Nuclear magnetic resonance approach to the characterization of siloxane–silica network-like structures

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This work deals with mesh size properties of network-like structures associated with random siloxane–silica mixtures. The transverse magnetic relaxation function of protons is shown to obey a superposition property controlled by the silica concentration C_{Si}, in the range $0 \leqslant C_{Si} \leqslant 0.50$ (w/w). Correspondingly, its invariant mathematical structure is governed by the average residual energy $\hbar \Delta_e$ of dipole–dipole interactions only. The parameter Δ_e is given the role of a timescale shift factor; it is related to the average mesh size of a given network. Nuclear magnetic resonance measurements show that silica aggregates do not induce any strong deviation from the primary entanglement system established in a pure siloxane melt. Whether infinite siloxane–silica clusters are swollen by polymer chains or whether finite size clusters are diluted in a siloxane melt, the resulting networks are described by similar distribution functions of elementary chains connecting neighbouring entanglements; these functions are shifted towards smaller mesh sizes upon addition of silica. These properties hold for several high molecular weight samples: $\bar{M}_w = 6.1 \times 10^5$, 2.4×10^5 and 1.6×10^5, respectively.

INTRODUCTION

Random mixtures resulting from the saturated adsorption of high molecular weight siloxane upon silica aggregates are known to create network-like structures. The main purpose of the present work was to attempt to characterize the average mesh size of these networks, and whether they are temporary or not. The theoretical characterization of random systems is known to be founded upon the existence of at least one correlation length λ, also called screening length. This usually obeys scaling properties which are closely related to the very nature of the observed medium[1,2]. Accordingly, any experimental characterization must first confirm the existence of a screening length and then determine the scaling laws that it obeys. These are usually induced by varying the concentration of one species of the random system:

$$\lambda = \lambda_0 (C/C_0)^\alpha$$

where α may be a critical exponent and λ, a so-called semi-local space scale, ranges from 50 Å to about 500 Å.

N.m.r. has been extensively used to investigate statistical properties of crosslinked chain systems and polymer melts[3–5]. This technique is well suited to studies concerning the fractal nature of polymer chains. The screening length, closely associated with the nuclear spin-system response, is the average length of the vector joining two neighbouring entanglements in a melt or two crosslinks in a gel. Contrary to thermodynamic approaches, the n.m.r. observation does not necessitate the use of any solvent to let the actual volume of a given chain skeleton form a contrast to the statistical volume it

occupies under thermal fluctuations. Magnetic interactions between nuclear spins located on different chain segments are negligible; accordingly, a single chain nuclear magnetization is observed. The fractal nature of a chain in a melt is thoroughly seen from this linear density of magnetization.

The main problem encountered in observing physical properties of gel-like systems from n.m.r. concerns the analysis of the complex mathematical structure of the spin-system response. In most cases, the observed relaxation function of the transverse magnetization $M_x(t)$ is not necessarily described by a single-exponential time function. It may, however, exhibit homogeneous properties within its whole time interval of variation. In such a case, the mathematical structure of the relaxation function may be invariant under induced changes of external parameters determining the equilibrium state of the gel system. As a result of such invariance, the relaxation function must present a superposition property described by a simple shift factor s of the timescale of variation. The relaxation function is generally expressed as:

$$M_x(\Delta(\xi \zeta)t)$$

where $\Delta(\xi, \zeta)$ is the reference frequency scale of time dependence of the relaxation process, and ξ and ζ are two possible relevant external parameters. The ratio $s = \varepsilon(\xi_1, \zeta_1)/\varepsilon(\xi_2, \zeta_2)$ is the shift factor corresponding to two different physical states of the gel.

The first step of the present work was to confirm the superposition properties of the relaxation function of the transverse magnetization observed in siloxane–silica

mixtures. Then, the dependence of the shift factor s upon silica concentration was determined.

The main properties of random siloxane–silica mixtures are recalled in the second section of this paper. A simple basis of the n.m.r. approach is described in the third one. Measurements are analysed in the fourth section, while effects of chain molecular weight variations are considered in the fifth one. Properties concerning samples prepared from a treated silica surface are discussed in the sixth section. All the results are discussed in the last one.

RANDOM SILOXANE–SILICA MIXTURES

The random siloxane–silica mixtures studied throughout the present work were obtained from a mechanically induced sorption process of siloxane upon silica aggregates. The experimental procedure used for sample preparation has already been described in a previous paper[6], hereafter referred to as I. Also, it has been shown in that paper that the average number of polymer chains n_f bound to aggregates per unit mass of silica did not depend upon the chain molecular weight of siloxane[6]. This fundamental results was established by measuring the residual amount of polymer Q_r^l left bound to silica after removal of all polymer chains free to move throughout the random mixture. More precisely, the linear dependence of Q_r^l upon the number average molecular weight $\bar{M}_n$ yielded both the quantity n_f and the average area σ_f of a chain binding site, taking the specific area of silica into consideration: $\sigma_f = 5.4 \times 10^3$ Å^2.

Since the average number of silanol groups per unit mass of silica was known, the number f of such groups participating in a chain binding site could be estimated: $f \simeq 10^2$. Therefore, assuming that the binding mechanism of a chain onto silica occurs through hydrogen bonding, it was considered that the number of monomeric units involved in such a process was at least equal to $f = 10^2$. Values of the quantities Q_r^l, n_f, σ_f and f were derived from siloxane–silica mixtures characterized by low silica aggregate concentrations and chain molecular weights smaller than $\bar{M}_n \simeq 3.6 \times 10^5$. In other words, any poly(dimethylsiloxane) PDMS) chain was assumed to be bound to one aggregate only. The concentration of polymer chains simultaneously bound to two particles or more was considered negligibly small. Such random mixtures will be considered throughout the present work as solutions of finite size siloxane–silica clusters in siloxane. Some of these clusters may form microgels.

