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Vulcanized Siloxane Chains Swollen by Polymer Chains. NMR Investigations into Free-Chain Dynamics

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ABSTRACT: Dynamical properties of free siloxane chains self-diffusing in siloxane gels are characterized by observing the nuclear magnetic relaxation of protons attached to methyl groups. Transverse relaxation functions associated with free chains are shown to obey a property of superposition by applying an appropriate shift factor to the time scale of evolution. The dependence of the shift factor upon the free-chain concentration is analyzed by introducing a free volume effect. It is supposed that the free volume fraction decreases upon an increase of the cross-link density. Numerical values of the free volume fraction at 298 K are found to be 0.20, 0.18, and 0.16 in gels characterized by numerical values of the swelling ratio Q_m equal to 5.8, 4.2, and 2.4, respectively. The free volume fraction in the polymer melt at 298 K is 0.223.

I. Introduction

This work deals with the NMR observation of dynamical properties of polymer chains free to move in polymeric gels.

The quantitative description of gel behavior under external perturbations such as swelling or stretching is still controversial.[1,2] However, NMR has proved to be a good tool to investigate the statistical structure of gels.[3] NMR properties of protons attached to the polymer chains have been studied under swelling or stretching.[4,5] The cross-link formation was also observed in several polymer systems.[6,7] The purpose of this work is to describe the dynamics of free chains in polymeric gels, using NMR. This study focuses on a polymer whose weight-average molecular weight is below the characteristic molecular weight, M_C. The effects of the cross-link density and of the concentration of free chains were studied. Low molecular weight poly(dimethylsiloxane) chains were added to functional poly(dimethylsiloxane) chains, and after cross-linking of the latter, the dynamics of the free chains was investigated from the relaxation process of the nuclear magnetization of protons linked to these chains. No isotopic labeling was necessary: the large difference between relaxation rates in the gel and in the polymer allows a complete description of the dynamics of the free chains.

II. Experimental Section

Samples. Three species of gels were studied. They were obtained from the mixing of a vinyl-functionalized polymer (polymer E or F) with a silane-functionalized polymer (polymer D). Random cross-links between these low molecular weight PDMS chains resulted from a hydrosilylation reaction between silane and vinyl groups in the presence of platinum. Gels A and B were obtained from the mixing of polymer D with polymer E or F, respectively. Gel C is a commercial product (RTV 141), and it cannot be fully described herein. It is also obtained from the mixing of two components. These two components and polymer samples were supplied and characterized by the Rhone-Poulenc Co. (France). Polymer samples are described in Table I.

Platinum was first added to polymers E and F, with the help of a hexane solution (0.01% platinum w/w). The samples were then dried to eliminate traces of hexane. The platinum content was fixed to 10^{-4} mol of Pt/mol of vinyl.

Polymeric gels were prepared by mixing the two polymers at stoichiometric conditions with a variable weight fraction ϕ_f of unreactive chains (polymer H) in order to obtain free chains in the gel. The content of unreactive polymer ϕ_f was varied from 0.2 to 0.8 (w/w). After mixing, all samples were kept in an oven at 373 K for 1 month to achieve the conversion of vinyl groups.

Table I
Sample Content, Number-Average Molecular Weight M_n, and Ratio I_p of Weight- to Number-Average Molecular Weights M_w/M_n

polymer	Si–H, 10^{-5} mol/g	Si–vinyl, 10^{-5} mol/g	M_n	I_p
D	122	0	7 650	1.9
E	0	14.8	12 500	2
F	0	7.4	15 700	2.9
H	0	0	10 300	2.06

Gel Fraction and Equilibrium Swelling. The gel fraction G of samples was defined as the ratio of the weight of the dry extracted gel to the weight of the original sample. The sol was extracted in methylcyclohexane at room temperature for 3 days, the solvent being renewed three times. Samples were thoroughly dried after removing the sol fraction.

The swelling ratio Q_m of each sample was defined as the ratio of the volume of the swollen gel over the volume of the dry extracted gel. It was measured at the end of the extraction performed in methylcyclohexane, at 295 K, by a weighing method. Q_m was calculated from the weights of the swollen and of the dry extracted sample and the values of the density of the solvent and of the polymer. The reproducibility of the gel fraction and swelling measurements was good, and the precision was about 5–10%.

NMR Measurements. NMR measurements were carried out by using a pulsed Bruker spectrometer, operating at 60 MHz. All relaxation functions were recorded at 298 K.

