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Reversible Swelling of Gel-Like Silica-Filled Siloxanes. NMR Approach to Static Scaling Properties

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ABSTRACT: This work deals with the gel-like behavior of systems resulting from mechanical mixing of high molecular weight siloxane chains with silica particles. Statistical properties of polymer chains were probed by measurement of the magnetic relaxation of protons after removing all free siloxane chains. The specific residual amount of polymer bound to silica was varied from 1.2 to 2.4 (w/w); the fractal character of siloxane chains bridging particles and dangling chains was enhanced by using a swelling agent (chloroform). The spin–lattice relaxation of protons was shown to be insensitive to silica concentration variations; it was also insensitive to the addition of solvent, at polymer concentrations smaller than about 2.4 (w/w). These two results were assigned to the presence of dynamic screening domains analogous to those originating from entanglements in a pure melt. Scaling properties of these domains were probed in a semilocal space scale from the transverse magnetic relaxation of protons. Results observed in these systems are in very strong contrast to those observed for calibrated gels: (a) no packing condition effect was observed and (b) no affine property was induced by reversibily swelling silica-filled siloxane systems.

I. Introduction

This work describes an NMR investigation attempting to characterize the unfolding mechanism of polymer chains in a gel-like structure, i.e., a system where mineral filler particles serve the function of interlinkages; in addition to these junctions, physical combinations of chains are also mediated by trapped entanglements. The present study concerns siloxane chains linked to silica particles through hydrogen bonding; the size and the concentration of silica particles, on the one hand, and the average chain molecular weight, on the other hand, were chosen in a way appropriate to the formation of a network structure. The unfolding effect of polymer chains connecting silica particles was induced by a swelling agent. Although siloxane chains are not covalently linked to particles, the random mixture resulting from a saturated adsorption onto the silica surface may be reversibly swollen by using a suitably good solvent. The mixture may be shown to behave like a permanent gel because interlinkages provided by hydrogen bonds are strong compared with the strength of silica–solvent interactions.

It has been long recognized that elementary chains in a gel have a fractal character: they store the elastic energy of the system. Also, the statistical volume pervaded by a given elementary chain is much larger than the volume of the corresponding condensed material.[1] Polymer chains are known to be swollen by one another in a pure melt. Elementary chains in a gel are likewise intertwined, notwithstanding the presence of cross-links.[2] The collective fractal character of a gel can be perceived from its elastic equation of state,[3] whereas the individual fractal character of elementary chains cannot be observed without contrasting some of them with neighboring chains which serve the function of a swelling agent.

The contrast may be created by a partial deuteriation of the network.[2] This labeled system has been used to illustrate a fundamental property of polymeric gels: the mean square dimension of the chain segment joining two successive covalent links is governed by Gaussian statistics. It is equal to that measured from a similar chain segment embedded in a pure melt. The observation of swelling effects of a network structure is a convenient way often used to explore gel properties because it magnifies the fractal character of elementary chains. The maximum swelling, obtained at equilibrium with a pure solvent, reflects the full unfolding of elementary chains taking excluded volume effects into consideration.[4] The maximum swelling effect obeys the C*-theorem propounded by De Gennes. Correspondingly, the elastic modulus of a swollen gel is weakened.[4] However, it may be worth emphasizing that, in the presence of solvent, there is a lack of information about specific properties resulting from a strong interpenetration of elementary chains and involving an enhancement of orientations of monomeric units.[5]

It has been recently shown that fractal properties of elementary chains, in a melt or in a gel, can be investigated by observing the magnetic resonance of protons attached to polymer chains.[6] Effects of topological constraints exerted on chain segments by entanglements or by cross-links are reflected in a specific mechanism of relaxation of the transverse magnetization of nuclei. The NMR investigation has been already applied to the following types of polymer systems.

(1) In an uncross-linked melt, low-frequency contributions to fluctuations of chain segments connecting entanglements were characterized, observing effects of chain molecular weight variations in concentrated solutions.[7]

(2) Four qualitative features of calibrated gels come out from NMR investigations of systems obtained from end-linked siloxane chains.[8]

(i) Relative fluctuations in space of two junctions connected by a chain segment are not isotropic. From the NMR point of view, a gel system represents an isotropic average of nonisotropic individual properties of elementary chains. These are induced by a hindered translational diffusion of junctions, while the isotropic average results from the absence of external constraints. NMR is known to be appropriate to the observation of nonisotropic properties of subsystems, notwithstanding the powder average applied to them.[9]

(ii) When the number of junctions per unit volume in a dry gel is decreased, both the nuclear magnetic relaxation rate, δ, and the elastic modulus, E, decrease.

(iii) When a gel is swollen, using a good solvent, the NMR behavior is in contrast to the elastic properties: the modulus, E, is decreased, whereas the relaxation rate, δ, is increased. This result indicates that junctions move only in a limited region of space. The unfolding of elementary chains keeps junctions away from one another; elementary chains are slightly stretched.

(iv) The progressive unfolding of elementary chains was shown to occur in two steps. The first was assigned to a disengagement of chains analogous to that observed in a pure melt, by adding small amounts of solvent. The second step was supposed to correspond to a smooth evolution from the concentrated state to the dilute state defined by the maximum swelling.

(3) Finally, NMR was applied to the study of random silica–siloxane systems resulting from mechanical mixing.[10] The purpose of this NMR approach was to characterize polymer chains in the presence of silica without observing the filler particles. The network structure obtained by increasing the silica concentration was shown to derive from the temporary network structure determined from entangled siloxane chains in the pure melt. The increase of the relaxation rate, δ, measured upon addition of silica was associated with an enhancement of the elastic properties of the polymer system, whereas the surface treatment of silica particles appropriate to the elimination of hydrogen bonds was found to induce only slight changes of elastic properties of the pure polymer system.

The purpose of the present work was to use NMR to compare the swelling process of random mixtures, observed after removing free polymer chains, with that of covalent gels formed from end-linked chains.