In a second paper[7], hereafter referred to as II, the multiple aggregate binding process of a chain was analysed using higher concentrations of silica, longer polymer chains and controlled extents of treated silica surface to vary the actual number of chain binding sites per unit mass of mineral filler[7]. The probability p_B that a chain is simultaneously bound to two aggregates was found to be equal to 0.7 in a random mixture corresponding to an initial silica concentration in siloxane equal to $C_{Si} = 0.29$ (w/w), with $\bar{M}_n = 3.6 \times 10^5$. The relative number of dangling chains was 0.3, while the relative number of chains simultaneously bound to three aggregates was about 0.5. A treated silica surface was used to analyse possible collective aspects concerning the binding mechanism of a single chain. After removing all polymer chains free to move throughout the mixture, the

resulting system was found to behave like a permanent gel: it could be reversibly swollen using a good solvent like chloroform or toluene; its shape was invariant under swelling. Random siloxane–silica mixtures characterized by an initial concentration $C_{Si} = 0.29$ (w/w) and an average chain molecular weight $\bar{M}_n \simeq 3.6 \times 10^5$ will be considered as infinite clusters swollen by polymer chains. For a lower silica concentration ($C_{Si} = 0.17$ (w/w)) and the same average chain molecular weight, the resulting sample also behaved like an infinite cluster. Furthermore, for a silica concentration $C_{Si} = 0.29$ (w/w) and a smaller chain molecular weight $\bar{M}_n \simeq 1.3 \times 10^5$, the resulting sample was also found to behave like a permanent gel.

NUCLEAR MAGNETIC RESONANCE APPROACH BASIS

Many details of the present n.m.r. approach have already been reported in several previously published papers[8,9]. The main features concerning this approach are given in the present work.

Spin system

Molecular probes used to investigate the properties of siloxane–silica mixtures are methyl groups attached to siloxane chains. The corresponding n.m.r. probes are three-spin systems determined from protons linked to methyl groups; the proton spin is $I = \frac{1}{2}$. Three-proton spin systems have been extensively studied, taking their internal dipole–dipole interactions H_D into consideration[10]. Matrix elements describing the adiabatic part of these dipole–dipole interactions are easily expressed using a basis defined from eigenfunctions of the Zeeman energy. Adiabatic dipole–dipole interactions H_D existing in a methyl group are divided into two parts. One of them, $H_D(\theta)$, only depends upon the orientation θ of the c-axis of symmetry of a methyl group, with respect to the steady magnetic field direction. The other part, $H_D(\theta, \alpha)$, depends upon both the c-axis orientation and the azimuthal angle α defining the rotation of the methyl group around its own axis of symmetry. Furthermore, it is currently assumed that the rotational diffusion of this group occurs according to two well defined steps. The first one is associated with diffusional rotation of the group around its own c-axis. In polymer systems, this is considered to be much faster than rotational diffusion of the c-axis occurring during the second step. This latter process is closely related to the random diffusion of long chain skeletons governed by very slow disentanglement mechanisms. As a result of such a two-step motion of methyl groups, dipole–dipole interactions within these groups are averaged to zero according to two steps, too. The part $H_D(\theta, \alpha)$ is averaged to zero during short time intervals ($\simeq 10^{-8}$ to 10^{-11} s) because of rotation around the c-axis. The motional averaging of the $H_D(\theta)$ part necessitates a more detailed analysis. This has recently been discussed in several papers[8]. Considering, first, short chains in a melt, the rotational diffusion of a macromolecule observed as a whole is fast enough compared with the timescale $|H_D(\theta)|^{-1}$ to average the dipolar part $H_D(\theta)$ to zero; whereas, considering very long chains in a melt, the rate of disentanglement is quite small so that the rotational diffusion of a whole macromolecule is too long compared with $|H_D(\theta)|^{-1}$ to average this part of the interactions to zero. This leads to a partial average, only: $\langle H_D(\theta) \rangle \neq 0$; this is now discussed.

Temporary network structure

Considering viscoelastic properties, any high molecular weight polymer melt is currently pictured as a temporary network structure determined from topological constraints[11,12]. The mesh size is related to the average concentration of entanglements. The average mass M_e of chain segments connecting any two neighbouring entanglements is derived from the plateau value G_N^0 of the relaxation modulus:

$$M_e = \rho RT/G_N^0 \qquad (1)$$

where ρ is the mass of polymer melt per unit volume and T is the temperature ($R = 8.32 \, \text{J K}^{-1}$). The mesh size is independent of the chain molecular weight. Chain segments connecting two neighbouring entanglements are called submolecules. The lifetime of the temporary network structure is closely related to the translational diffusion of polymer chains in the melt. This diffusion process is usually described from a broad relaxation time spectrum which consists of two dispersions Ω_1 and Ω_2 separated from each other by a wide cut-off. The dispersion Ω_1 is associated with high relaxational frequency motions occurring within a chain segment connecting neighbouring entanglements; Ω_1 is independent of the chain molecular weight[11,12]. It has negligible effects concerning the diffusion of a macromolecule. The dispersion Ω_2, is also called the terminal relaxation spectrum, describes collective diffusional motions occurring along a whole polymer chain; it exhibits a strong chain molecular weight dependence. The dispersion Ω_2 has mainly been derived until now from the reptational model proposed by De Gennes[13]. It is not the purpose of the present work to show how the reptational model can be connected to nuclear magnetic resonance[14]. However, the main property underlying the present n.m.r. approach is the existence of a wide cut-off separating the two dispersions Ω_1 and Ω_2. For very long chains, the terminal relaxation spectrum has no effects on n.m.r., because corresponding chain relaxation times are far too long compared with molecular correlation times supposed to induce significant effects on the irreversible motion of the magnetization. Considering n.m.r. properties, any high molecular weight polymer melt is perceived as a permanent network structure. It is like assuming that entanglements are frozen during the timescale of n.m.r. observation. In other words, by assuming that the Ω_2 dispersion is not involved in n.m.r. measurements, it is inferred that no diffusional motion of any part of a chain can be observed over a timescale corresponding to the whole chain relaxation spectrum. The chain motion is not perceived from n.m.r. as a full isotropic diffusion process. On the other hand, high relaxation frequency motions of short segments (Ω_1) dispersion) are well observed from the relaxation process of the longitudinal component of the nuclear magnetization. It is currently shown that this relaxation process is independent of the chain molecular weight[15].

