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NMR and Viscoelastic Investigations into the Structure and Dynamics of Emulsion Copolymer Gels

J. P. Cohen-Addad and F. Desbat

Laboratoire de Spectrométrie Physique, Université Joseph Fourier (Grenoble I),
BP 87, 38402 St. Martin d'Hères Cedex, France

J. Richard[*]

Centre de Recherches d'Aubervilliers, Rhône-Poulenc SA, 52 rue de La Haie-Coq,
93308 Aubervilliers Cedex, France

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ABSTRACT: This work deals with structural and dynamical properties of copolymer gels containing free branched chains which were prepared by styrene–butadiene emulsion copolymerization. The gel fraction of the emulsion copolymers was varied within a large range (15–90%) by adding different chain transfer agents during the polymerization process. NMR experiments were performed on homogeneous polymer films obtained by coalescence of the particles upon drying of the dispersions. Properties of dry extracted gels, gels swollen by free chains, or gels fully swollen by a good solvent were investigated to bring out the statistical structure of the gels. A time–temperature superposition principle was found to provide a good analysis of the time dependence of the transverse magnetic relaxation functions. The temperature dependence of the scale factors reveals the strong role played by the free chains in the system. Finally, through the description of the state of constraints encountered by chain segments, NMR and viscoelastic features of these partly cross-linked systems are shown to be consistently interrelated.

I. Introduction

The purpose of this work was to investigate structural and dynamical properties of copolymer gels prepared by emulsion polymerization; investigations were based on NMR and dynamic viscoelastic measurements. It is now well established that NMR properties of protons attached to entangled chains or covalent gels reflect the state of constraints encountered by chain segments embedded in the network;[1] then, through the description of statistical properties of chain segments, this semilocal approach to the network structure complements the viscoelastic measurements which are a macroscopic probe for elasticity.[2] In a previous work,[3] the viscoelastic properties of partly cross-linked polymer films obtained from styrene–butadiene emulsion copolymers were reported with a special emphasis on the chain dynamics in the system. However, the average macroscopic character of most of the network features derived in this work has been identified as the main restriction of the approach and has prevented us from getting an accurate image of the structure. In the present work, attention is focused on the same kind of systems and investigations are mainly based on semilocal observations resulting from the magnetic relaxation of protons located on the chain segments.

Homogeneous polymer films can be obtained from latexes through water evaporation and coalescence of the particles.[4,5] In the present case, the particles consisted of covalent gels which were built up during emulsion radical polymerization and which were swollen by free branched chains.[6] The effect of cross-linking density was studied and the statistical structure of the polymer network was investigated from the proton transverse relaxation combined with swelling effects. Another purpose of the work was then to bring out connections between the NMR parameters and the physical quantities derived from viscoelastic and swelling investigations.

Table 1. SB Copolymer Particle Contents

latex	av SB comp (wt %)	CTA type	CTA concn (wt %)
1	S = 69	Cl	0
2	B = 27	Cl	0.4
3		Cl	0.8
4		Cl	1.25
5		Cl	2
6	S = 69	C2	0.4
7	B = 27	C2	0.8
8		C2	1.6
9		C2	3.2
10	S = 41 B = 55	Cl	1.6
11	S = 54 B = 42	Cl	1.6
12	S = 59 B = 37	Cl	1.3
13	S = 81 B = 15	Cl	0.8

II. Experimental Section

(a) Samples. A series of latexes with different compositions of styrene (S) and butadiene (B) comonomers were prepared with various concentrations of two different chain transfer agents (CTA). The emulsion polymerization process used in this work has been previously described.[6] It was carried out in a semicontinuous way, where monomers are added to an initial load. The feed rate of the monomer mixture was chosen to result in starved conditions; i.e., the polymerization rate is equal to or higher than the addition rate. The radical polymerization initiator was ammonium persulfate. The volume fraction of polymer in water at the end of polymerization was close to 50%. We used classical chain transfer agents to vary the cross-linking density of the polymers: an alkyl mercaptan (C1) and a polyhalogenated organic compound (C2). The stability of the colloidal dispersions was obtained by copolymerizing a small amount of an acrylic-type comonomer. The average particle size of all the latexes was found to be ~0.18 μm with a narrow width of the size distribution. Latex features are given in Table 1. Polymer films were prepared by dehydration of these dispersions. After degassing and concentrating under a moderate vacuum, they were cast in nonsticking smooth silicone molds. These concentrated dispersions were then dried at 50 °C in an oven for

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[*] Author to whom correspondence should be addressed.

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6 h. Homogeneous transparent solid films were achieved in this way. They were stored under vacuum in a desiccating vessel prior to use.

(b) Gel Fraction and Equilibrium Swelling. Polymer films contained both covalently cross-linked networks and free branched chains. We used the classical definition for the gel fraction G, i.e., the ratio of the weight of dry extracted gel to that of the original sample. The sol was extracted at room temperature in three solvents: chloroform, toluene, or dimethylformamide (DMF). To avoid the breaking of samples during the experiments, films were carefully put onto appropriate filters of controlled porosity, which were dipped in the solvent. They were then allowed to swell for 48 h at room temperature before the solvent containing the free chains was removed. The filters containing the swollen gels were weighed. Afterward, new solvent was added, and the extraction procedure was repeated until equilibrium values were obtained for the weight of the swollen gels. The total period of time needed for the extraction was typically 4 days, the solvent being renewed twice. Swollen gels were dried for 24 h at 60 °C after removing the sol fraction. The whole procedure for extraction enabled us to make sure that the large sol molecules, which were the most difficult to extract and yet contribute to the sol fraction, were actually removed.

For each film, the extraction experiment was performed on three different samples for each solvent. The results of the measurements were found to be reproducible within a 10% accuracy, except for samples with low gel fraction values ($G <$ 60%), which exhibit an unreproducible puzzling behavior in DMF only and which were not considered in the rest of the study.

The ratio of the swollen gel volume to the dry extracted gel volume was taken as the definition for the equilibrium swelling ratio of the samples Q_m. It was measured at the end of the extraction performed at 295 K in the three solvents (chloroform, toluene, or DMF). After the swollen and the dry extracted samples were weighed, Q_m was derived using the density values for the solvent and polymer. The accuracy of the measurements was found to be ~10% for the swelling ratio Q_m, as long as it remained <30; for higher values of Q_m, the accuracy was only 15%. The reproducibility of Q_m measurements was checked to be satisfactory, except for samples with G values lower than 60% in DMF, which were not considered in the rest of the study.

(c) NMR Measurements. NMR measurements were carried out on a CXP Bruker spectrometer operating at 34 MHz which was equipped with an attachment for temperature control. Relaxation functions of all samples were recorded between 45 and 120 °C. All samples were placed in sealed NMR tubes in a nitrogen environment. Two kinds of samples were investigated for their proton relaxation behavior. The former were the gels in their reaction bath; i.e., they consisted of the as-polymerized systems which contain the cross-linked networks swollen by the free branched chains and which formed polymer films upon dehydration. The latter were the dry extracted gels obtained after solvent extraction of the free chains in these films and drying.