II. NMR Probe. Fractal Chain Character

1. **Methyl Groups.** NMR probes used to investigate swelling the properties of random siloxane–silica mixtures are determined by methyl groups attached to poly(dimethylsiloxane) chains. From the point of view of NMR, a methyl group defines a spin system comprising three identical nuclear magnetic moments; each of them is characterized by a spin $I = {}^1/_2$. A feature of any methyl group, originating from its 3-fold symmetry, is the specific expression of dipole–dipole interactions established between the three nuclei, considered all together. The adiabatic part of these dipole–dipole interactions is known to be split into two parts D_1 and D_2. Only part D_2 depends on the angle, θ_c, that the $\vec{C}$ axis of symmetry of the methyl group makes with the steady magnetic field direction, while the other one, D_1, depends upon both angle θ_c and the azimuthal angle of rotation of the methyl group about its own $\vec{C}$ axis.[11]

2. **Siloxane Chains.** Another feature of methyl groups concerns their random motions; when they are attached to long siloxane chains, the time scale of these motions is necessarily split into two well-separated intervals. Starting the observation at an initial time, t_i, the first one is associated with the fast rotational diffusion of a methyl group about its $\vec{C}$ axis of symmetry. Correlation times characterizing this motion are known to range from 10^{-11} to 10^{-9} s. The second time interval corresponds to slow motions of the $\vec{C}$ axis, induced by the migration process of a chain as a whole. These two types of motions are stochastically independent of each other. As a consequence of the splitting of the time scale of random motions, the two parts of the adiabatic dipole–dipole interactions of nuclei within a methyl group are averaged in two different ways. During short time intervals ($\simeq 10^{-7}$ s), D_1 is averaged to zero, whereas D_2 is constant because the orientation of the $\vec{C}$ axis may be considered as fixed in space. Dipole–dipole interactions are only partly averaged. The full motional averaging process requires long time intervals because it must be completed by skeletal motions of a chain.[6] The transverse nuclear magnetization resulting from such random motions of a methyl group has been shown to consist of two parts of equal amplitude; the reversible dynamics of the first contribution, $m_2(t)$, is only governed by time fluctuations of the angle, $\theta_c(t)$, that the $\vec{C}$ axis makes with the steady magnetic field direction:

$$m_2(t) = {}^1\!/_2\left\langle \cos\left(D_p \int_0^t [3\cos^2\theta_c(t') - 1]\,\mathrm{d}t'\right)\right\rangle \qquad (1)$$

with $D_p = 10^5$ rad·s^{-1} for a methyl group. $\langle\ \rangle$ denotes a time average over all orientations of the $\vec{C}$ axis. The other contribution to the magnetization, $m_1(t)$, is only sensitive to fast random motions of the methyl group about its $\vec{C}$ axis; it usually corresponds to a long time scale ($\simeq 1$ s).

However, in the case of long siloxane macromolecules, the second step of the motional averaging is not perceived from NMR because they do not move rapidly enough, in comparison with the time scale of NMR measurements.[12] In the case of polymeric gels, this second step is likewise not observed by NMR because junctions do not move rapidly in all directions of space. Any elementary chain connecting two successive junctions may be considered on average as having a fixed end-to-end vector in space.

3. **Chain of Specified End-to-End Vectors.** The sensitivity of NMR to the fractal character of elementary chains originates from nonisotropic monomeric motions occurring within a chain segment whenever it has a fixed end-separation vector, $\vec{r}_e$, different from zero.[6] These nonisotropic motions do not average to zero tensorial spin–spin interactions of nuclei. The average value

$$\epsilon_e = D_p\langle 3\cos^2\theta_c(t) - 1\rangle_e \qquad (2)$$

must be calculated over all chain conformations compatible with the non-zero end-separation vector, $\vec{r}_e$. It is generally expressed as a function of $\vec{r}_e$ and the number, Ne, of skeletal bonds in the chain segment; for a state of weak stretching,

$$\epsilon_e \propto \beta D_p(3\cos^2\theta_c - 1)r_e^2/\text{Ne}^2a^2 \qquad (3)$$

Here, a is the mean skeletal bond length; the coefficient β accounts for the flexibility properties of the chain segment; θ_c is the angle that the end-separation vector, $\vec{r}_e$, makes with the steady magnetic field direction.[13,14] There is a residual energy of spin–spin interactions. Accordingly, the expression of the contribution to the transverse magnetic relaxation function of a given methyl group (formula 1) must be replaced by

$$m_2^e(t) = \tfrac{1}{2}\exp(i\epsilon_e t)\phi_2^e(t) \qquad (4)$$

$\phi_2^e(t)$ is associated with random motions of the C axis about its mean orientation determined by the fixed end-to-end vector, $\vec{r}_e$. The function, $\phi_2^e(t)$, usually decays over a time interval much larger than ϵ_e^{-1}. It has a negligible effect on $m_2^e(t)$, and it will be omitted:

$$m_2^e(t) \simeq \tfrac{1}{2}\exp(i\epsilon_e t) \qquad (5)$$

Neglecting all magnetic interactions between methyl groups and assuming that the distribution of end-separation vectors is isotropic, the signal resulting from formula 5 is averaged over the whole gel sample:

$$M_2(t) = \overline{\tfrac{1}{2}\exp(i\epsilon_e t)} \qquad (6)$$

The average is calculated over all end-separation vectors; it reflects nonisotropic properties of elementary chains, albeit the distribution of $\vec{r}_e$ vectors is isotropic. The foregoing description may be associated with a permanent gel where $\vec{r}_e$ vectors join junctions having small amplitude fluctuations about their mean positions. It may likewise represent the situation of a temporary network structure determined from entangled long siloxane chains; entanglements are considered frozen during the time scale of NMR measurements.

4. Fractal Aspects. It is not the purpose of the present paper to describe the quantitative connection of the spin-system response, $m_2^e(t)$, with the fractal properties of a chain segment. However, this property can be discussed in the following qualitative way.