Residual spin–spin interactions

High molecular weight samples will be considered as permanent network structures throughout the present work. They are supposed to be built from submolecules which have fixed end points, from the point of view of

n.m.r.; they connect two neighbouring entanglements; their average molecular weight is M_e. Now, the rotational diffusion of any monomeric unit is non-isotropic whenever it occurs within a chain segment which has fixed end points. Considering that most spin–spin interactions inducing n.m.r. properties observed in polymer melts are dipole–dipole interactions, these tensorial functions of space variables of nuclei are not averaged to zero by non-isotropic rotational diffusion of monomeric units. There is a residual energy of spin–spin interactions, $\hbar\varepsilon_e$. The irreversible dynamics of the transverse component of the magnetization is only governed by partial motional averages of spin–spin interactions. They reflect pure symmetry properties resulting from hindered motions associated with the Ω_1 dispersion within short segments connecting entanglements. This property has been easily described using a simple model built from a freely jointed chain segment[8]. Every bond was assumed to carry a proton pair. However, nuclear magnetic interactions between proton pairs were neglected. The calculated residual energy of spin–spin interactions is expressed as:

$$\hbar\varepsilon_e = \hbar\beta\Delta_G r_e^2 (3\cos^2\theta_e - 1)/N_e^2 a^2 \qquad (2)$$

where $\hbar\Delta_G$ is the energy of spin–spin interactions which should be observed in a glass ($\Delta_G \simeq 10^5 \, \text{rad s}^{-1}$), N_e is the number of skeletal bonds defining the chain segment connecting two neighbouring entanglements, a is the average length of a bond, r_e is the temporarily fixed end-to-end vector of the observed chain segment, θ_e defines the orientation of r_e with respect to the steady magnetic field direction, and β is a numerical factor close to unity.

Semi-local n.m.r. probe

In a melt, the residual energy $\hbar\varepsilon_e$ must be averaged over all end-to-end vectors of the temporary network structure resulting from the presence of entanglements. The distribution function is usually assumed to be Gaussian:

$$\overline{r_e^2} = C_\infty N_e a^2 \qquad (3)$$

where C_∞ is the characteristic ratio of the chain segment.

This is a static average. Correspondingly, the average residual energy calculated over the whole sample is written as:

$$\hbar\Delta_e = \hbar(\overline{\varepsilon_e^2})^{1/2} \qquad (4)$$

or

$$\Delta_e = 2\beta\Delta_G C_\infty/N_e\sqrt{3} \qquad (5)$$

Formulae (2) and (3) clearly show that collective properties of monomeric units are probed by n.m.r. over a space scale determined by $(\overline{r_e^2})^{1/2} \simeq 61 \, \text{Å}$; with $a \simeq 1.5 \, \text{Å}$, $C_\infty \simeq 7$ and $N_e \simeq 238$. This is a semi-local space scale. Correspondingly, an estimate of Δ_e can be given from formula (5):

$$\Delta_e \simeq 3.4 \times 10^3 \, \text{rad s}^{-1}$$

with $\Delta_G \simeq 10 \, \text{rad s}^{-1}$, $C_\infty \simeq 7$, $N_e \simeq 238$ and $\beta \simeq 1$. This corresponds to a resonance linewidth value usually measured from flexible polymer chains in a melt. The foregoing numerical values could apply to

poly(dimethylsiloxane) chains, where M_e is known to be equal to about 8.8×10^3. The G_N^0 value derived from formula (1) is 2.8×10^6 dyn cm^{-2}; tabulated values give 2.3×10^6 dyn cm^{-2}. From formulae (1) and (5) the average residual energy is expressed as a linear function of G_N^0:

$$\Delta_e = 4\beta \Delta_G C_\infty G_N^0 / \omega_m RT \sqrt{3} \qquad (6)$$

where $1/\omega_m$ is the molar volume of one monomer unit.

The presence of a residual energy of spin–spin interactions has been extensively studied using several n.m.r. approaches. The simplest one is based on a spectrum-narrowing effect induced by sample rotation around an axis perpendicular to the steady magnetic field direction[5,16].

Specific methyl group properties

Formula (6) can be extended to real poly(dimethylsiloxane) chains, in the following way. First, the factor C_∞ is assumed to account reasonably for flexibility effects along observed chain segments. Secondly, specific properties of three-proton spin systems are taken into consideration. The spin-system response associated with the transverse component of the magnetization consists of two signals of equal amplitude. The dynamics of one of them (signal I) is controlled by the $H_D(\theta,\alpha)$ part of spin–spin interactions, already mentioned. It mainly reflects high-frequency motions of short segments and it roughly depends upon the correlation function:

$$\langle H_D(\theta,\alpha_1)H_D(\theta,\alpha_2)\rangle$$

where α_1 and α_2 are two azimuthal angles corresponding to two times t_1 and t_2. The relaxation process occurs in a time interval defined by a timescale $T_2(I)$. In a hogh molecular weight PDMS melt, the other half of the signal (signal II) is governed by the residual energy of spin–spin interactions within a methyl group. The strength of the part $H_D(\theta)$ is exactly expressed as that of a proton pair, $3\gamma^2 h/2b^3$, where γ is the gyromagnetic ratio of a proton and b is the distance between protons within either a pair or within a methyl group. The timescale of the relaxation process is $T_2(II) \simeq \Delta_e^{-1}$. We are mainly interested in this part of the signal to explore mesh size properties of random siloxane–silica mixtures.

MESH SIZE OF NETWORK-LIKE STRUCTURES

Before describing n.m.r. measurements, it may be worth emphasizing that the number of monomeric units linked to the silica surface gives rise to a negligible signal compared with the amplitude of the magnetization observed from the whole sample. Monomeric units are supposed to be linked to silica through hydrogen bonding. The average number of hydrogen bonds per unit area of silica has already been estimated; it is equal to 1.8×10^{-2} Å^{-2}. The specific area of silica is 150 m^2 g^{-1}. Therefore, considering saturated adsorption onto silica, the average mass of monomeric units bound to the surface is 3.3×10^{-2} g per unit mass of silica. The most concentrated samples observed throughout the present work correspond to 1.6 g of polymer per unit mass of silica. Although some monomeric units located near the surface can also be temporarily held fixed in space, the

corresponding amplitude of their signal cannot be larger than about 10% of the whole magnetization.

All relaxation functions of the transverse magnetization were recorded from spin-echo experiments performed by using a Bruker CXP 100 spectrometer.