Transverse magnetic relaxations were observed by applying a Carr–Purcell sequence to the spin system to overcome the effect of inhomogeneities usually present in polymeric systems. The pseudosolid spin echo was obtained from the following four-pulse sequence:[3]

$$(\pi/2)_y-\tau/2-(\pi)_y-\tau/2-(\pi/2)_x-\tau_1/2-(\pi)_y-\tau_1/2$$

where $(\alpha)_y$ denotes a rotation of angle α around the y axis in the rotating frame. The pulse $(\pi)_y$ is used to focus the transverse magnetization previously dispersed by the effect of sample inhomogeneities.

III. Gel Fraction and Equilibrium Swelling Effect

(a) Gel Fraction. When the gelation process was achieved, the gel fraction G was measured to check that all functional chains were actually cross-linked; then the final system was considered as a gel swollen by free chains. The sol fraction $1 - G$ is plotted versus the weight fraction

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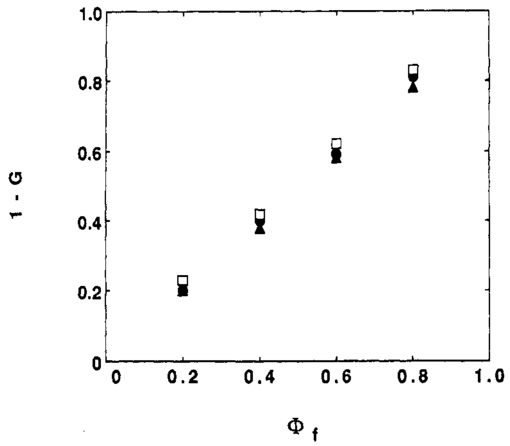

Figure 1. Sol fraction measured after cross-linking of functional PDMS chains, in the presence of unreactive PDMS chains, at concentration ϕ_f, as a function of ϕ_f. Gel series A (●), B (□), and C (▲).

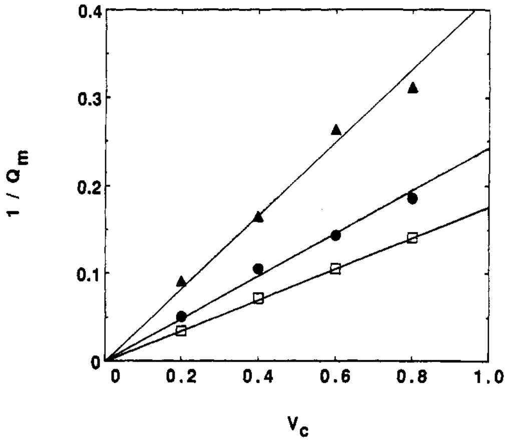

Figure 2. Inverse of the equilibrium swelling ratio in methylcyclohexane, measured in gels synthesized with unreactive chains at concentration $1 - V_c$, as a function of V_c. Gel series A (●), B (□), and C (▲).

ϕ_f of unreactive polymer in the initial reaction bath in Figure 1. It is clearly seen from Figure 1 that these two quantities are equal to each other:

$$1 - G = \phi_f$$

This result means that all functional chains are connected to one another through the sample, in either one of the two following ways. One chain may be linked to the infinite cluster, or it may belong to a finite size cluster trapped in the network, which was not washed out by the solvent.

However, it will be assumed throughout this study that the fraction of low molecular weight polymer in the sol consists mainly of the unreactive chains added to functional chains before the beginning of the cross-linking process.

(b) State of Maximum Swelling. The equilibrium swelling ratio was measured as a function of the concentration of functional chains $V_c = 1 - \phi_f$. V_c is supposed to be equivalent to a concentration in the reaction bath, the solvent being here the unreactive polymer. However, it must be kept in mind that the polymer statistics is Gaussian during the cross-linking process, since the gelification is performed in a melt; no excluded volume effect is involved in the description of the reaction bath.

Variations of the inverse of the swelling ratio as a function of V_c are reported in Figure 2. The solid lines represent a linear variation passing through the axis origin.