Consider first an ideal chain segment with a fixed-end-separation vector, $\vec{r}_e$, equal to zero. The statistical volume pervaded by this segment comprising Ne freely jointed bonds is

$$v_e \propto \text{Ne}^{3/2}a^3$$

The average radius, R, of this volume is set equal to $\text{Ne}^{1/2}a$. Furthermore, assuming that a molecular weight, m_a, is assigned to each chain unit, the total mass, m_T, of the chain is expressed as

$$m_T \propto \text{Ne}\,m_a$$

or

$$m_T \propto R^2$$

The fractal exponent of the chain segment is 2. Correspondingly, the average value given by formula 3 is zero; the spin-system response expressed by formula 5 describes an infinitely long decay.

Consider now a fully stretched ideal chain segment. Its end-separation vector, $\vec{r}_e$, is fixed in space and has a length equal to Nea. The volume pervaded by this chain segment is Nea^3; its fractal character is completely lost. All bonds are oriented along the direction of $\vec{r}_e$. Consequently, there is no motional averaging of dipole–dipole interactions. ϵ_e has a maximum value in accordance with the orientation of $\vec{r}_e$ with respect to the magnetic field direction. The resulting spin-system response expressed by formula 5 must describe a very short decay. Going from $|\vec{r}_e| = 0$ to $|\vec{r}_e| = \text{Ne}a$, all intermediate situations are associated with a fractal character of the chain segment, of less and less importance.

5. Real Chains. The foregoing approach relies on the assumption that nuclear moments of different methyl groups were not interacting with one another. In the case of real chains embedded in a polymeric gel, these interactions cannot be neglected. Hence, it is now considered that nuclear magnetic interactions exist between methyl groups along a given chain segment and also between methyl groups attached to different intertwined chain segments. It is still assumed that any elementary chain domain is fully characterized by its end-to-end vector, $\vec{r}_e$. Also, the expression of the residual energy of all spin–spin interactions existing within such a domain is assumed to have axial symmetry with respect to the vector, $\vec{r}_e$. This residual energy is an additional contribution to the relaxation mechanism of $M_1(t)$ of the magnetization. It can drastically shorten the relaxation process of the contribution, $m_2(t)$, to the transverse magnetization, which was assumed to have a very long decay, in the absence of interactions between methyl groups. Finally, it will be assumed throughout this paper that the total residual energy, ϵ_T, governing the $M_2(t)$ part of the signal is still expressed as

$$\epsilon_T = \beta(3\cos^2\theta_e - 1)r_e^2/(\text{Ne}^*)^2a^2 \qquad (7)$$

where Ne* is now an effective number of degrees of freedom participating in the definition of the elementary chain domain. Formula 7 will be used as the basis of interpretation of the NMR properties observed in random silica–siloxane mixtures.

III. Random Silica–Siloxane Mixtures

Silica-filled polymers studied in this work were prepared from mechanical mixing of siloxane chains with silica particles. The random character of these mixtures results both from the broad distribution of silica aggregate sizes and from the high polydispersity, I, of siloxane chains ($I \simeq 2$). Furthermore, silica aggregates are distributed at random in space. A saturated adsorption of siloxane chains onto the silica surface arises from the mechanical mixing procedure. The noncovalent adsorption process of PDMS chains on silica aggregates has been investigated in previous papers,[15,16] considering that it occurs through hydrogen bonding. In ref 15, mixtures were characterized by a low concentration of silica ($C_{\text{Si}} \leq 0.17$) and chain molecular weights smaller than $M_n = 3.6 \times 10^5$. The residual amount of polymer, Q_r, still bound to silica after removal of all free macromolecules from the mixture, was found to obey a linear dependence upon the chain molecular weight, $\bar{M}_n$. Accordingly, the average number, n_f, of polymer chains bound to the silica surface per unit mass of silica was considered constant: $n_f = 2.82 \times 10^{18}$ g^{-1}. Any macromolecule is bound to one aggregate through a binding site which presents a multiple-link structure; the average area of one binding site is $\sigma_f \simeq 5.4 \times 10^3$ Å^2; an estimate of the number, f, of monomeric units participating in the chain binding is $f = 10^2$. Mixtures characterized by a higher silica concentration and long PDMS chains ($\bar{M}_n \gtrsim 1.3 \times 10^5$) have been analyzed in ref 16. A multiple-aggregate chain-binding process has been shown to occur; this process has been investigated from chemical treatment of the silica surface, to vary the number of binding sites per unit mass of silica. In a random mixture obtained from a silica concentration $C_{Si} = 0.29$ (w/w) and PDMS chains of average molecular weight $\bar{M}_n = 3.5 \times 10^5$, most siloxane macromolecules are bound to two aggregates (20%) or three aggregates (50%); the remaining macromolecules are dangling chains.

These systems may exhibit gel behavior after removal of all free chains; they can be reversibly swollen by a solvent. It may be worth emphasizing that in addition to bridges originated from the presence of silica, physical combinations of polymer chains are also mediated by entanglements which necessarily arise from mixed long macromolecules.

IV. Experimental Section

Materials. Siloxane–silica mixtures were provided by Rhône-Poulenc Company (France). Poly(dimethylsiloxane) samples are commercially available polymers. Two different weight-average molecular weights were used: $M_w = 6.1 \times 10^5$ and 2.4×10^5, respectively. Corresponding polydispersity indices were $I = 1.7$ and 1.8, respectively. Fumed silica (Aerosil; specific surface area, 150 $m^2\,g^{-1}$) was bought from Degussa (West Germany). The ultimate particle size corresponds to a sphere diameter equal to about 140 Å, but particles are covalently bound to one another into aggregates.

Silica-filled polymers were prepared by mechanical mixing performed on a two-roll stainless steel mill at room temperature until homogeneous samples were obtained. Three different mixtures were studied. They were characterized by the following initial silica concentrations: $C_{Si} = 0.17$, 0.23, and 0.29 w/w, respectively.

