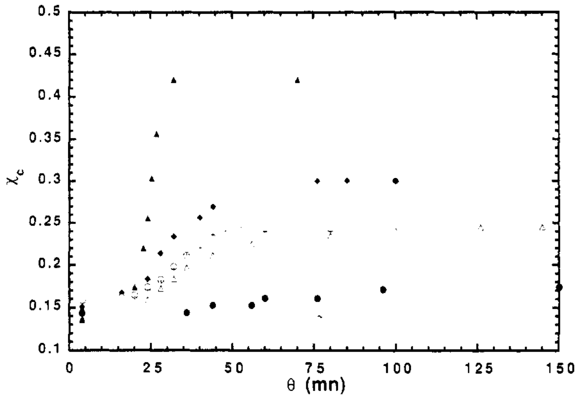


Figure 5. Evolution of χ_c as a time function for several sulfur concentrations: 0.01 g/g (▲); 0.005 g/g (◆); 0.0045 g/g (○); 0.004 g/g (+); 0.0035 g/g (△); 0.002 g/g (●).

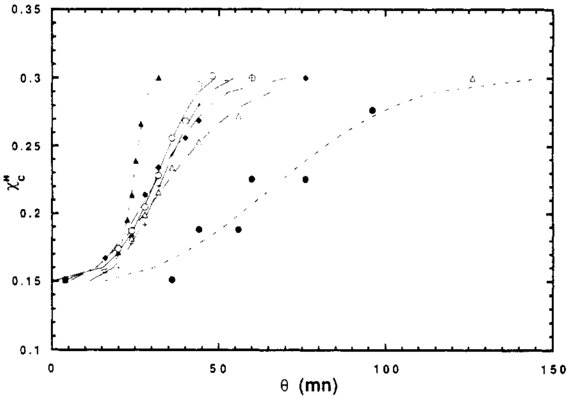


Figure 6. Experimental curves reported in Figure 5 given the same amplitudes: 0.01 g/g (▲); 0.005 g/g (◆); 0.0045 g/g (○); 0.004 g/g (+); 0.0035 g/g (△); 0.002 g/g (●).

The shift factor a_c is supposed to be proportional to the concentration γ_c^s. All curves drawn by applying the factor a_γ are shown in Figure 7A. They are not found to exhibit exactly the same steepness. Experimental curves are more easily compared with one another when the value of the shift factor is set arbitrarily equal to $1.5\gamma_c^s/\gamma_c^s(\max)$. It is clearly seen in Figure 7B that curves of gelation kinetics cannot be superposed. Therefore, there is a weak effect of the sulfur concentration upon the kinetics observed by NMR. However, a property of partial superposition can be observed at low concentration of cross-links; this is illustrated by considering transverse relaxation functions which correspond to the same value of the ratio $\chi_c(\theta) = 0.2$ with $\theta = 21$ min for $\gamma_c^s = 0.01$ g/g, $\theta = 25$ min for $\gamma_c^s = 0.005$ g/g, and $\theta = 30$ min for $\gamma_c^s = 0.0045$ g/g (Figure 8). Although initial concentrations of cross-linking reagents are different, relaxation functions reflect identical NMR

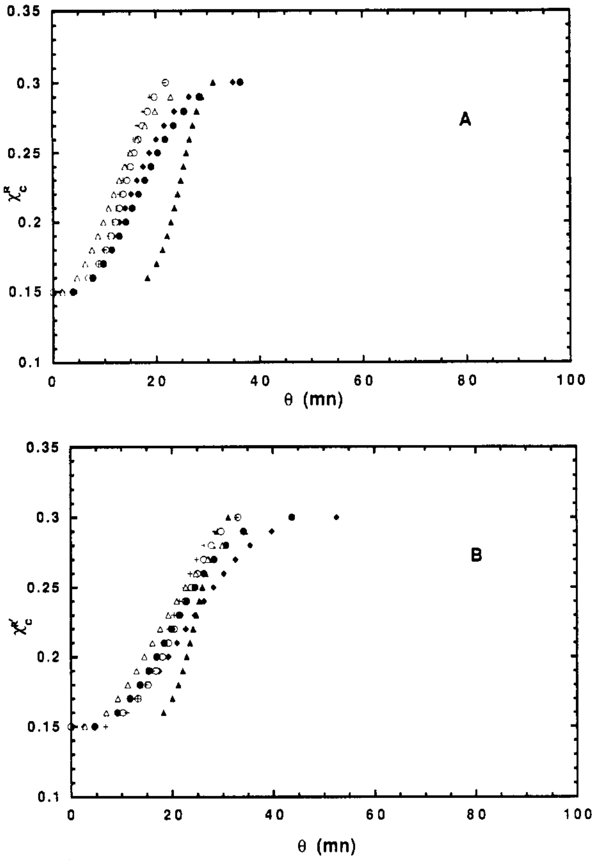


Figure 7. (A) Shift factor proportional to the sulfur concentration applied to the time scale of each kinetics curve: 0.01 g/g (▲); 0.005 g/g (◆); 0.0045 g/g (○); 0.004 g/g (+); 0.0035 g/g (△); 0.002 g/g (●). (B) No property of exact superposition observed when applying a shift factor equal to 1.5 γ_c^s: 0.01 g/g (▲); 0.005 g/g (◆); 0.0045 g/g (○); 0.004 g/g (+); 0.0035 g/g (△); 0.002 g/g (●).

properties within an uncertainty smaller than 3.5%. The property of partial superposition of curves of gelation kinetics is shown in Figure 9A. Experimental curves were translated until they were partly in coincidence with one another; they were drawn without changing amplitudes. Variations of the shift factor of the time scale are reported as a γ_c^s function in Figure 9B. The dependence of a_γ is found to be reasonably linear up to a concentration of sulfur of about 0.005 g/g. The property of partial superposition of curves of gelation kinetics, on the one hand, and the linearity of the parameter χ_c in the final state of gelation, on the other hand, show that deviations from the property of full superposition of normalized curves cannot be associated with the NMR observation. These deviations originate from chemical properties which govern the kinetics of cross-link formation.