Table II

gels	$\langle Q_m V_c \rangle$	f_p/B, %	$\Delta f/B$, %	K/B, %	f_g/B, %
A	4.2	22.3	4.4	2.0	18
B	5.8	22.3	2.7	1.0	19.6
C	2.4	22.3	6.1	0.3	16.2

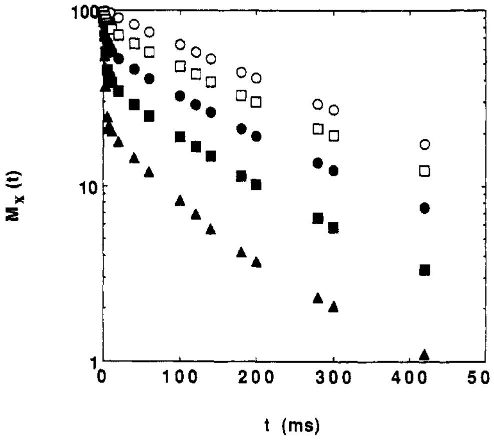

Figure 3. Relaxation functions recorded in the gel series A, at 298 K, for different concentrations of free chains: $\phi_f = 1$ (○), 0.8 (□), 0.6 (●), 0.4 (■), and 0.2 (▲).

It can be noted that, in the three gels, the product $Q_m V_c$ is independent of the concentration in the reaction bath. The maximum deviation between this variation and the experimental determination is less than experimental uncertainty. The average values $\langle Q_m V_c \rangle$ of the product $Q_m V_c$ are reported in Table II.

Comparing A and B gels with each other, it is found that the swelling is increased as vinyl-terminated chains are lengthened. The range of variations of the molecular weight is small, and polydispersity indices are high; therefore, it is not proposed to describe the mass dependence of the swelling degree of the gels. The only point is that the three siloxane gels investigated herein have different cross-link densities, the value $\langle Q_m V_c \rangle$ being a characterization of the concentration of cross-links.

IV. Gel Fraction: NMR Observation

(a) Two-Component Relaxation Functions. Typical magnetic relaxation functions recorded in sample A swollen by polymer chains at various concentrations are reported in Figure 3. They correspond to free-chain content values equal to 1, 0.8, 0.6, 0.4, and 0.2 from top to bottom. The relaxation curves exhibit a split into two well-separated decays: a rapid component, whose time scale is around 1 ms, and a slow one with a time scale a hundred times larger. Following measurements of the gel fraction described previously, the relaxation function is written as

$$M_x(t,\phi_f) = C_g(\phi_f)\, R_g(t,\phi_f) + (1 - C_g(\phi_f))R_1(t,\phi_f)$$

where $R_g(t,\phi_f)$ is the relaxation function associated with chains which form the gel. It depends actually on the concentration of unreactive polymer ϕ_f. This dependence will be investigated in a future paper.

$R_1(t,\phi_f)$ is the relaxation function corresponding to free chains in the gel. It is also affected by variations of the concentration of free chains; it is the purpose of the present study to analyze this behavior. It must be noted that $R_1(t,\phi_f)$ is not an exponential decay: this is due to the typical response of methylene groups.[8]

The weight factor $C_g(\phi_f)$ is the contribution of the gel to the amplitude of the magnetization observed over the whole sample.

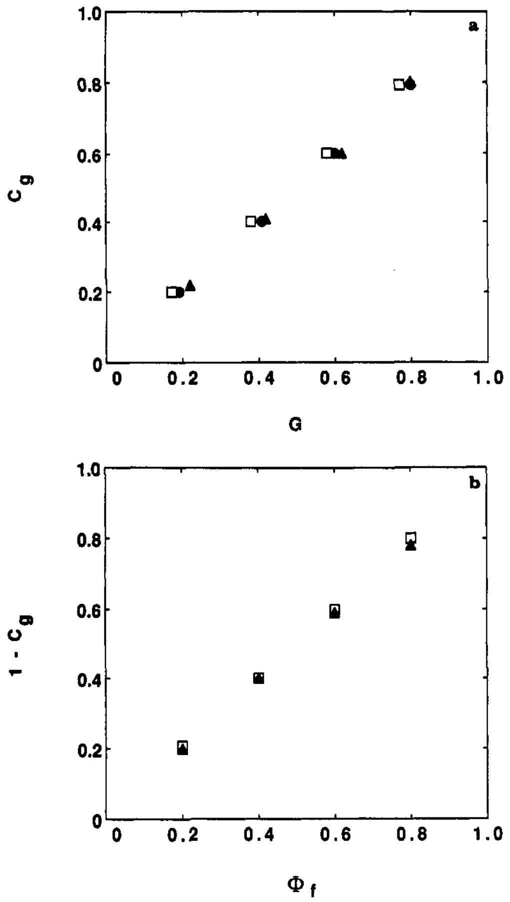

Figure 4. (a) Relation between NMR measurement of the gel fraction C_g and the gel fraction measured by a weighing method G. (b) Fraction of the slow component, associated with free chains, in the relaxation function, $1 - C_g$, as a function of the free-chain concentration measured by a weighing method, before the cross-linking process. Gel series A (●), B (□), and C (▲).