Free polymer fractions were removed from silica–siloxane mixtures by exhaustive extraction at room temperature, using chloroform (RP Normapur, 99.2–99.6%, $CHCl_3$, 5×10^{-4}% acidity in HCl, 5×10^{-2}% H_2O). A few cubic samples (4 mm in size) were immersed in 30 mL of solvent. The solution was renewed with pure solvent twice a day, over a period of 5 days. Samples were then vacuum dried at 370 K for 48 h. The residual amount of polymer, Q_r, per unit mass of silica was determined from microanalytical measurements of the carbon content in the final product.

NMR measurements were performed using samples swollen by deuteriated solvents (chloroform, C.E.A. France; methylcyclohexane, Merck, West Germany). Swollen samples were kept in sealed NMR tubes in equilibrium with solvent vapor. Several intermediate swollen states, from a dry network to the maximum swelling resulting from the equilibrium with the liquid solvent, were studied. The swelling ratio values were determined from a weighing method.

NMR Experiments. All NMR measurements were performed by using a Bruker CXP 100 spectrometer operating at 60 MHz. Transverse relaxation measurements were carried out by the spin–echo technique. They were numerically analyzed as the sum of two exponential functions of equal amplitude, as explained in section II.

V. Unfolding of Elementary Chains

This section concerns silica-filled polymers observed after removing all free macromolecules. They are considered to be permanent gels. NMR measurements were performed on these systems in order to characterize the statistical properties of the elementary chains joining silica aggregates. This approach was based on the chain unfolding effect resulting from the progressive swelling process of the gels. Intermediate swelling states were reached by adding small controlled amounts of solvent to a given dry gel. Then all samples were kept in sealed NMR tubes. Investigations were focused on three random network structures, hereafter referred to as A, B, and C. Sample A was defined from the initial silica concentration of $C_{Si} = 0.29$ w/w; the average molecular weight of siloxane chains was $\bar{M}_w = 6.1 \times 10^5$. Sample B was obtained with the same siloxane chains but the silica concentration was $C_{Si} = 0.17$ w/w. Finally, sample C was prepared from an initial silica concentration of $C_{Si} = 0.29$, while the average molecular weight of the siloxane chains was $\bar{M}_w = 2.5 \times 10^5$.

It may be worth emphasizing that these permanent gels are built from junctions characterized by high functionality. They also contain numerous dangling chains. Furthermore, entanglements which are not trapped are eliminated by removing free macromolecules. However, new entanglements formed by intertwined loops can be created.

The NMR analysis will rely on the following qualitative feature: the relaxation rate, δ_2, of the NMR signal, $M_2(t)$, defined by formula 6, reflects the degree of anisotropy of the spatial region explored by monomeric units through diffusional rotations.

1. Residual Amount of Polymer. Residual amounts of polymer still bound to silica particles after removing all free chains were found to be equal to $Q_r = 1.7$, 2.4, and 1.2 w/w for A, B, and C samples, respectively. The value 1.7 obtained for sample A must be compared with the ideal value $Q_r^i = 2.4$ which would be obtained from the linear dependence of the quantity Q_r, already observed from systems characterized by shorter chains (ref 15). It is assumed that the comparatively small value of 1.7 results from a strong multiple-aggregate chain binding process occurring in sample A. More than two particles are probably bound to one single chain. Also, because of the high silica concentration, the remaining dangling chains are probably short. Considering now sample B, compared with sample A, the value $Q_r = 2.4$ reflects fewer multiple-aggregate chain-binding processes involving more than two aggregates. It also reflects more and longer dangling chains. Finally, comparing sample C with samples A and B, there probably exist two-aggregate chain-binding processes, but structures involving more than two aggregates can probably be ignored because polymer chains are short; also, dangling chains are shorter than in samples A or B.

Correspondingly, relaxation rates of $M_2(t)$ NMR signals were found to be $\delta_2^0 = 0.3$, 0.25, and 0.5 s^{-1} for samples A, B, and C, respectively. There is no significant difference between samples A and B, whereas there are probably more topological constraints exerted on monomeric units in sample C.

2. Maximum Swelling. Maximum swelling ratio values were found to be equal to $Q_m = 6.5$, 8.2, and 5.2 for samples A, B, and C, respectively (Q_m is defined as the ratio of the swollen gel volume over the dry gel volume; the volume of silica was subtracted in both cases). Without entering into too many details, it can be asserted that elementary chains joining aggregates in sample B are longer than those defining sample A because of the lower initial silica concentration defining B. They also are longer than in sample C because the initial chains used to prepare mixture B are longer than those defining sample C.

3. Progressive Swelling Process. Variations of the relaxation rate, δ_2, of the $M_2(t)$ part of the transverse magnetization are reported as a function of the swelling ratio of sample A in Figure 1. Two swelling agents, chloroform and methylcyclohexane, were used. Two parallel straight lines are observed. The progressive swelling process of sample B, observed from the relaxation rate, δ_2, is shown in Figure 2; the parameter δ_2 obeys the power law

$$\delta_2 - \delta_2(0) \propto Q^{2.2}$$

with good accuracy. Finally, variations of δ_2 for sample C are reported in Figure 3; it is found to obey the relation

$$\delta_2 - \delta_2(0) \propto Q^{0.5}$$

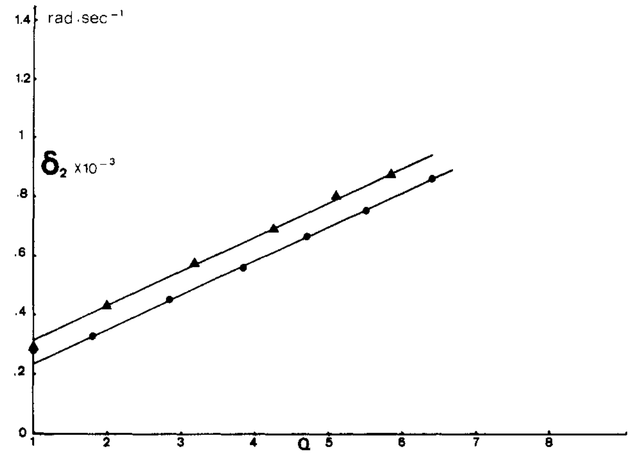

Figure 1. Variations of the relaxation rate, δ_2, measured as a function of the swelling ratio, Q, of sample A (room temperature): (▲) deuteriated chloroform; (●) deuteriated methylcyclohexane.