Transverse magnetic relaxations were observed by applying a Carr–Purcell sequence to overcome the dispersal effect of precession rates arising from inhomogeneities of the samples. To probe the magnetic relaxation mechanism and the effect of topological constraints exerted on the chains, pseudosolid spin-echo measurements were also performed applying the pulse sequence proposed recently.[2,7]

(d) Viscoelastic Measurements. Dynamic micromechanical analysis (DMA) was performed using the Rheometrics RDS-LA viscoelastometer described previously.[3,8] Isothermal master curves of the extension moduli were obtained by sweeping the frequency of the sine deformation between 10^{-1} and 500 rad s^{-1} at different temperatures close to the glass transition temperature (T_g) of the samples and shifting the spectra along the frequency axis until a reliable superposition was obtained for the three viscoelastic functions (E', E'', $\tan \delta$). Criteria of the applicability of this method were checked to be fulfilled for our samples.[3,9] The strain amplitude ranged between 5×10^{-4} and 3×10^{-3}, which was checked to lie in the linear viscoelastic regime. The samples were long rectangular strips of well-controlled dimensions cut from the dried polymer films.

Table 2. Gel Fraction Values Obtained in Chloroform (G_c), Toluene (G_t), and DMF (G_d) for the Series of SB Copolymer Films

film	G_c (wt %)	G_t (wt %)	G_d (wt %)
1	89.5	80	94
2	76	84.5	86.5
3	69.5	65.5	67
4	43.5	42.5	ND[a]
5	15	15	ND
6	81.5	81	78.5
7	71.5	72	69.5
8	40	47.5	ND
9	17	26	ND
10	55	62	74.5
11	44	44	ND
12	50.5	54	ND
13	72.5	76.5	69.5

[a] ND = not determined because of poor reproducibility.

III. Gel Fraction

Gel fraction values of the whole series of polymer films were measured by washing samples with chloroform, toluene, or DMF. Values obtained from chloroform (G_c), toluene (G_t), DMF (G_d) are reported in Table 2. As previously noticed, only a few results were obtained in DMF because of poor reproducibility of the measurements. The origin of this behavior is not well understood; however, it could be related to the rather high polarity of the solvent, which could induce strong interactions with the particle–particle interfaces within the films, these regions being more polar than the core of the particles.[10] For this reason, DMF is expected to preferentially swell the particle–particle interfaces, and this inhomogeneous diffusion of solvent in the film is expected to give rise to a redispersion of the individual particles in the solution rather than extraction of free chains. The occurrence of this phenomenon appeared to be very sensitive to the gel fraction of the polymers and to be enhanced for low gel fraction samples which were definitely broken in DMF. On the contrary, the integrity of almost every sample was preserved in chloroform and toluene, whatever the gel fraction value. Moreover, comparison of the values of G_t and G_c shows that, except for a slight scattering of experimental points in the high-G region (within 12%), the two series of values are close to each other. Thus only the value of G_t will be considered in the rest of this section. Let us focus now on the series of samples (1–9) prepared from the same S/B ratio (69/27) and discuss the variations of G_t as a function of CTA content γ_C (Figure 1a for CTA C1 and Figure 1b for CTA C2). First, it is worthwhile noticing that $G(\gamma_C)$ does not tend to unity, even when γ_C is equal to zero: the polymerization process without chain transfer agent does not produce chains all attached to one another. Second, it is also clearly seen from Figure 1 that the gel fraction G is a decreasing function of the CTA content γ_C. This behavior can be predicted using a theoretical model developed recently.[6] Apart from the distribution of branching and cross-linking in styrene–butadiene emulsion copolymers that this work brought out, the following key points concerning the gel formation process are worth noting. In these systems, cross-linking mainly occurs through the coupling of free growing radicals to pendent vinyl groups resulting from 1,2 addition on butadiene (Figure 2), the residual double bonds in the main chains being unreactive toward cross-linking reactions. However, the reactivity of the 1,2 pendent vinyl groups is rather low, since their reactivity ratio for various styrene–butadiene comonomer compositions has been found to be $\sim 2 \times 10^{-3}$.[6] This low value appears to be quite consistent with our results which show that, even

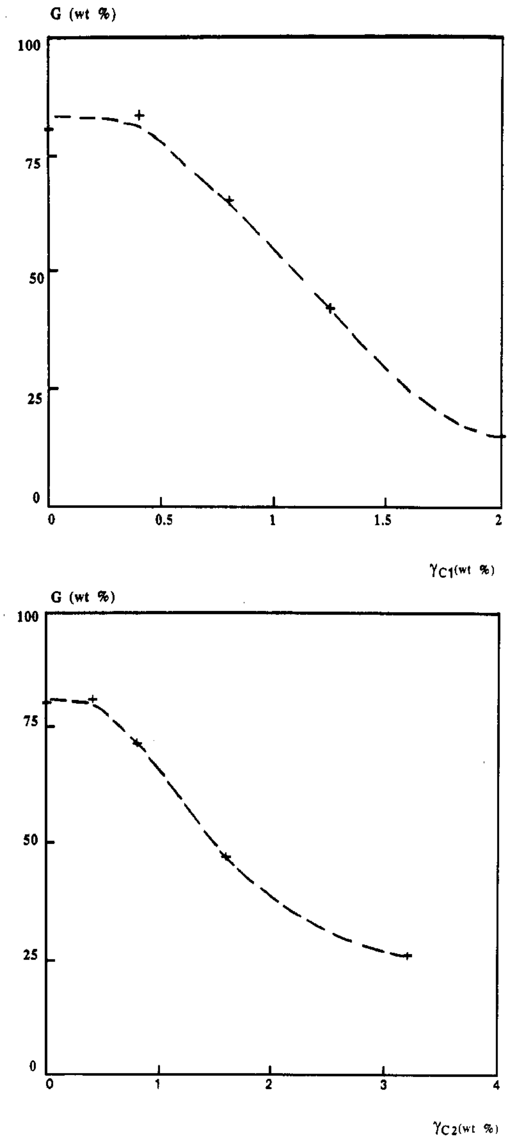

Figure 1. Variations of the gel fraction G (wt %) as a function of the content of (a, top) CTA C1 (γ_{C1} (wt %)) and (b, bottom) CTA C2 (γ_{C2} (wt %)) for the samples of S/B ratio 69/27 (wt/wt).