Pure melt

As a first step, the n.m.r. observation started from pure molten polymers characterized by number average weights $\bar{M}_n = 3.6 \times 10^5$ and 1.3×10^5, respectively (polydispersity indices were $I = 1.7$ and 1.8, respectively). Corresponding relaxation functions of the transverse magnetization of protons are reported in *Figure 1*. They obey a superposition property over a variation interval of the decay amplitude equal to about 70%. The tail of the signal associated with the molecular weight $\bar{M}_n = 1.3 \times 10^5$ describes small effects induced by a disentanglement process. However, this is not fast enough to perturb the whole signal; as is usually predicted, it starts increasing the time constant of the relaxation function tail, only. The upper parts of both signals exhibit a sample rotation effect already mentioned[3]. They should be in coincidence with each other without any timescale shift, because the average molecular weight of chain segments connecting neighbouring entanglements is independent of the chain molecular weight in a monodisperse sample. However, observed systems are not monodisperse polymers ($I = 1.7$ and 1.8, respectively) and they have different distributions. Consequently, temporary network structures are swollen in different ways by low molecular weight parts of the chain distributions. These n.m.r. results show that the temporary network structure is dependent upon the polydispersity to some extent. From formula (5), this should also be reflected by plateau values of the relaxation modulus G_N^0, for these two melts.

Finite size clusters, infinite clusters

Polymer samples ($\bar{M}_n = 3.6 \times 10^5$) containing increasing amounts of silica were observed. Corresponding relaxation functions of the transverse magnetization were recorded; they were found to obey a superposition property which is illustrated by *Figure 2a*. The reference curve was recorded from a sample characterized by an initial silica concentration $C_{Si} = 0.29$ (w/w). Such a sample was already known to give rise to a permanent network structure by eliminating all polymer chains free to move. Then, the curve recorded from a less concentrated
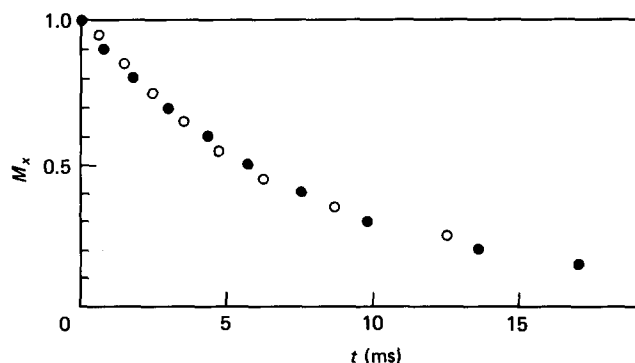

Figure 1 Pure melt: superimposed relaxation functions of the transverse magnetization of protons linked to siloxane chains. The reference curve corresponds to $\bar{M}_n = 3.6 \times 10^5$ ($\bullet$); the shift factor corresponding to $\bar{M}_n = 1.3 \times 10^5$ is $s = 0.44$ ($\bigcirc$)
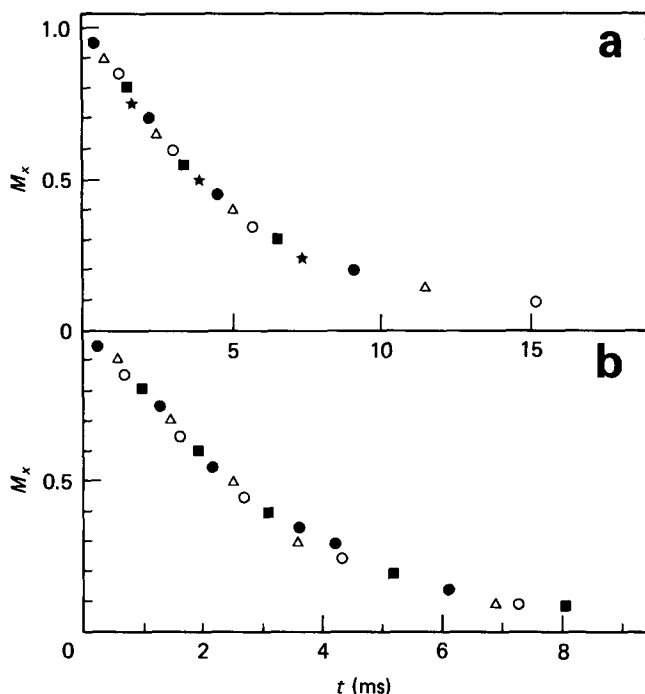
Figure 2 Silica-filled siloxanes ($\bar{M}_n = 3.6 \times 10^5$): superposition property of relaxation functions corresponding to different silica concentrations, C_{Si}. (a) $C_{Si} = 0.29$ (w/w) (●), reference curve; shift factors 0.17 (△), 0.09 (○), 0.05 (■), 0.0 (★). (b) $C_{Si} = 0.45$ (●), reference curve; shift factors 0.41 (△), 0.3 (○), 0.2 (■)

siloxane–silica mixture ($C_{Si} = 0.17$ (w/w)) was brought into coincidence with the reference curve using a single factor s to shift its whole timescale. Such a sample was also known to behave like a permanent network structure by eliminating all free polymer chains. Shifted relaxation functions corresponding to silica concentrations $C_{Si} = 0.09$, 0.04 and 0, respectively, are also drawn in *Figure 2a*. All variations of the timescale shift factor s are reported as a function of the silica concentration C_{Si} in *Figure 3a*. It obeys a striking linear dependence upon C_{Si} although the three less concentrated samples do not exhibit any gel limit behaviour. They only consist of clusters and microgels.

This partial result clearly shows that the mathematical structure of magnetic relaxation functions is kept invariant under increase of the silica concentration within the range $0 \leqslant C_{Si} \leqslant 0.29$. The only change induced by the presence of silica aggregates concerns the decrease of the relaxation timescale. Starting from a pure melt, it is considered that network structures obtained by adding silica are still governed by entanglements, in the concentration range $0 \leqslant C_{Si} \leqslant 0.29$. According to formula (5), the decrease of the relaxation timescale must be related to a slightly reduced average size of the statistical mesh of the network structure. Topological constraints are more and more trapped by silica aggregates, but they are all perceived as frozen from n.m.r. The only effect induced by silica is a slight shift of the distribution function of elementary chains connecting neighbouring entanglements, towards shorter chain segments.

Infinite clusters

In a third step, the n.m.r. observation started from a random siloxane–silica mixture ($\bar{M}_n = 3.6 \times 10^5$), characterized by a silica concentration C_{Si} equal to 0.29 (w/w). Then, several samples were prepared by removing increasing amounts of polymer chains free to move

throughout the initial mixture. The reference relaxation curve was recorded in a sample characterized by the limit silica concentration $C_{Si}^l = 0.45$ (w/w). The resulting sample behaved like a permanent gel; it necessarily contained dangling chains. Relaxation curves associated with intermediate silica concentrations equal to 0.41, 0.315 and 0.305, respectively, were brought into coincidence with the reference curve, using an appropriate shift factor *Figure 2b*). Corresponding variations of the shift factor are shown in *Figure 3b*. Samples characterized by concentrations ranging from 0.45 to 0.29 (w/w) may be considered as permanent gels partly swollen by polymer chains. Nevertheless, the mathematical structure of magnetic relaxation functions is still kept invariant upon swelling of the permanent gel.