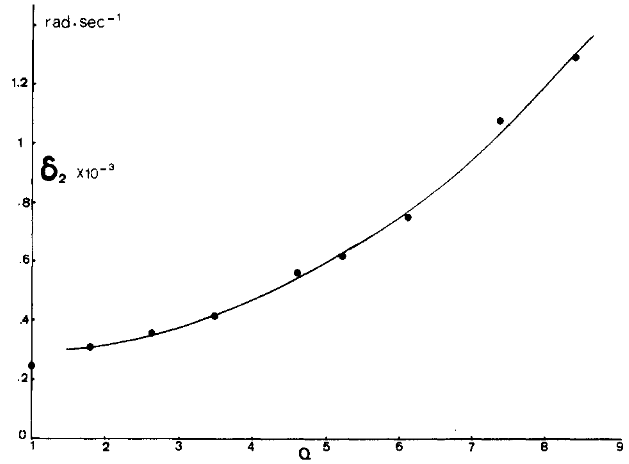

Figure 2. Variations of the relaxation rate, δ_2, measured as a function of the swelling ratio, Q, of sample B. The swelling agent is deuteriated methylcyclohexane (room temperature).

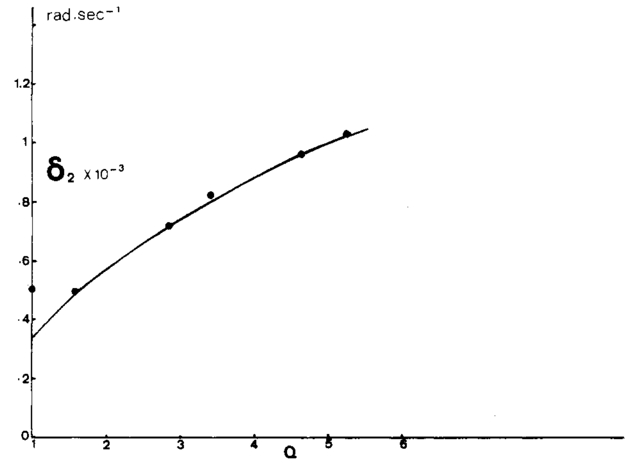

Figure 3. Variations of the relaxation rate, δ_2, measured as a function of the swelling ratio, Q, of sample C. The swelling agent is deuteriated methylcyclohexane (room temperature).

The three types of samples are readily distinguishable from each other on the basis of their NMR properties. The three exponents differ significantly.

4. Comparison with Calibrated Gels. Discussion. It is not the purpose of the present work to give a thorough description of the swelling properties of silica–siloxane mixtures. However, the NMR can be qualitatively discussed in the following way.

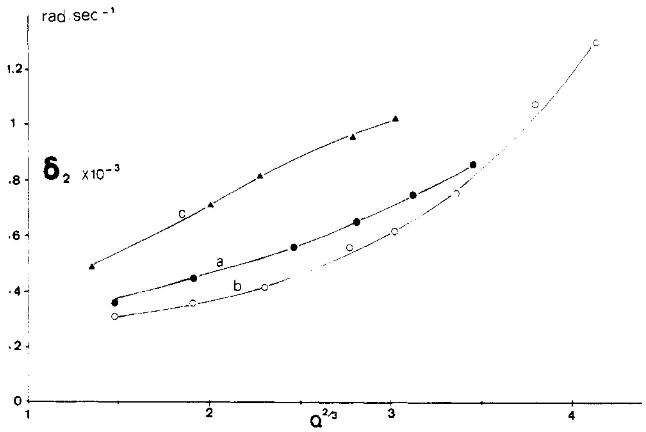

Figure 4. Variations of relaxation rates, δ_2, reported as a function of $Q^{2/3}$: (a) sample A, (b) sample B, and (c) sample C.

The main feature observed Figures 1–3 is the strong increase of relaxation rates induced by the addition of solvent to the dry gels. This result is in strong contrast to the usual effect of dilution observed for polymer systems. However, the increase of the relaxation rate of the transverse magnetization has been already observed upon swelling of calibrated PDMS gels.[8] These tetrafunctional systems were obtained from end linking of chains.[17] By use of several swelling agents and different initial concentrations, ω_c, of cross-linking reactions, the relaxation rate, δ, was found to obey a single scaling law:

$$\delta \propto Q^{2/3}\omega_c^{5/3} \tag{8}$$

Formula 8 is obtained in a straightforward way from formula 3 by assuming that elementary chains obey a packing condition and that the number, Ne, of monomer units in an elementary chain is determined from trapped entanglements.[4] The packing condition states that the total volume of the swollen gel is proportional to the sum of volumes of all swollen elementary chains. Thus, if any individual volume is equal to $\bar{r}_e^3$,

$$Q \propto \bar{r}_e^3/\mathrm{Ne} \quad \text{or} \quad \bar{r}_e^2 \propto Q^{2/3}\mathrm{Ne}^{2/3}$$

Trapped entanglements determine Ne:

$$\mathrm{Ne} \propto \omega_c^{-5/4}$$

Such a dependence upon Q implies that junctions fluctuate within small lmited regions of space. More precisely, amplitudes of displacements of junctions are not large compared with mean chain dimensions. Consequently, no average procedure can be applied to the positions of junctions, as if, for example, they obeyed Gaussian statistics. Junctions must be characterized by nonisotropic displacements of small amplitude in accordance with the phantom network description.[18] If we now consider random silica–siloxane mixtures, it cannot be assumed that silica particles fluctuate in space. Elementary chains have fixed points. Furthermore, the nature of silica–siloxane mixtures is far more complex than that of calibrated PDMS gels. Accordingly, it cannot be assumed that these random mixtures obey a packing condition.