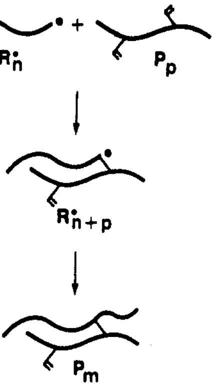

Figure 2. Schematic drawing of the cross-linking process through the coupling of a free growing radical to pendent double bonds in radical polymerization.

without chain transfer agent, the polymerization process does not produce a network containing all chains attached to each other. The addition of CTA during polymerization delays the onset of gel formation toward the period of high monomer conversion. Furthermore, the above experimental results clearly show that γ_C should be larger than a few percent to preclude it totally. Another interesting point is that the instantaneous cross-link density dramatically increases only at monomer conversions higher than 90%. In other words, the cross-linking process becomes highly efficient in the high-conversion regime, when the probability for the growing radical to come into a pendent vinyl group becomes at least comparable with that for the same radical to come into a monomer.

Taking account of these data, we can now attempt to describe the properties of our gels within the framework of percolation, as has been recently worked out fruitfully for the description of vulcanized polybutadiene chains.[11] These systems can be considered as polymer chains cross-linked at random, the cross-linking process being limited by the transfer reaction to CTA. The probability p to attach one chain to another one through the addition of a growing macroradical onto a pendent double bond has been expressed as a function of the CTA content γ_C.[6] More precisely, from kinetic considerations of the radical polymerization mechanism, p is known to vary as an inverse law of the rate for transfer reaction R_{tr}, which can be written as[6]

$$R_{tr} = k_{tr}\gamma_C[R_0] \qquad (1)$$

where k_{tr} is the rate constant for transfer reaction and $[R_0]$ is the concentration of growing radicals. For this reason, p is expected to vary as an inverse law of the CTA content γ_C, with a nonunique relationship between these two parameters, since k_{tr} depends on the type of CTA used. Thus, one of the simplest approaches is to choose a γ_C^{-1} representation for G. Experimental values of G are reported as a function of γ_{C1}^{-1} and γ_{C2}^{-1} in parts a and b of Figure 3, respectively. These curves strongly suggest that there exists a threshold value for the CTA contents γ_{C1} and γ_{C2}, above which gelation cannot occur during emulsion polymerization. Moreover, just above the threshold, G is actually found to increase very rapidly as a function of γ_C^{-1}. However, it appears rather difficult to connect the experimental threshold to percolation theory, since the precise relationship between p and γ_C is not known.

IV. State of Maximum Swelling

The state of maximum swelling is characterized by the swelling ratio Q_m. The process to reach it involves the disengagement of chain segments from one another followed by the swelling of each segment under the osmotic pressure induced by the solvent.[10] Swelling ratio values obtained for the whole series of polymer films in chloroform (Q_m^c), toluene (Q_m^t), and DMF (Q_d^m) are given in Table 3. It is worth noting that samples which exhibit swelling ratios higher than ~30 in chloroform or toluene lose their shape and integrity in DMF, likely due to redispersion of some particles in the solution. An interesting way of dealing with the obtained data is to plot the values of Q_m as a function of G^{-1} (Figure 4), so as to tentatively disclose the possible existence of a uniform behavior whatever the gel nature. Inspection of Figure 4 reveals that whatever the composition of the copolymer and the nature of CTA (C1 or C2) the representative points of all gels with G values higher than 0.4 can be put on the same curve. It is then inferred that the structure of the covalent network formed during emulsion polymerization is very similar in all the samples and strikingly does not depend on the composition of the copolymer and the nature of the CTA. However, no power law can be deduced for the entire range of G values investigated, ruling out any simple scaling law for the swelling ratio.

V. Proton Transverse Relaxation

In this section, the transverse magnetic relaxation of protons linked to chain segments is analyzed as a tem-

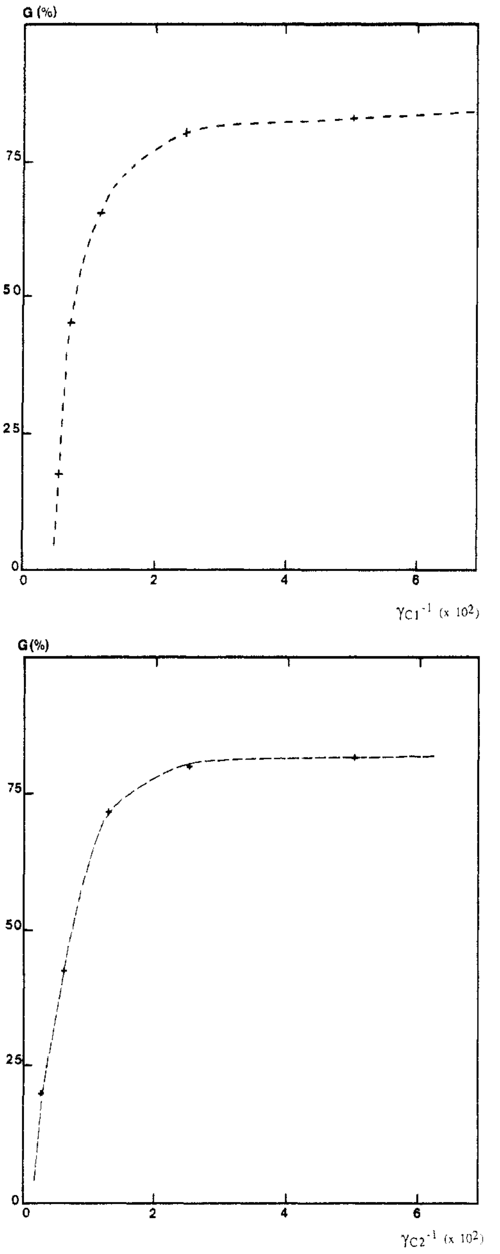

Figure 3. Variations of the gel fraction G (wt %) as a function of (a, top) γ_{C1}^{-1} ($\times 10^2$) and (b, bottom) γ_{C2}^{-1} ($\times 10^2$) for the samples of S/B ratio 69/27 (w/w).

Table 3. Swelling Ratio Values Obtained in Chloroform (Q_m^c), Toluene (Q_m^t), and DMF (Q_m^d) for the Series of SB Copolymer Films

film	Q_m^c	Q_m^t	Q_m^d	film	Q_m^c	Q_m^t	Q_m^d
1	10	7	3.5	8	28	24.5	ND
2	12	7.5	4	9	39	28.5	ND
3	16.5	17.5	15	10	24.5	16.5	6.5
4	30.5	25	ND	11	29	26	ND
5	ND[a]	43.5	ND	12	26	23	ND
6	11.5	7.5	7.5	13	12.5	12	12
7	16.5	15	13.5				

[a] ND = not determined because of redispersion of the particles in the solvent, resulting in the destruction of the sample.

perature function, considering gels before and after the extraction of free chains, hereafter referred to as gels in the reaction bath and dry extracted gels, respectively.