Another series of samples was prepared by removing increasing amounts of free polymer chains from an initial siloxane–silica mixture ($\bar{M}_n = 3.6 \times 10^5$) defined by the concentration $C_{Si} = 0.16$ (w/w). Relaxation curves corresponding to several concentrations 0.32, 0.25 and 0.2, respectively, were found to again obey a superposition property (*Figure 2b*). The sample obtained by removing all free chains from the initial mixture also behaved like a permanent gel ($C_{Si}^l = 0.32$). Shift factors are reported in *Figure 3b*. Samples with silica concentrations ranging from 0.32 to 0.2 also correspond to permanent gels swollen by polymer chains.

Finally, all shift factors were determined from the more concentrated sample ($C_{Si}^l = 0.45$ (w/w)); their variations are reported in *Figure 3c*.

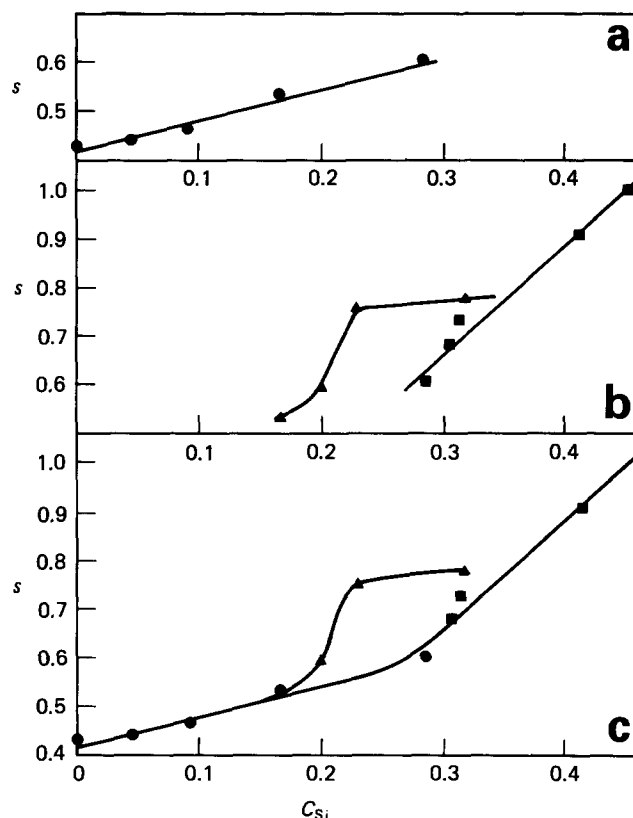It is clearly seen that permanent network structures prepared from samples characterized by two different

Figure 3 Shift factor variations derived from *Figure* 2($\bar{M}_n = 3.6 \times 10^5$). (a) Samples obtained by adding silica to pure melt. (b) Samples obtained by removing free polymer from the mixture defined by the initial concentrations $C_{Si} = 0.29$ (■) and $C_{Si} = 0.17$ (▲). (c) Shift factors referred to the highest silica concentration ($C_{Si} = 0.45$)

initial concentrations ($C_{Si} = 0.29$ or $C_{Si} = 0.17$) can be thoroughly distinguished from each other, using n.m.r. Referring to formula (5), the mesh size of the low silica concentration sample ($C_{Si}^l = 0.32$) is actually perceived from n.m.r. as larger than that of the high silica concentration one ($C_{Si}^l = 0.45$) because the ratio of corresponding shift factors is 1.33. The lower limit of silica concentration $C_{Si}^l = 0.32$ necessarily corresponds to neighbouring silica aggregates connected by chain segments longer than those existing in the sample defined from the higher limit of silica concentration. However, the ratio of shift factors different from unity is interpreted in the following way. Both the low silica concentration sample and the more concentrated one probably present a permanent structure derived from the primary temporary network determined from entanglements in a pure melt. But, the less concentrated sample contains more dangling chains associated with the low molecular weight part of the chain distribution than the more concentrated system. Accordingly, whatever the swelling mechanism induced by dangling chains, the latter sample must be less swollen than the low silica concentration system. Then, *Figure 3b* shows the swelling of both samples by free polymer does not induce identical effects.

The main conclusion of this first part of the n.m.r. observation is that entanglements governing the mesh size of network-like structures determined by addition of silica are derived from the primary structure built from entanglements existing in the pure melt.

CHAIN MOLECULAR WEIGHT VARIATIONS

N.m.r. observations similar to that described in the foregoing section were also made for lower molecular weight siloxane samples ($\bar{M}_n = 1.3 \times 10^5$ and $\bar{M}_n = 0.9 \times 10^5$; both polydispersity indexes were $I = 1.8$).