(i) In order to investigate possible affine behavior of chain segments, the relaxation rates were plotted as a function of $Q^{2/3}$ instead of Q (Figure 4). The observation of three different curves suggests that either nonaffine properties or nonlinearity, induced by extensive stretching of elementary chains, could influence the residual energy of spin interactions. The order of magnitude of relaxation rates measured in samples A, B, and C is 10^3 rad·s^{-1}. This value must be compared with the absolute strength of dipole–dipole interactions of protons, in a methyl group: 10^5 rad·s^{-1}. Therefore, observed dipole–dipole interactions are strongly reduced by nonisotropic motions of chain segments. From formula 3, the reduction factor roughly corresponds to $|r_e| \simeq 10^{-1}\mathrm{Ne}a$; this does not describe a strong stretching of chain segments. Hence, nonlinearity effects which would be associated with the residual energy must be eliminated.

(ii) Curves a–c in Figure 4 represent nonaffine properties of elementary chains as reflected in the quantity r_e^2/Ne^2a^2. This nonaffine character may concern end separation vectors, $\vec{r}_e$, and also the effective number of monomeric units Ne*. This effect probably results from the mixture of dangling chains and chains bridging silica particles. Dangling chains strongly contribute to the free energy of mixing with the swelling agent. However, they cannot freely expand because of the increase of the elastic free energy resulting from the expansion of the network structure and they undergo a confinement effect. In this work, it is assumed that dangling chains and chains joining silica particles form network structure derived from entanglements existing in the pure melt. In other words, the mesh size is not solely determined by the average distance of silica particles. It also results from entanglements. The addition of solvent is assumed to change both end-separation distances, $|\vec{r}_e|$, and the average number of monomeric units, Ne*. For the sake of simplicity and without any further information, it is suposed that $|\vec{r}_e|$ distances obey affine properties, while the effective number obeys approximate power laws given by $\mathrm{Ne}^* \propto Q^{-0.2}$, $\mathrm{Ne}^* \propto Q^{-0.8}$, and $\mathrm{Ne}^* \propto Q^{0.1}$ for samples A, B, and C respectively. According to this arbitrary assumption, the Q dependence of Ne* may serve as a rough estimate of the strength of topological constraints exerted on chain segments. This will be discussed in a subsequent paper.

VI. Local Motions

Qualitative properties of local motions occurring in random siloxane–silica mixtures in the presence of solvent were investigated using the spin–lattice relaxation rate, T_1^{-1}, of protons of the methyl groups. Measurements were performed on the three silica-filled polymers already mentioned.

1. Swelling Effects. Experimental results are reported in Figure 5a, which shows the observed typical dependence of T_1^{-1} upon the swelling ratio, Q. A principal feature of the curve drawn in Figure 5a is the absence of significant effects of the silica concentration on local motions. Such an effect could not be seen by NMR within the accuracy of measurements. The swelling agent was deuteriated chloroform.

Another feature of the curve drawn in Figure 5a concerns the existence of two well-defined concentration ranges. The first one corresponds to Q values going from 1 to about 2.0; it is associated with a strong decrease of the relaxation rate, T_1^{-1}. Within the second range ($2.0 \lesssim Q \lesssim Q_m$), the experimental curve exhibits a plateau ($T_1^{-1} \simeq 0.54$ s^{-1}). Starting from the dry mixture, it is assumed that the addition of solvent hastens diffusional local motions, regardless of their actual complexity. This probably requires a description involving several correlation times.[19,20] Nonetheless, the decrease of the relaxation rate, T_1^{-1}, observed upon a decrease of local correlation times indicates that these are shorter than the rough estimate given by the inverse of the Larmor frequency ($\omega_0^{-1} \simeq 1.5 \times 10^{-9}$ s). When spin–lattice relaxation rate variations measured in polymer systems as a function of a given variable (temperature or concentration) are represented by a curve which shows a maximum, they usually exhibit a Larmor frequency dependence observed on each side of the curve about the maximum. This property is generally attributed to a broad distribution of molecular correlation times. It was again observed in silica-filled systems by varying the Larmor frequency from 60 to 100 MHz (Figure 5b).