(b) NMR Measurement of the Gel Fraction. The NMR parameter $C_g(\phi_f)$ represents the fraction of protons attached to chains belonging to the gel; $C_g(\phi_f)$ is also a weight fraction of the gel since only siloxane monomers are present in the samples. It can be measured from the semilogarithmic plot of $M_x(t,\phi_f)$, as shown in Figure 3. The slowly decaying component can be linearly extrapolated to $t = 0$, the intercept being a measure of $1 - C_g(\phi_f)$.

The NMR determination of the gel fraction $C_g(\phi_f)$ is compared to the value G obtained by a weighing method, in Figure 4a. It is clearly seen that $C_g(\phi_f)$ is equal to $G(\phi_f)$. Thus, combining this with the previous result, we have

$$1 - C_g(\phi_f) = \phi_f$$

as shown in Figure 4b. This was checked for the three gels investigated in the present study. It is worth emphasizing that this result confirms the assumption made in section III: the sample consists of two well-defined species. It reinforces the assignment of the slow component to the unreactive chains added to the reaction bath. Thus it is possible to study the properties of magnetic relaxation of protons linked to these chains in gels without any ambiguity. No isotopic labeling is necessary, the contrast here being given by the large difference which exists between relaxation rates of the two species.

V. Transverse Magnetic Relaxation of Free Chains

(a) Chain Dynamics. Pseudosolid spin echoes were used to analyze the magnetic response of the free chains.

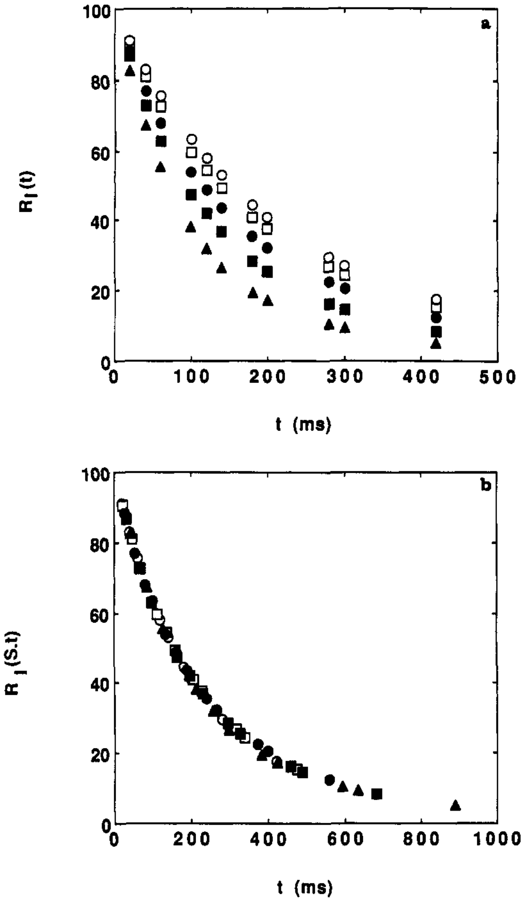

Figure 5. (a) Relaxation functions associated with the free chains in the gel series A, as a function of free-chain content: $\phi_f = 1$ (○), 0.8 (□), 0.6 (●), 0.4 (■), and 0.2 (▲). (b) Superimposed functions obtained in the gel series A, resulting from a shift of the time scale of the relaxation functions. The reference function is the relaxation decay recorded in the melt of free chains ($\phi_f = 1$). Same symbols as in Figure 5a.

It is well-known from polymeric systems that the magnetic relaxation can be governed either by the residual energy of dipole–dipole interaction or by chain dynamics. In the first case, low-frequency fluctuations are not perceived because of the freezing effect due to topological constraints exerted on the chains. Then the spin system exhibits pseudosolid spin echoes, with typical properties of symmetry.[3]

In the second case, low-frequency fluctuations are observed in the relaxation process and no pseudosolid spin echo is detected. In an intermediate situation, pseudosolid spin echoes are observed but they are no longer symmetric.