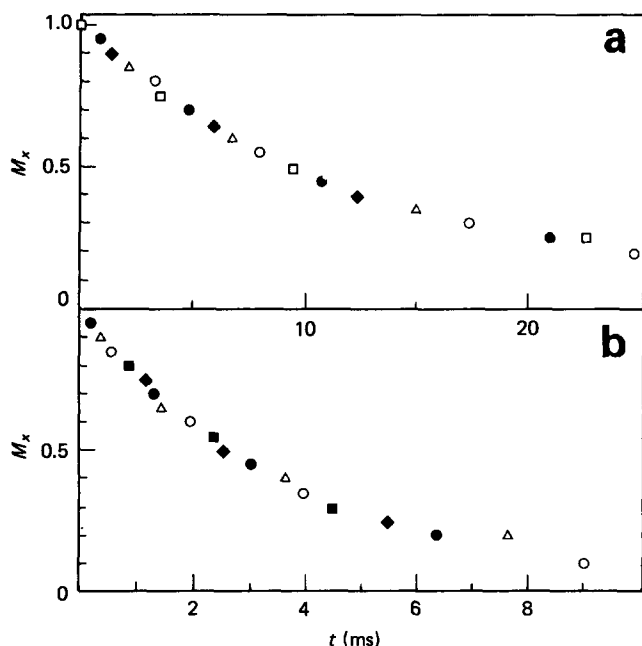**Figure 4** Silica-filled siloxanes ($\bar{M}_n = 1.3 \times 10^5$); superposition property of relaxation functions corresponding to different silica concentrations. (a) $C_{Si} = 0.17$ (●), reference curve; shift factors 0.09 (◆), 0.05 (△), 0.0 (○), 0.29 (□). (b) Samples prepared by removing free polymer from an initial concentration $C_{Si} = 0.29$ until $C_{Si} = 0.53$ (●); 0.29 (△); 0.49 (○). Further samples prepared from an initial concentration $C_{Si} = 0.17$ until $C_{Si} = 0.41$ (■); 0.25 (◆)
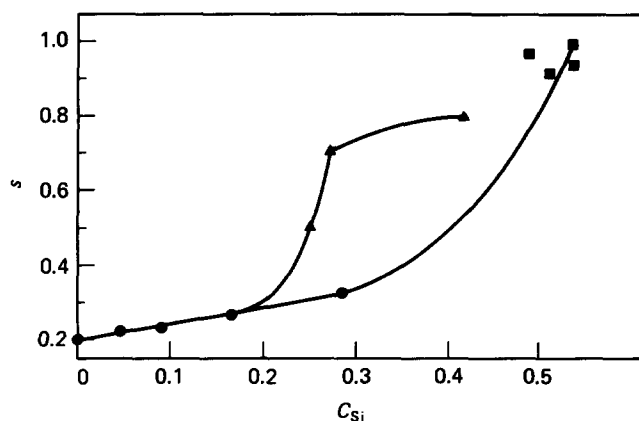

Figure 5 Shift factor variations derived from *Figure 4*. Silica added to pure melt (●); samples prepared from the initial concentrations $C_{Si} = 0.29$ (■) and $C_{Si} = 0.17$ (▲)

Intermediate molecular weight siloxane

Starting from a pure melt ($\bar{M}_n = 1.3 \times 10^5$), the silica concentration was varied until $C_{Si} = 0.29$ (w/w). The superposition property was observed with a satisfactory accuracy over a relative range of variations of decay amplitude equal to 60% (*Figure 4a*). Also, samples with higher silica concentrations were obtained by removing free polymer chains from the initial mixture ($C_{Si} = 0.29$ (w/w)). The limit silica concentration was $C_{Si}^l = 0.53$ (w/w); it corresponded to an infinite cluster, reversibly swollen by using a good solvent. The limit concentration $C_{Si}^l = 0.53$ is higher than that obtained from longer chains ($C_{Si}^l = 0.45$). This result only indicates that the multiple aggregate binding process occurs to an extent which is smaller in low molecular weight siloxane samples than in high molecular weight ones. Relaxation functions of the transverse magnetization were also found to obey a superposition property (*Figure 4b*). All shift factors are reported in *Figure 5* (the reference curve corresponds to $C_{Si}^l = 0.53$ (w/w)).

Another series of measurements was obtained by removing free polymer chains from a sample characterized by an initial concentration $C_{Si} = 0.17$ (*Figure 4b*). Shift factor values are reported in *Figure 5*. The limit concentration ($C_{Si}^l = 0.42$ (w/w)) did not correspond to any permanent gel. The sample only contained microgels which were not necessarily connected with one another: there was a negligible multiple aggregate binding process.

Once again, network-like structures, whether they are permanent or not, derived from the initial concentrations $C_{Si} = 0.17$ or $C_{Si} = 0.29$ are not swollen by polymer chains in the same way. Referring again to formula (5), the mesh size is larger on average in the lower silica concentration sample than in the higher one: the ratio of shift factors is 1.25.

Low molecular weight siloxane

Starting from a low molecular weight polymer sample ($\bar{M}_n = 0.9 \times 10^5$ and $I = 1.8$) relaxation functions were recorded from mixtures characterized by the following silica concentrations: $C_{Si} = 0.17, 0.29, 0.45, 0.47, 0.49, 0.5$, 0.53 and 0.55, respectively (*Figure 6*). The last six concentrations were obtained by extracting polymer chains from the silica filled siloxane characterized by the initial concentration $C_{Si} = 0.29$ (w/w). Variations of the shift factor are drawn in *Figure 7*. The limit concentration
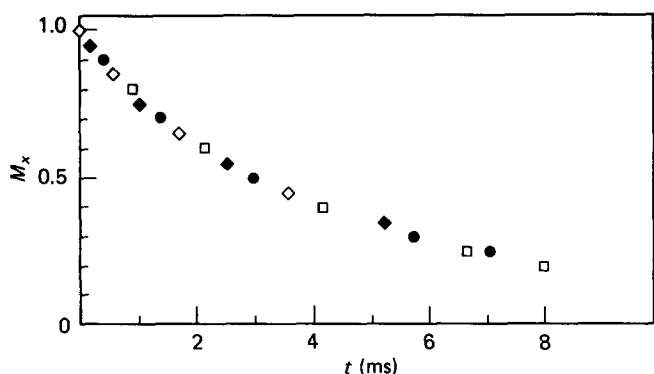
Figure 6 Silica-filled siloxanes $(\bar{M}_n = 0.9 \times 10^5)$; superposition property of relaxation functions corresponding to different silica concentrations, C_{Si}. Samples obtained from the initial concentration $C_{Si} = 0.29$ (◆); $C_{Si} = 0.45$, reference curve (●); $C_{Si} = 0.55$ (□). Further sample obtained from the initial concentration $C_{Si} = 0.17$ (◇)
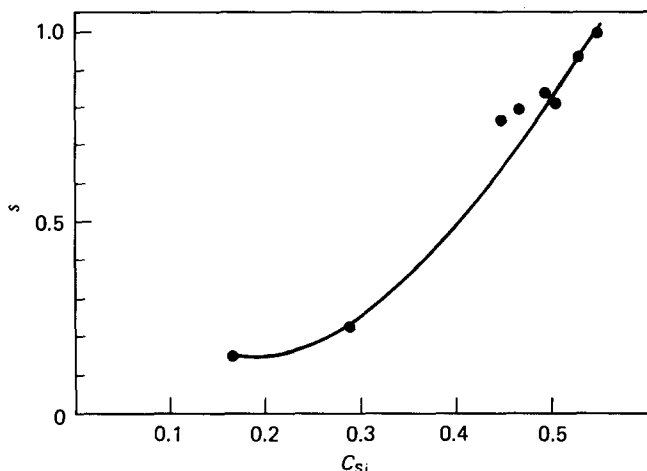

Figure 7 Shift factor variations derived from *Figure 6*

was not found to correspond to any permanent network-like structure.