1. Property of Superposition. Most proton transverse relaxation processes observed in polymeric systems above the glass transition temperature are known to be described by nonexponential time functions. Deviations from an exponential behavior arise not only from complex dynamical properties of polymer chains but also from residual tensorial interactions between nuclear spins induced by topological constraints exerted on chains. The difficult problem encountered in describing magnetic relaxation functions can be overcome by noting that these normalized functions obey a property of superposition observed when the time scale is multiplied by an appropriate factor. This property applies above the glass transition temperature and reveals an invariance of relaxation functions which holds whenever the polymeric systems belong to a well-defined family. Any proton relaxation function can be expressed in a general way as

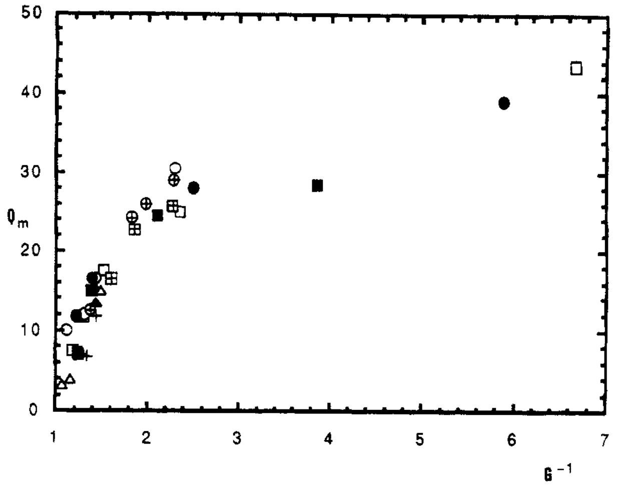

Figure 4. Representation of the maximum volumic swelling ratio Q_m as a function of G^{-1} for the whole series of SB copolymers in different solvents: (□) samples 1–5 in toluene; (■) samples 6–9 in toluene; (□) samples 10–13 in toluene; (○) samples 1–5 in chloroform; (●) samples 6–9 in chloroform; (⊕) samples 10–13 in chloroform; (△) samples 1–5 in DMF; (▲) samples 6–9 in DMF; (+) samples 10–13 in DMF.

$$M_x(t,T_0) = f(\Delta(T_0)t) \qquad (2)$$

in which $\Delta(T_0)$ depends on the physical state of the polymer system which protons are attached to. Then the property of superposition leads to

$$M_x(t,T) = f(\Delta(T)t) \qquad (3)$$

with a scale factor defined by

$$\Delta(T) = \Delta(T_0)\, s(T,T_0) \qquad (4)$$

Then

$$M_x(t,T) = f(\Delta(T_0)\, s(T,T_0)t) \qquad (5)$$

or

$$M_x(t',T) = f(\Delta(T_0)t') \qquad (6)$$

with

$$t' = s(T,T_0)t \qquad (7)$$

The $\Delta(T)$ parameter contains the physical characterization of the polymeric system.

2. Dry Extracted Gels. Typical relaxation functions recorded after extracting free chains from gels are shown in Figure 5 (sample 3); these normalized functions were found to obey a property of superposition by multiplying the time scale of observation by an appropriate factor hereafter called $s_d(T,T_0)$. The T_0 reference temperature can be arbitrarily chosen above the glass transition temperature. It was set equal to 358 K for all studied

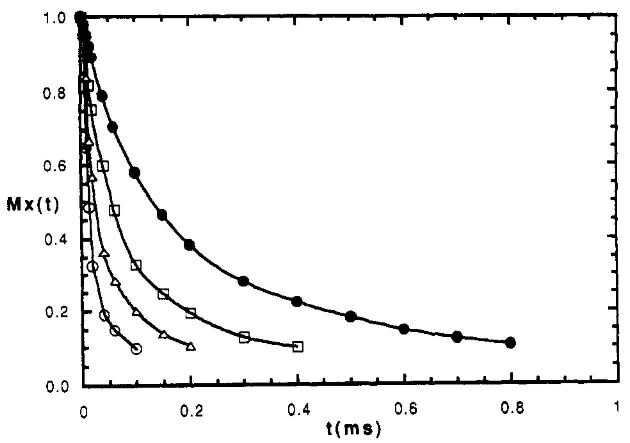

Figure 5. Relaxation functions recorded from the dry gel 3 at different temperatures: 318 (○), 335 (△), 344 (□), and 358 K (●).

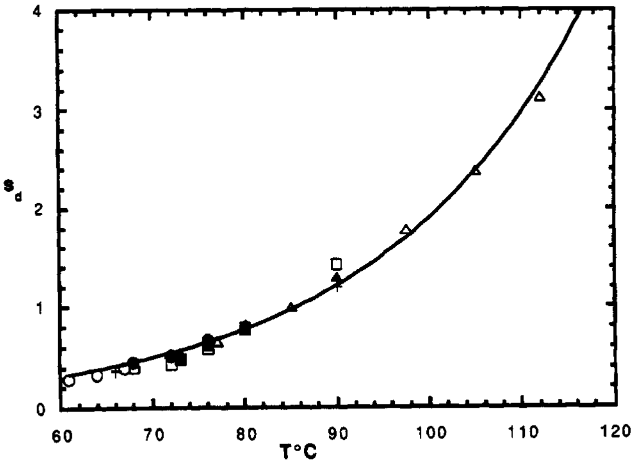

Figure 6. Evolution of NMR scale factor s_d induced by temperature variations determined for dry gels. Gels are represented by their gel fractions in toluene ($G = G_t$), which are 42.5 (●), 54 (○), 65.5 (△), 72 (■), 80 (▲), 81 (□), and 84.5% (+). The reference temperature T_0 is set equal to 358 K.

polymeric systems whatever the gel fraction. T is the temperature of observation. Then, scale factors were found to determine a single curve drawn as a temperature function in Figure 6. This striking result clearly shows that relaxation functions of all gel systems behave in the same way when the temperature is varied, even though the relaxation functions exhibit great differences from one system to another. Consequently, a single scale factor $s_d(T,T_0)$ is defined for the series of gel systems synthesized with CTA C1. The evolution of the scale factor induced by temperature variations was found to be in agreement with an analysis based on an Arrhenius law (Figure 7); the activation energy is equal to 51 kJ mol^{-1}. This uniform behavior leads us to conclude that the dry extracted gels, i.e., the covalently cross-linked polymeric networks formed during the emulsion polymerization process, belong to the same well-defined family.

3. Gels in the Reaction Bath. (a) Liquid-like Behavior. The property of superposition was found to apply also to proton relaxation functions recorded from gel systems without extracting free chains; a scale factor $s_b(T,T_0)$ was determined from all observed gel systems by choosing a reference temperature still equal to 358 K. The dependence of the scale factor on temperature variations is shown in Figure 8. Once again, a single curve can be drawn through experimental points; results were found to fit a free volume law representation while the agreement with an Arrhenius analysis was worse. The free volume effect was supposed to be described according to the WLF equation.[9] The classical representation of this equation is illustrated in Figure 9; experimental values of parameters are $f_0 = 0.2$ for the free volume fraction at 358 K and $\alpha = 2 \times 10^{-3}$ K^{-1} for the thermal expansion coefficient. Protons attached to the network structure cannot be distinguished from those linked to free chains. NMR observations concern chain segments which belong to either of the two kinds of polymeric systems: reaction bath or network structure.