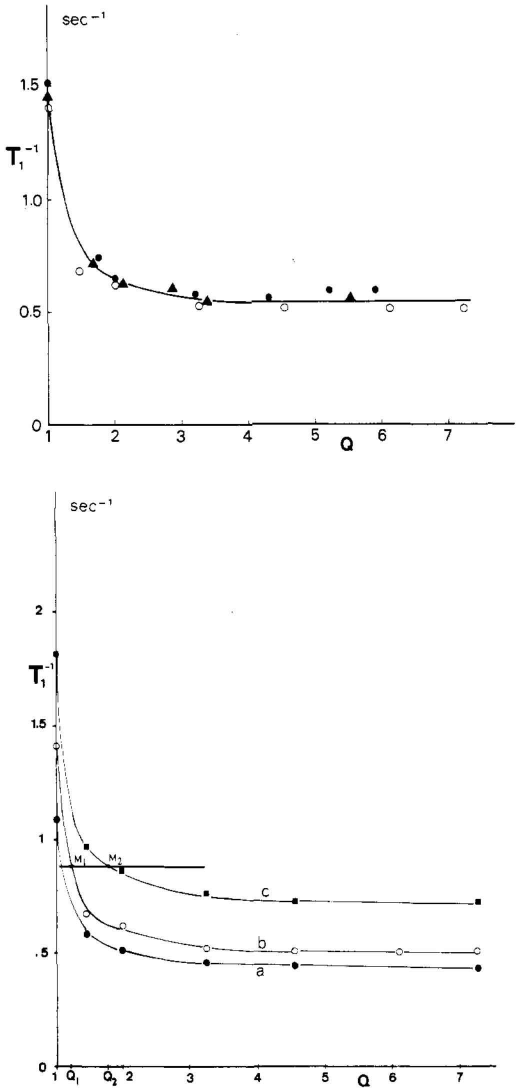

Figure 5. (a, top) Spin–lattice relaxation rates measured as a function of the silica concentration and the swelling ratio, Q: (●) sample A, (○) sample B, and (▲) sample C. (b, bottom) Spin–lattice relaxation rates measured at two Larmor frequencies, as a function of the swelling ratio of sample B: (a) 100 MHz, (b) 60 MHz, and (c) the relaxation rate multiplied by 100/60.

2. Dynamical Crossover. The most striking result concerns the splitting of spin–lattice relaxation rate variations into two concentration ranges.[21] It may be worth emphasizing that such a property also characterizes other molten polymer–solvent systems, regardless of the presence of mineral fillers in the medium. This was observed in systems containing long *cis*-1,4-polybutadiene, polystyrene, or polyisobutylene chains.[22] Furthermore, proton spin–lattice relaxation rates are usually independent of chain molecular weights, except for very short chains ($\bar{M}_w \simeq M_c$; M_c is the characteristic molecular weight). In the case of polymer solutions, the observation of a plateau extending to the dilute regime, combined with this chain molecular weight independence, unambiguously shows that local motions are fully shielded from long-range fluctuations of a chain, whether it is embedded in a temporary network or not. It is believed that the two concentration ranges observed in uncross-linked systems reflect a dynamical crossover from a concentrated solution regime to a semidilute solution regime. In other words, the description of local dynamical properties governing the relaxation rate, T_1^{-1}, is assumed to parallel the temperature–concentration phase diagram concerning static averages of fluctuations in a binary solvent–polymer system, although the crossover concentration might be slightly shifted toward smaller or higher values. It is generally stated that three-body-type interactions of monomer units participate in fluctuation properties in concentrated solutions, while two-body-type interactions contribute to fluctuation properties in more dilute solutions. It is considered that variations of T_1^{-1} observed in random mixtures upon swelling reflect likewise a dynamical crossover from a concentrated solution regime to a semidilute one, regardless of the presence of silica particles. In other words, basic dynamical parameters governing the high-frequency viscoelastic behavior of swollen silicone–silica mixtures should not vary when the polymer volume fraction becomes smaller than $Q_c^{-1} \simeq 0.5$.

Without presenting a thorough discussion of local dynamical properties, which would be beyond the scope of the present work, it may be of interest to qualitatively analyze T_1^{-1} curves in the following way. It is well-known that most formulas describing spin–lattice relaxation rates obey a homogeneity property when they are multiplied by the Larmor frequency, ω_0. For molecular processes involving a single correlation time, τ_c, the homogeneous variable is $\omega_0\tau_c$:

$$\omega_0 T_1^{-1} = F(\omega_0\tau_c)$$

F represents a linear combination of spectral densities describing nucleus random motions. This applies to complex molecular systems, too. Values of T_1^{-1} multiplied by the ratio of Larmor frequencies 100/60 are reported in Figure 5b; they can be compared with values measured at 60 MHz. A line drawn parallel to the Q axis which intersects both curves b and c in two points $K_1(Q_1)$ and $K_2(Q_2)$ gives the relative variation of correlation times corresponding to a ratio of Larmor frequencies equal to 1.66.

To conclude this section, it is considered that basic dynamical parameters governing the high-frequency response of a silica-filled siloxane to an external mechanical constraint should not vary with the silica content, provided all silica particles are bridged by chains. Furthermore, the addition of solvent should have negligible effects on this high-frequency response when the polymer volume fraction is smaller than about 0.5.

VII. Enhanced Orientational Interactions of Monomeric Units

Finally, the last NMR parameter used to investigate swelling properties of random silica–siloxane mixtures was the relaxation rate, δ_1, of the second part, $M_1(\delta_1 t)$, of the transverse magnetic relaxation function of methyl groups. $M_1(\delta_1 t)$ is a sum over the whole sample of all contributions, $m_1(t)$, given by individual methyl groups, whether they interact with one another or not. Variations of δ_1 as a function of both the silica concentration and the swelling ratio, Q, are reported in Figure 6. T_1^{-1} and δ_1 curves parallel each other, although they correspond to very different orders of magnitude: δ_1 is about 20 times larger than T_1^{-1}. There is a negligible effect induced by variations of the silica concentration while two solvent concentration ranges are clearly observed. Within the first one ($1 \lesssim Q \lesssim 2$), δ_1 decreases upon addition of solvent; then, a plateau value is reached. a similar behavior has already been observed in qualitative gels. the qualitative analysis of the δ_1 curve relies upon two features.

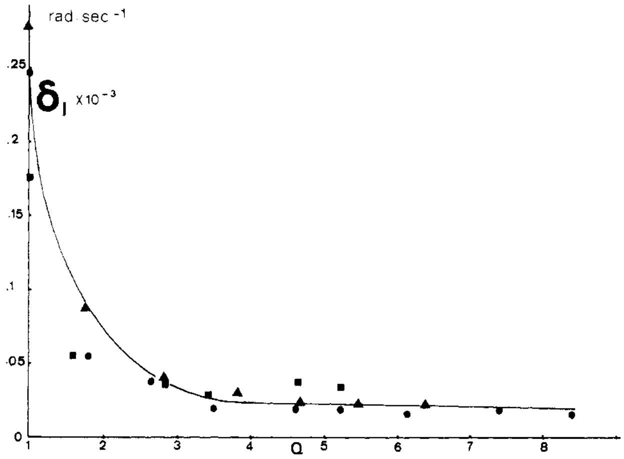

Figure 6. Variations of the relaxation rate, δ_1, measured as a function of the swelling ratio, Q: (▲) sample A, (●) sample B, and (■) sample C.