The addition of silica to this low molecular weight siloxane does not induce any drastic change of the distribution function governing the random mesh size of the temporary network-like structure existing in the pure polymer; it is only shifted towards smaller values.

TREATED SILICA SURFACE

Finally, the n.m.r. investigation was applied to mixtures characterized by a constant silica concentration $C_{Si} = 0.29$ ($\bar{M}_n = 3.6 \times 10^5$) and various extents of surface treatment of aggregates. Silica silanol sites were converted to non-functional trimethylsilyl groups according to an experimental procedure already described in II. The timescale of the magnetic relaxation function was found to increase by increasing the extent of surface treatment. Observed fractions of converted free silanols were 0.17, 0.22, 0.59 and 0.74, respectively. Corresponding superimposed functions are drawn in *Figure 8*. This result clearly indicates that the binding effect of polymer chains onto silica partly governs properties of the network-like structure although the silica concentration is kept constant.

DISCUSSION

Figure 9 connects relaxation functions obtained from different chain molecular weight series of silica-filled

siloxanes. They also obey a superposition property ($C_{Si} = 0.17$ and $\bar{M}_n = 3.6 \times 10^5$, 1.8×10^5 and 0.9×10^5, respectively). The most striking feature concerning the foregoing analysis is the general superposition property of the relaxation function of the transverse component of the magnetization, observed upon addition of silica. All shift factors are represented in *Figure 10*. The reference curve starts from the permanent gel structure ($C_{Si}^l = 0.45$); it is characterized by the largest residual energy Δ_e^0. Any shift factor is then written as $s = \Delta_e/\Delta_e^0$; therefore, according to formula (6), it is proportional to the plateau value of the relaxation modulus of a given sample:

$$s = \Delta_e/\Delta_e^0 \propto G_N^0 \qquad (7)$$

More precisely, s is considered as an increasing function of G_N^0; formula (7) is probably a linear approximation. The superposition law is interpreted as showing that average properties of network-like structures are derived from the primary temporary network structure induced by entanglements existing in a pure melt. Accordingly, the behaviour of the probability distribution function of mesh sizes is considered as invariant upon addition of silica except for a shift towards smaller sizes related to an increase of G_N^0 values, i.e. of elastic properties of the polymer part of the mixture. Furthermore, a glance at *Figure 10* shows that a full treatment of the silica surface $C_{Si} = 0.29$ (w/w) gives rise to a mixture characterized by a residual energy value close to that of a mixture defined from a low concentration of silica ($C_{Si} \simeq 0.04$) without any surface treatment of aggregates. Therefore, mesh size
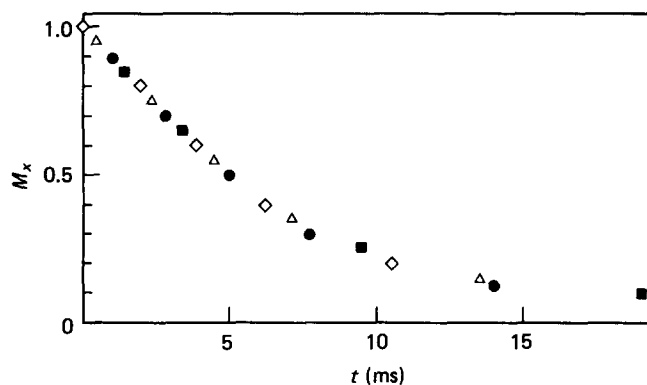

Figure 8 Silica-filled siloxanes $(\bar{M}_n = 3.6 \times 10^5)$, $C_{Si} = 0.29$. The silica surface of aggregates was treated to various extents. Ratio of converted silanol groups: 0.75 (●) reference curve; 0.6 (◇); 0.3 (△); 0.0 (□)
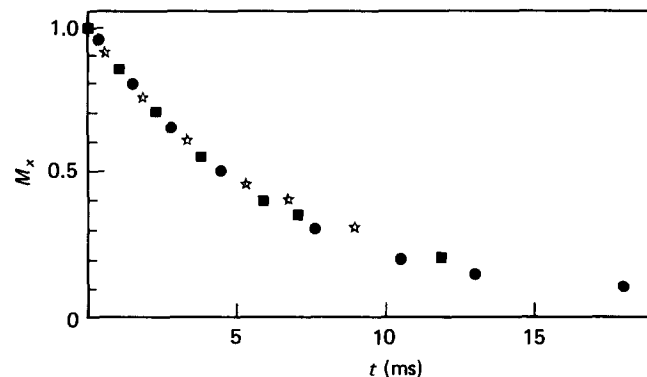

Figure 9 Superimposed relaxation functions corresponding to several number average chain molecular weights ($C_{Si} = 0.17$). $\bar{M}_n = 3.6 \times 10^5$ (●), reference curve; 1.3×10^5 (■); 0.9×10^5 (★)
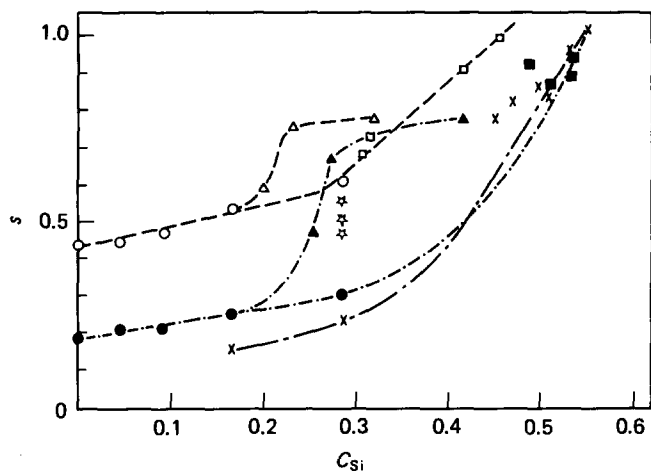
Figure 10 All shift factors referred to the silica concentration $C_{Si}=0.45$. $\bigcirc$, $\square$, $\triangle$, $\bar{M}_n=2.6\times10^5$; $\bullet$, $\blacksquare$, $\blacktriangle$, $\bar{M}_n=1.3\times10^5$; $\times$, $\bar{M}_n=0.9\times10^5$; $\bigstar$, treated silica surface ($\bar{M}_n=3.6\times10^5$)

static properties of the network are governed more by the binding of siloxane chains upon silica than by the presence of silica. This does not greatly modify the geometrical structure resulting from topological constraints, whether they are trapped or temporary. However, low relaxational frequencies are expected to be perturbed by the presence of treated as well as non-treated silica.