These results clearly show that, in the gels in their reaction bath, chain segments exhibit a liquid-like behavior whatever the nature of the systems they belong to, whereas

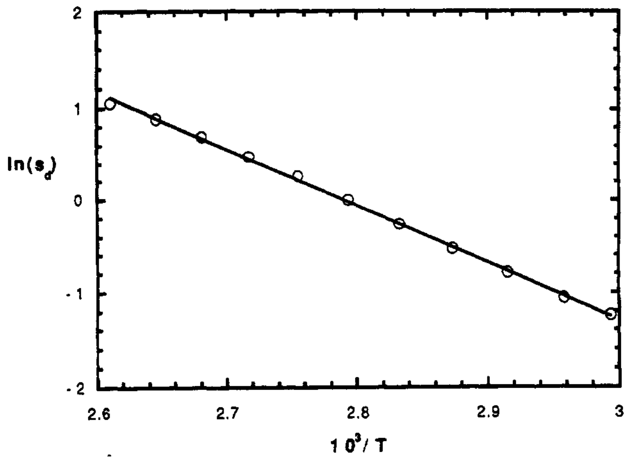

Figure 7. Representation of the Arrhenius law for s_d corresponding to the dry extracted gels.

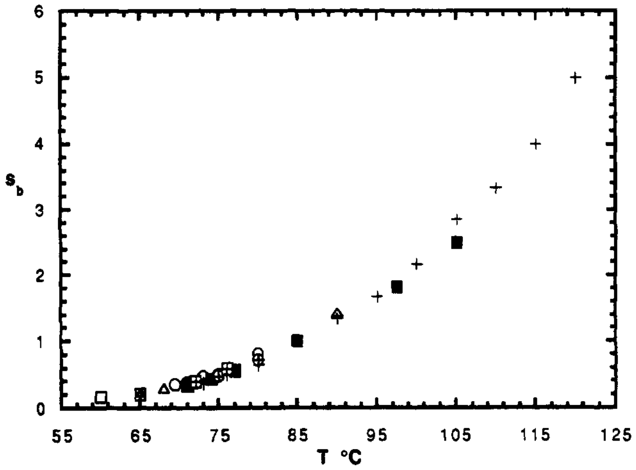

Figure 8. NMR scale factor s_b as a function of temperature for gels in the reaction bath. Gels are represented by their gel fractions in toluene, which are 15 (□), 26 (□), 42.5 (⊕), 47.5 (+), 65.5 (■), 72 (○), 80 (▲), 81 (△), and 84.5% (●).

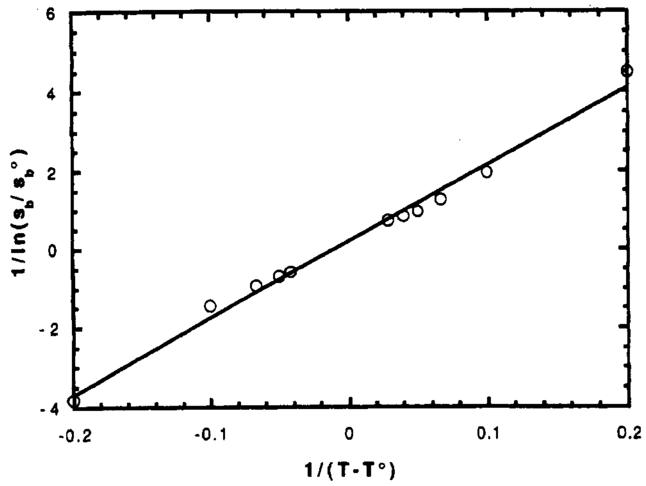

Figure 9. Represnetation of the free volume law for the mean curve of $s_b(T)$, corresponding to gels in the reaction bath.

the extraction of free chains from these systems gives rise to strong constraints, which are described in a reasonable way by introducing a local potential barrier. In other words, the presence of free chains results in the decrease of the constraints existing in the covalent network, and this behavior clearly shows that free chains contained in the reaction bath act as a swelling agent of the covalent network.

(b) State of Constraints. For samples in their reaction bath which exhibited the same S/B ratio (69/27), another interesting way to investigate the behavior of these polymeric gels and to probe the state of constraints encountered by chain segments is to compare and focus on the relaxation functions obtained for each sample at the same fixed temperature T. Samples were only defined by their gel fraction G, and the corresponding evolution of the relaxation functions $M_x,T(t,G)$ as a function of time obviously depended on the value of G. Then, the proton relaxation function $M_x,T(t,G)$ can be expressed in a general way as

$$M_x,T(t,G) = g(\Delta(G)t) \tag{8}$$

in which $\Delta(G)$ characterizes the physical state of the polymeric gel at temperature T. For a reference gel value G_0, which is arbitrarily chosen among those of the series of samples, it leads to

$$M_xT(t,G_0) = g(\Delta_0 t) \tag{9}$$

with

$$\Delta(G) = \Delta_0 s_T(G,G_0) \tag{10}$$

Then

$$M_{x,T}(t,G) = g(\Delta_0 s_T(G,G_0)t) = M_{x,T}(t',G_0) \tag{11}$$

with

$$t' = s_T(G,G_0)t \tag{12}$$

This means that the normalized relaxation functions $M_x,_T(t,G)$ can be superimposed by multiplying the time scale of observation by an appropriate factor hereafter called $s_T(G,G_0)$. When the temperature T was appropriately chosen for all the considered samples to be well above their glass transition temperature, $s_T(G,G_0)$ was experimentally found to be independent of the time of observation, and then superposition was checked to be valid at each time of observation for the relaxation process. From the physical point of view, $s_T(G,G_0)$ can be considered as an isothermal scale factor giving a semiquantitative representation for the state of constraints existing within the polymeric gels at temperature T, compared to the reference system with gel value G_0. The dependence of the isothermal scale factor $s_T(G,G_0)$ on gel fraction variations is shown in Figure 10 for samples 1–5 and samples 6–9 synthesized with CTA C1 and CTA C2, respectively. Inspection of this diagram reveals that the variations of the scale factor as a function of G depend on the nature of the CTA used, since in the low gel fraction region (G < 55 wt %), two well-separated curves can be drawn. For a given amount of cross-linked chains involved in the covalent network and lower than 55 wt %, the level of constraints encountered by chain segments is found to be higher in gel systems synthesized with CTA C2. More precisely, it appears that, even when the CTA C2 concentration is increased to 3.2 wt %, leading to a value of G of 26 wt %, $s_T(G,G_0)$ is almost not affected and remains very close to 1: in this sample, the constraints still exhibit the same level as in the sample synthesized with 0.8 wt % of CTA C1. The additional constraints should be induced by the free chains which are embedded in the covalent network, since for a given value of the gel fraction, the structural and dynamical properties of the covalent networks (dry extracted gels) were found to be similar. Hence, this result brings out the key part played by the free chains in the dynamical properties of these systems, depending on the nature of the CTA used to restrict the covalent cross-linking density. In addition, it points out the limits of the above uniform behavior, evidenced for these gel systems from the observation of a single scale factor $s_b(T,T_0)$.