(i) It has long been established that the irreversible dynamics of $M_1(\delta_1 t)$ is mainly governed by dipole-dipole interactions concerning nuclei located on different methyl groups.[11] Contributions of high frequency motions to the relaxation mechanisms of $M_1(\delta_1 t)$ can be established from T_1^{-1}; they are negligible.

(ii) Furthermore, it has been previously shown that the strength of pseudosolid spin–echoes observed in calibrated gels is maximum within the first range of swelling ratio values ($1 \lesssim Q \lesssim 2$) but is weakened by the addition of solvent when swelling ratio values correspond to the plateau part of the curve ($Q \gtrsim 2$).[22]

These two features clearly show that the parameter δ_1 reflects nonisotropic motions of monomeric units located on different chain segments. Those located on the same chain segment are also involved, provided they are close enough to each other, because the chain segment forms a loop. It must be kept in mind that dipole–dipole interactions rapidly decrease when the distance b between nuclei is increased. They vary as b^{-3}. It is considered that the nonisotropic character of relative diffusional motions of chain segments probably corresponds to an enhancement of orientational constraints exerted on monomeric units and resulting from internal stretching of chain segments. From both δ_1 and T_1^{-1} curves, it is inferred that the strength of physical interactions of monomeric units is weakened by the addition of solvent to the polymer system but is unchanged when concentrations of chains are smaller than about 0.5 (w/w). Two effects are observed by NMR: on the one hand, relative diffusional motions of chain segments are more isotropic upon addition of solvent; on the other hand, the average distance between monomeric units is lengthened.

VIII. Conclusion

This work deals with silica-filled siloxane systems obtained by mechanical mixing of high molecular weight siloxane chains with silica particles. When the silica concentration is high enough, these random mixtures can form permanent gels after removing all free polymer chains. They can be reversibly swollen provided solvent–silica interactions are weaker than the strength of polymer–silica bonds. The main question arising from the study of such permanent gels concerns the characterization of the network structure actually governing macroscopic properties.

It has already been shown from previous work that before removing free polymer chains the network structure of the mixture is mainly derived from the temporary network structure existing in a melt in the absence of silica.[10] The addition of silica does not greatly disturb the whole geometry of the network structure. It only subtracts degrees of freedom of the polymer system and induces more and more hindrances to monomeric motions. The net result is an improvement of elastic properties.

After free polymer chains are removed, some initial entanglements are eliminated; some others are trapped. However, when a random mixture reaches its thermodynamic equilibrium, new entanglements are formed to define a network structure. The existence of domains of dynamical correlations is clearly demonstrated by the present NMR approach. On the one hand, local high-frequency motions are independent of the silica concentration. Hence, silica particles do not cause correlation domains. These result from the intrinsic properties of polymer systems. Incidently, the high-frequency mechanical response of random mixtures should be insensitive to the presence of silica. On the other hand, local high-frequency motions are independent of the presence of swelling agent, for polymer concentrations smaller than about 0.5 (w/w). This is a common property of uncrosslinked molten polymers.

Domains characterized by high-frequency dynamical properties screened from the presence of silica or solvents were also studied by observing the transverse nuclear relaxation instead of longitudinal relaxation.

Statistical properties of end-separation vectors joining junctions, whether these are temporary or not, were probed by adding solvent to mixtures to increase the fractal character of the domains. No affine property and no packing condition was found to apply to correlation domains. These two results are in strong contrast to properties observed in calibrated gels; they were assigned to the presence of numerous dangling chains in random mixtures. The result concerning the packing condition is easily accepted, whereas the behavior of end-separation vectors observed in some mixtures is more striking: end-separation distances correspond to average stretchings much larger than average distances corresponding to affine extensions.

A more quantitative approach will be given in a subsequent paper. The purpose of the present work was to give evidence for the presence of domains unaffected by variations of the silica concentration. Hence, the role of mineral particles is mainly to improve elastic properties and to shift viscoelastic terminal relaxation spectra toward lower frequencies.

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Transport Properties of Substituted Poly(acetylenes)

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ABSTRACT: Ac and dc conductivities of poly(*tert*-butylacetylene), poly(phenylacetylene), and poly(methylacetylene) have been investigated. Undoped polymers show dc conductivities smaller than $10^{-15}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, with a weak thermal dependence of ac conductivity which can be explained by a phonon-assisted hopping mechanism. Upon doping with iodine, dc conductivities in the 10^{-5}–10^{-3} range are obtained for all polymers. However, the values of conductivity decrease under a constant bias, indicating the presence of an ionic mechanism. These values stabilize to a reduced level which is a function of the size of the substituent, bulkier substituents giving lower values. This stable region is governed by two electronic mechanisms; at low temperatures, a phonon-assisted hopping mechanism is observed, whereas at higher temperatures, a thermally activated hopping mechanism becomes dominant. Different configurational structures of poly(*tert*-butylacetylene) have no effect on its electrical properties. The relative low conductivity values observed for substituted poly(acetylenes) as compared to unsubstituted poly(acetylene) can be explained by their nonplanar conformations and the presence of substituents which increase the distance between the chains.

Introduction

Poly(acetylene) is the simplest conjugated polymer. Pristine poly(acetylene) exhibits a low value of electrical conductivity which increases upon doping to reach values of about 1000 $\Omega^{-1}\ \mathrm{cm}^{-1}$.[1] Many studies have been devoted to the electrical properties of poly(acetylene) but its mechanisms of conduction are still incompletely resolved.[2–11]

For lightly doped poly(acetylenes) (concentrations lower than 0.01 dopants per carbon atom), an intersoliton electron hopping mechanism has been proposed by Kivelson; this theory leads to predictions which are in good agree-

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