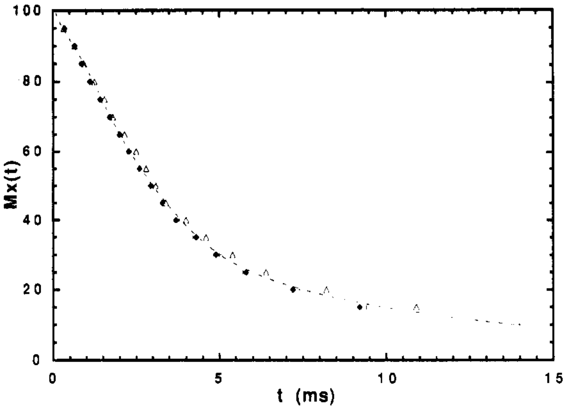


Figure 8. Superposition of the transverse relaxation functions corresponding to the same value of χ_c = 0.2: θ = 21 min for γ_c^s = 0.01 g/g (△); θ = 25 min for γ_c^s = 0.005 g/g (+); θ = 30 min for γ_c^s = 0.0045 g/g (◆).

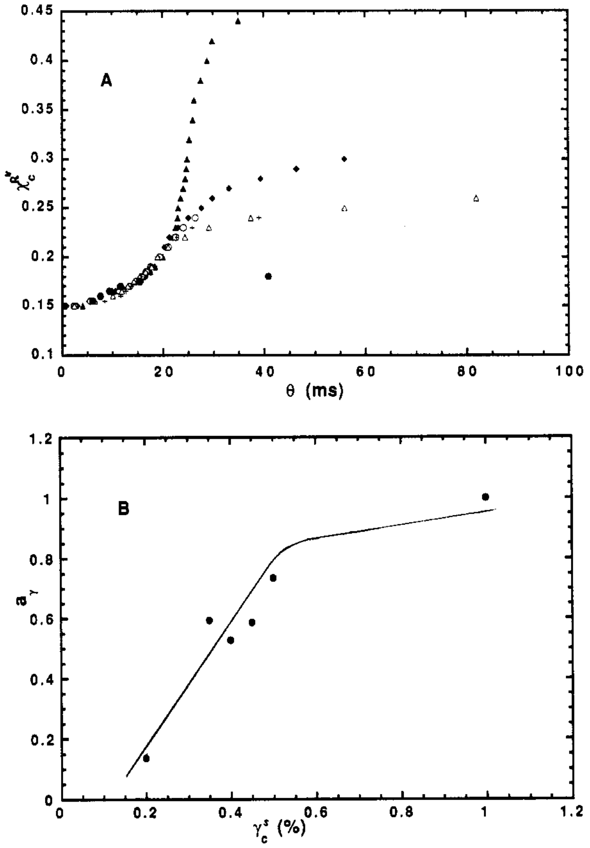


Figure 9. (A) Superposition of curves of gelation kinetics drawn from Figure 5. Sulfur concentrations are as follows: 0.01 g/g (▲); 0.005 g/g (◆); 0.0045 g/g (○); 0.004 g/g (+); 0.0035 g/g (△); 0.002 g/g (●). (B) Variation of the shift factor a_γ applied to the time scale of curves of gelation kinetics to obtain a partial superposition.

IX. Conclusion

The plateau behavior which characterizes the shear modulus of relaxation of any high polymer melt is usually associated with the existence of a temporary network structure. Such a picture is used to account for the presence of long-range topological constraints. Strands corresponding to short segments can adjust rapidly, but considerably more time is required for entire molecules to slip around the contour of one another. Long-range constraints vanish according to a relaxation process strongly dependent upon the chain molecular weight whereas random motions which occur within short segments are insensitive to chain-length variations; there is a so-called effect of the dynamic screening of long-range chain fluctuations. The lifetime of the transient network structure is usually much longer than the time scale of NMR observations; consequently, properties of the transverse relaxation of protons attached to polymer chains are analogous to those observed in permanent gels. These properties originate in nonisotropic rotations of skeletal bonds. In the case of polybutadiene, the presence of permanent cross-links gives rise to an enhancement of the anisotropy effect, which appears as a linear function of the concentration of the cross-linking agent. This enhancement results from more and more restricted chain fluctuations. It is of interest to note that there is no discontinuity between NMR properties observed in highly entangled chains and those observed in cross-linked chains and extrapolated to zero concentration of cross-links. The partial orientational property is found to affect all skeletal bonds throughout the whole polymer system within the range of sulfur concentration studied in this work. This probably reflects a collective orientational behavior of skeletal bonds in polybutadiene. Highly entangled chains or cross-linked polymers observed by NMR can be described as an ensemble of partly extended segments. In systems of cross-linked chains, they are permanently extended on average, even in the absence of any external constraint.

Within the framework of interpretation of NMR properties it must be considered that covalent coupling junctions are uncrossable; in other words, the end-to-end vector of any segment joining two consecutive cross-links is different from zero on average, over a time interval of at least 10 ms.

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