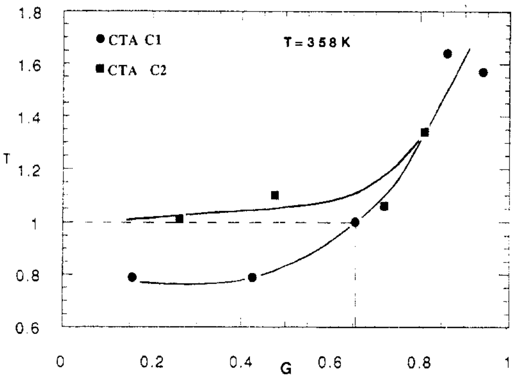

Figure 10. Isothermal NMR scale factor $s_T(G,G_0)$ as a function of the gel fraction G (wt %) at fixed temperature T = 358 K for the series of samples in their reaction bath with the same S/B ratio [(●) samples 1–5; (■) samples 6–9]. G_0, which corresponds to s_T = 1, is chosen to be 65.5%.

VI. Correlations between Viscoelastic and NMR Features

In the above sections, new information at the semilocal scale was obtained through the NMR approach, concerning the statistical structure and dynamics of the network. Moreover, the role of the free chains embedded in this network was pointed out. Then, on one hand, from a theoretical point of view it has recently been shown that the restoring force appearing in a gel system under stretching can be related to the relaxation rate of transverse magnetization of nuclei attached to polymer chains.[1] On the other hand, in a previous work, methods to perform a quantitative analysis of DMA spectra recorded on latex films have been proposed and checked to be valid[3] for this kind of polymer film. They have enabled us to determine parameters characterizing the network structure and dynamics at different scales. It is now interesting to study how NMR and viscoelastic data are connected with each other.

1. Density of Elastically Effective Network Strands (ν_c) and NMR Scale Factor $s_T(G)$. One of the most important parameters at the chain scale that viscoelastic measurements can give access to is the density of elastically effective network strands between coupling loci ν_c. For polymer films obtained from gels in their reaction bath, these coupling loci arise from either covalent multifunctional links or physical intermolecular interactions such as hydrogen bonding between carboxylic comonomers or topological constraints. For the sake of simplicity, it will be assumed that the total concentration of effective strands is derived taking into account the additivity of contributions from covalent cross-links and molecular interaction loci.[9]

(a) Variations of ν_c against Gel Fraction. Parts a and b of Figure 11 show the isothermal master curves recorded for the frequency dependence of the moduli E'

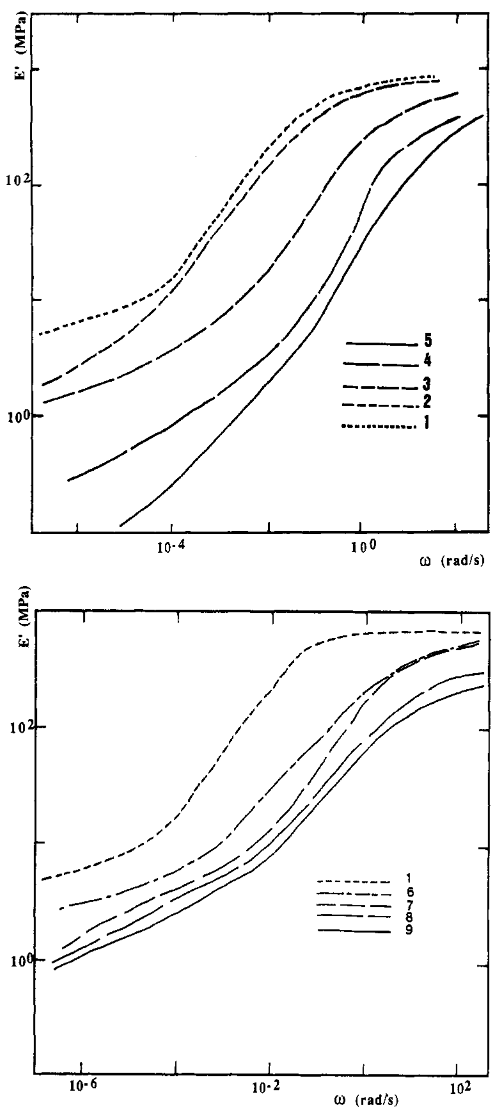

Figure 11. (a, Top) log–log plot of the isothermal master curves obtained for the storage modulus E' of samples 1–5 (synthesized with CTA C1) at 28 °C using the time–temperature superposition method. (b, Bottom) log–log plot of the isothermal master curves obtained for the storage modulus E' of samples 6–9 (synthesized with CTA C2) at 28 °C using the time–temperature superposition method. The corresponding curve for sample 1 ($\gamma_C = 0$) is reported for comparison.

of latex films synthesized with CTA C1 and CTA C2, respectively. All these curves exhibit the typical strong relaxation from a glass-like behavior in the high-frequency range toward a rubber-like one in the lower frequency region. The effect of CTA content on the viscoelastic behavior of the films, which has been previously described,[3] is twofold: (i) First, it is responsible for a shift in the location of the transition zone on the frequency scale, reflecting an alteration of the relaxation times. (ii) Second, it determines the level of the elastic modulus in the low-frequency region, which represents the modulus of the rubber-like network, whose coupling knots arise from either covalent cross-links or physical intermolecular interactions. Then combining the classical rubber elasticity theory and the phenomenological Marvin–Oser expression as previously proposed,[3] we were able to determine the value of ν_c for the series of samples with the same S/B ratio (69/27) and different CTA contents γ_C (samples 1–9). The corresponding values of ν_c are reported in Figure 12 versus the gel fraction G_c, together with the representative point for sample 12, whose S/B ratio is different from that of samples 1–9.

(b) Additional Coupling Loci Induced by Free Chains. The diagram of Figure 12 appears to be quite informative concerning the role of free chains in the constraints encountered by chain segments. As a matter of fact, inspection of Figure 12 reveals that for a given value of the gel fraction G the density of elastically effective network strands between coupling loci ν_c depends on the nature of the CTA. In both cases, it is classically observed that ν_c decreases when G decreases, but this effect is shown to be much more pronounced when CTA C1 is used to restrict the cross-linking density of the polymers: for instance, for a G value of 15%, ν_c is found to only be 16 μmol/cm^3 for polymers synthesized with CTA C1, whereas the corresponding value of ν_c is 300 μmol/cm^3 when CTA C2 is used. This behavior clearly shows that, for the same amount of material involved in the covalent network, i.e., the same fraction of covalently cross-linked chains, the contribution from noncovalent molecular interaction loci to the elastic properties of the material depends on the nature of the CTA. Then, an extra part can be played by the free chains which are embedded in the covalent network. In particular, in the case of polymers synthesized with CTA C2, Figure 12 clearly shows that free chains create a high number of noncovalent intermolecular interactions which do not exist in polymers synthesized with CTA C1.