Finally, silica-filled siloxanes ($\bar{M}_n=3.6\times10^5$) observed in the concentration range $0.29\leqslant C_{Si}\leqslant0.45$ were considered as permanent gels partly swollen by free polymer chains. A swelling ratio Q was defined by dividing the total volume of polymer in the system by the volume of polymer corresponding to the limit silica concentration $C_{Si}^l=0.45$. The corresponding shift factor clearly exhibits a linear dependence upon Q. Silica-filled siloxane characterized by $\bar{M}_n=1.3\times10^5$ also presents a linear dependence of shift factors upon the swelling ratio Q (*Figure 11*). Furthermore, the random mixture defined from $\bar{M}_n=0.9\times10^5$ was also shown to exhibit the above property, although it cannot be considered as an infinite cluster. This result shows that swelling mechanisms of network-like structures are similar to one another whatever the initial state of the structure that is used to be swollen by free siloxane. In other words, initial structures defined from $\bar{M}_n=3.6\times10^5$, $C_{Si}^l=0.45$, $\bar{M}_n=1.3\times10^5$, $C_{Si}^l=0.53$ and $\bar{M}_n=0.9\times10^5$, $C_{Si}^l=0.55$, respectively, are probably derived from the same primary network. They are only swollen to different extents because of large differences between chain length distributions, but they are swollen according to the same mechanism by free chains. This reinforces the hypothesis that mesh size properties of silica-filled siloxanes mainly result from entanglements. The concentration of these topological constraints is varied by changing the amount of free siloxane.

Viscoelastic properties of filled polymers have been extensively investigated, for various systems such as polyisobutylene with different proportions of glass beads, poly(propylene ether) with sodium chloride particles, and rubber loaded with carbon black[12]. Several approaches have been proposed to relate the plateau value of the shear modulus of a composite to the shear moduli of the separated component materials. It may be worth emphasizing that, as a result of the pesent study, the network structure of the polymer part of the random

mixture cannot be considered as invariant upon addition of silica. This implies that the plateau value of the polymer component shear modulus should be introduced in theoretical formulations as a function of filler content.

CONCLUSION

Polymeric melts are knwon to present a dual mechanical behaviour: they are both viscous and elastic. The strength of each of these two characters depends upon the frequency of observation. The nuclear magnetic resonance response also exhibits such a dual property. This response presents a strong similarity with relaxation processes observed in solid state polymers (transverse component of the magnetization) and also a similarity with relaxation properties observed in liquid-like systems (longitudinal component). The purpose of the present work was to start elucidating the role of mineral fillers in siloxane using the transverse magnetic component of protons linked to polymer chains. More precisely, attention was focused on properties of the network-like structure existing in the presence of silica.

Siloxane–silica mixtures were probed in the semi-local space scale defined ($\simeq50$ Å) by the average distance between neighbouring entanglements. The most striking result arising from this n.m.r. observation is the invariance property of the mathematical structure of the transverse magnetic relaxtion function observed upon addition of silica. This implies that:

(i) The distribution function of elementary chains connecting neighbouring entanglements is also kept invariant upon addition of silica; it is only shifted towards smaller mesh size.

(ii) Network-like structures, whether they are temporary or not, are derived from the entangled chain system existing in a pure melt, without any drastic change. The shift effect towards smaller mesh sizes may be pictured as an affine isotropic deformation of the siloxane medium.

Furthermore, this shift effect is also considered as reflecting an enhancement of elastic properties of
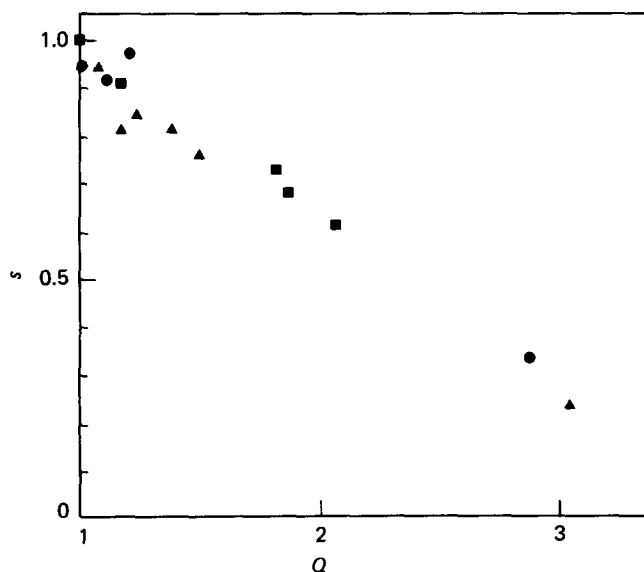

Figure 11 Linear variations of the shift factor as a function of the swelling ratio Q of network-like structures (the swelling agent is free siloxane; see text). $\bar{M}_n=3.6\times10^5$ ($\blacksquare$); 1.3×10^5 ($\bullet$); 0.9×10^5 ($\blacktriangle$). All samples were prepared from the initial concentration $C_{Si}=0.29$

siloxane–silica mixtures. This should be associated with an increase of the plateau value G_N^0 of the relaxation modulus[12]. More precisely, this enhancement is induced not only by the presence of silica but mainly by a binding process of the polymer chain upon aggregates, i.e. a reduction of entropy of the whole system resulting from a reduction of the number of degrees of freedom of the polymer component of the mixture.

The main feature to be pointed out from the present study is the possibility to discriminate elasticity properties of the polymer network structure from properties of the mixture considered as a whole from viscoelastic measurements. The residual energy of spin–spin interactions in a filled melt is assumed to be an increasing function of the plateau value G_N^0 of the shear modulus of the polymer component.

The present study could be conducted from neutron scattering measurements using partly labelled polymer chains. However, the main difficulty concerning such an approach arises from the partial labelling of a given chain: it does not necessarily correspond to the mean chain segment connecting two entanglements. In the same way, it is known that the labelling of elementary chains used to synthesized end-linking gels does not necessarily correspond to mean chain segment connecting trapped entanglements, although these have been shown to govern most gel properties[17,18]. The present approach could be extended to silica-filled polybutadiene and polyisoprene composites[19,20].

ACKNOWLEDGEMENTS

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