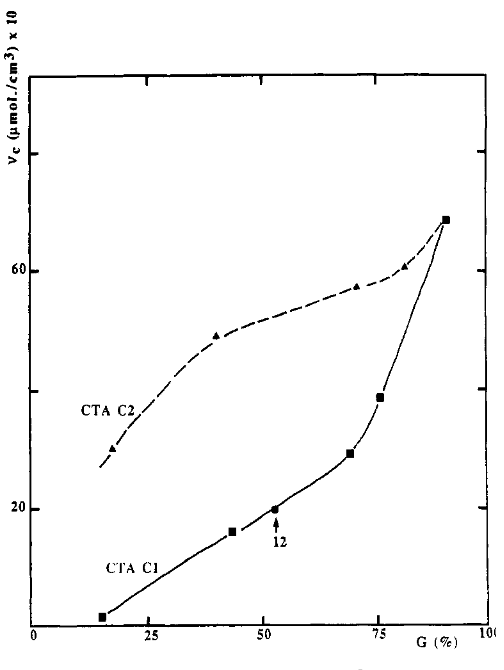

Figure 12. Plot of the variations of the density of elastically effective network strands derived from viscoelastic measurements ν_c versus the gel fraction G (in chloroform) for samples with the same S/B ratio (samples 1–9). The representative point for sample 12 (S/B ratio = 59/37) is also reported in this diagram.

(c) Correlations with NMR Behavior. Comparison of the diagram of Figure 12 with the dependence of the NMR scale factor $s_T(G,G_0)$ against G for the same series of samples (Figure 10) makes it possible to show that the two kinds of results are connected. More precisely, the plot of the NMR shift factor $s_T(G,G_0)$ versus G (Figure 10) enabled us to infer that, for a given value of G lower than 55%, polymers synthesized with CTA C2 exhibit a faster magnetic relaxation than polymers synthesized with CTA C1, since the corresponding values of s_T were found to be higher for the former polymers. This behavior is likely to be attributed to additional constraints created by the free chains in the gels when CTA C2 is used. Furthermore, as the structural properties of the covalent network were found to be rather regular and practically independent of the CTA content, both NMR and viscoelastic results lead us to conclude that CTA mainly affects the structure of the free chains.

Finally, we would like to stress that the representative point for sample 12, whose S/B ratio is 59/37 and which is synthesized with CTA C1, is located on the same curve in Figure 12 as representative points obtained for samples with the same CTA but a S/B ratio of 69/37. This behavior brings out an additional argument in favor of a rather regular structure of the gels (covalent network + free chains) for a given nature of CTA, which could be considered as practically independent of the polymer composition and the CTA content. Moreover, it clearly shows that only CTA controls the dynamical properties of the gel systems, its content reducing the gel fraction and its nature mainly governing the molecular interactions created by the free chains.

2. Monomeric Friction Coefficient ξ_0 against CTA Content. At this point, the dynamical properties of the gels have been investigated at the chain scale and semilocal scale, deriving parameters ν_c and s_T, respectively. Conclusions have been consistently drawn concerning the part played by the free chains in these properties, since these species were found to greatly affect the elastic response of our samples. From the standpoint of the information gained, NMR and viscoelastic measurements appear to give different descriptions of the same phenomenon. Then, to complete this work, it seems to be worthwhile to investigate the dynamical properties of the gel at the local monomer scale, to specify the influence of the CTA nature on the local features and to ascertain the consistency of local and semilocal properties. It has previously been emphasized that the local segmental dynamics can be correctly described using the monomeric friction coefficient ξ_0.[3] This parameter represents the average frictional force per monomer unit and unit velocity encountered by a monomeric segment as it moves through a medium consisting of other polymer chains. According to Ferry,[9] it can be derived from the low-frequency end of the transition zone appearing in Figure 11a,b. More precisely, as previously shown,[3,12] a more convenient way to meet the problem is to work with the frequency dependence of the complex compliance J^* ($J^* = 1/E^*$). Then the values of $a^2\xi_0$ can be determined experimentally (a is the root-mean-square end-to-end length per square root of monomer units) from the low-frequency end of the transition zone, where there is a segment of J' and J'' which conforms to the theoretical slope of $-^1/_2$.[3,9,12] The detailed procedure for the derivation of $a^2\xi_0$ in this way for the same kind of sample has been published in a previous work.[3]

(a) Variations of $a^2\xi_0$ against CTA Content. Figure 13 shows the plot of parameter $a^2\xi_0$ against the CTA content γ_C in the polymer obtained for the whole series of samples with the same S/B ratio (69/27). Two regions can be clearly distinguished in this diagram for both kinds of CTA used: at low CTA contents ($\gamma_C < 1$ wt %), the monomeric friction coefficient exhibits a strong dependence on the value of γ_C and is decreased by 2 orders of magnitude at least when CTA content is increased to ~ 1 wt %. This behavior means that addition of CTA to the polymer greatly reduces the friction encountered by the monomer moving in the network. Then, for values higher than ~ 1 wt %, another region can be observed where the local monomer dynamics is found to be almost unaffected by increasing CTA content in the polymer.

In the range of CTA concentration (γ_C) where the local monomer dynamics is almost unaffected, the values of $a^2\xi_0$ for polymers synthesized with C2 remain higher by 1 order of magnitude than those obtained for polymers synthesized with C1, even for very high CTA contents. This result clearly shows that in the former samples one monomer segment in its translatory motions is more constricted by the surrounding polymer chains than it is in the latter samples. These observations are quite consistent with results obtained from the above NMR investigations for the dynamics of the chain segments at the semilocal scale.

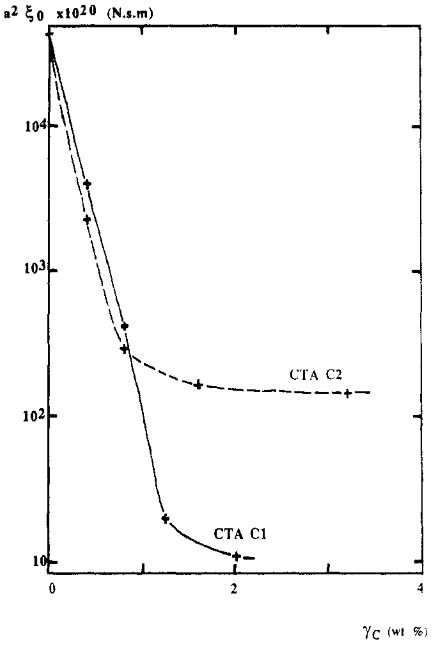

Figure 13. Plot of the variations of the parameter $a^2\xi_0$ against the CTA content γ_C (wt %) for the series of samples with the same S/B ratio (69/27): dashed line, CTA C1; solid line, CTA C2.

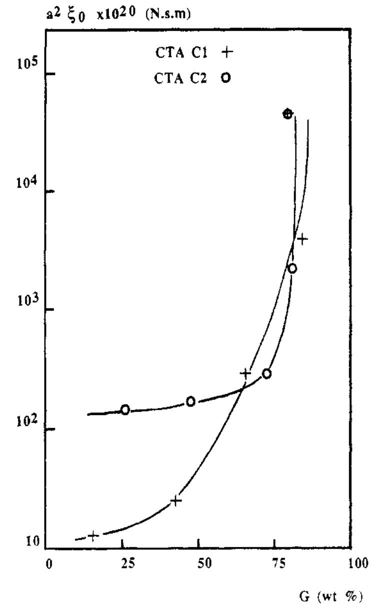

Figure 14. Plot of the variations of the parameter $a^2\xi_0$ against the gel fraction value G (wt %, in chloroform) for the series of samples with the same S/B ratio (69/27): (+), CTA C1; (O), CTA C2.

(b) Influence of Free Chains on the Local Dynamics. An interesting way to deal with the above data is to plot $a^2\xi_0$ against the gel fraction G for the same series of samples (Figure 14). It is clearly seen that $a^2\xi_0$ decreases when G decreases, and the effect is again found to be much more pronounced when CTA C1 is used to restrict the cross-linking density of the polymers. Then for the same amount of material involved in the covalent network, i.e., the same fraction of covalently cross-linked chains, the average frictional resistance encountered by a submolecule junction moving through its surrounding medium strongly depends on the nature of the CTA, especially when the gel fraction value becomes lower than 55%. This confirms that, in the case of polymers synthesized with CTA C2,

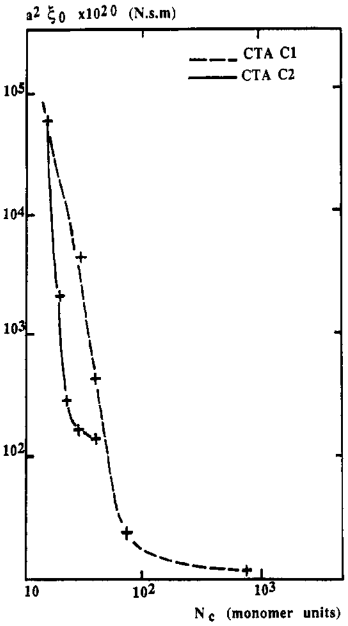

Figure 15. Plot of the variations of the parameter $a^2\xi_0$ against the average number of monomer units between coupling loci N_c for the series of samples with the same S/B ratio (69/72): dashed line, CTA C1; solid line, CTA C2.

additional constraints are created by the free chains which swell the covalent network. Furthermore, it suggests that these constraints are strong enough to greatly affect the local segmental mobility and hence the local dynamics of the chains. For this reason, it can be inferred that Figures 10 and 14 provide two pictures of the same phenomenon, the former at a semilocal scale and the latter at the local scale, i.e., the strong influence of constraints induced by the free chains on the dynamical properties of these gels consisting of partly cross-linked copolymers.

(c) Monomer Dynamics versus Network Tightness. Fruitful information concerning the monomer dynamics can be obtained by plotting $a^2\xi_0$ against the average number of monomer units between elastically effective coupling loci N_c for the same series of samples (Figure 15). N_c can be directly calculated from the value of the density of network strands ν_c using the following expression:

$$N_c = \rho/\nu_c M_0 \tag{13}$$

where ρ is the density of the polymer and M_0 is the monomer molecular weight equivalent to the weight of a statistical unit of the SB copolymer.

The curve obtained for polymers synthesized with CTA C1 has been published and discussed in a previous work;[3] however, it is reported in Figure 15 to allow a comparison with data obtained for samples synthesized with CTA C2. Inspection of Figure 15 reveals that in polymer films synthesized with the former CTA local monomer dynamics is controlled by the tightness of the network only when the average number of monomer units between coupling loci becomes smaller than 10^2; on the contrary, for higher values of N_c, the frictional resistance encountered by a submolecule junction moving through its surrounding medium levels off and does not significantly depend any more on the mesh size of the polymer network. In contrast, it appears that for samples synthesized with CTA C2, the network remains tight enough for the local monomer dynamics to be still significantly modified by molecular interactions: as a matter of fact, N_c remains lower than 10^2 monomer units, and then the region in which $a^2\xi_0$ could level off is never reached. Hence, it brings us to conclude that, even if CTA C2 acts as an efficient agent to control the covalent cross-linking process of the SB copolymer, it induces the formation of intermolecular interactions which greatly enhance the density of elastically effective network strands and strongly affects the dynamics of the polymeric gels, even at the local monomer scale. This effect was first suggested by the analysis of NMR data presented in section V.3. It brings out an additional argument to clearly illustrate the relationships existing between the viscoelastic properties of the gels and the magnetic relaxation of nuclei attached to the polymer chains. Hence, it leads us to conclude that effects appearing at the monomer local scale are closely interrelated with those which are detected at the semilocal scale through NMR experiments.

VII. Conclusions

The structural and dynamical properties of polymeric gels prepared by emulsion polymerization were investigated from transverse proton relaxation, swelling, and viscoelastic behavior. The structure of the covalent network formed during the polymerization process was inferred to be very similar for the whole series of samples, since a uniform behavior was disclosed from swelling measurements and a property of superposition, which reveals an invariance of relaxation functions, was evidenced for the transverse proton relaxation. Strikingly, this uniform structure did not appear to be affected either by the composition of the SB copolymer or by the nature of the chain transfer agent. The scale factors for superposition of relaxation functions were found to display a free volume behavior for gels in their reaction bath, whereas those obtained for dry extracted gels were found to obey a law of the Arrhenius type. This result emphasizes the key role played by the free chains in the dynamical properties of the system, the covalent network being actually swollen by these free chains. Then for a given composition of the copolymer with a fixed S/B ratio, it was shown that the state of constraints induced by the free chains in the systems can be characterized. More particularly, in the present systems, it was found to depend on the nature of CTA used to limit the covalent cross-linking density of the system. At high CTA contents resulting in gel fraction values G lower than 55 wt %, the organohalogenated CTA (C2) gives rise to additional intermolecular interactions which strongly affect the dynamics of the polymer chains. This effect was evidenced analyzing both NMR and viscoelastic data; moreover, it was found to remain valid and sensitive even at the local monomer scale. For this purpose, the description derived from viscoelastic measurements was emphasized to consistently complement the semilocal NMR approach.

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