Here, no pseudosolid spin echo, even nonsymmetric, was detected in the slow component $R_1(t,\phi_f)$. The relaxation function $R_1(t,\phi_f)$ of the free chains is thus entirely governed by chain dynamics, even at high gel fractions. Consequently the different functions $R_1(t,\phi_f)$ recorded at various concentrations ϕ_f should obey a homogeneity property: they should be identical after a shift of the time scale of variation. In other words, they should have the same mathematical structure; the variation of ϕ_f should only change the time scale of the relaxation decay.

(b) Property of Superposition. Typical relaxation functions corresponding to free chains in gel A are shown in Figure 5a. Five decays are presented; they correspond to ϕ_f equal to 1 (pure polymer), 0.8, 0.6, 0.4, and 0.2 (w/w). They were obtained by dividing the amplitude of an echo in the slow component of $M_x(t,\phi_f)$ ($t > 20$ ms) by the parameter $1 - C_g(\phi_f)$ determined in the previous section. Two features are perceived from Figure 5a.

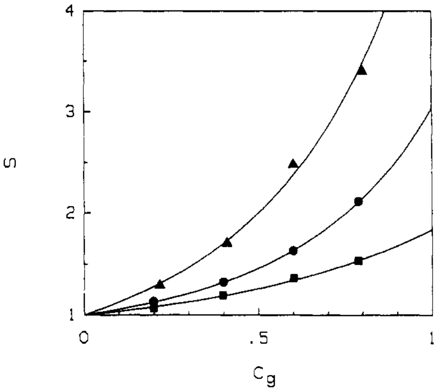

Figure 6. Shift factor variations with the gel fraction measured from NMR. The solid lines represent the theoretical variations computed from a least-mean-square procedure. Gel series A (●), B (■), and C (▲).

(i) As the gel fraction increases, or ϕ_f decreases, the relaxation rate of the free chains is increased: the time scale of $R_1(t,\phi_f)$ is shortened as the gel fraction is increased. This means that the chain dynamics is slowed down by the gel.

(ii) As predicted in the foregoing paragraph, the relaxation curves have indeed the same mathematical structure: they are identical after a shift of the time scale of variation. The superimposed functions corresponding to Figure 5a are presented in Figure 5b. The relaxation decay recorded in the pure melt ($\phi_f = 1$) was chosen as a reference function, and a shift factor $S(\phi_f)$ was applied to the function obtained in a sample at concentration ϕ_f, so that

$$R_1(t,\phi_f{=}1) = R_1(S(\phi_f)t,\phi_f)$$

According to this definition, $S(\phi_f)$, is proportional to the relaxation rate of the decay associated with the free chains. The invariance of the mathematical structure of the relaxation function means that the same mechanism is responsible for the relaxation process through the range of variations of the gel fraction. The inherent difficulty of the mathematical description of the relaxation decay is here overcome by the homogeneity property.

(c) Shift Factor Variations. The variations of the shift factors measured in the three gels investigated herein are reported in Figure 6, as a function of the NMR determination of the gel fraction $C_g(\phi_f)$. Two features arise from Figure 6:

(i) S is an increasing function of $C_g(\phi_f)$; in other words, the larger the gel fraction, the larger the relaxation rate. The chain dynamics of the free polymer chains is slowed down by the chains attached to the gel.

(ii) The chain dynamics is more affected in gel C than in gel B. More precisely, according to the swelling measurements reported in section III, the less the gel swells at equilibrium, the slower the chain dynamics at a given gel fraction.

VI. Free Volume Effects Induced by Cross-Linking

(a) Friction Coefficient. According to the invariance exhibited by the relaxation decays of the free chains under the variation of the gel fraction, the relaxation function can be generally expressed as

$$R_1(t,\phi_f) = R_1(\zeta(\phi_f),t)$$

where $\zeta(\phi_f)$ is the reference frequency scale of time dependence of the relaxation process. Since the relaxation process is entirely governed by chain dynamics, $\zeta(\phi_f)$ is a measure of the friction perceived by the free chains from the polymeric system characterized by ϕ_f.

It is proposed to describe the variations of $\zeta(\phi_f)$ with the variation of the volume fraction of free volume f in the mixture:[9]

$$\zeta(\phi_f) \propto \exp(B/f)$$

According to the definition of the shift factor, S is

$$S(\phi_f) = \exp(B/f - B/f_p)$$

where f_p is the fraction of free volume in the pure polymer melt.

(b) Gel Contribution to the Free Volume. It is now supposed that the gel contribution to the free volume is smaller than that of the polymer because of the presence of cross-links. By analogy with the description of dynamical properties of a polymer–solvent system, the free volume fraction in the mixture is expressed as

$$f = f_p(1 - G) + f_g G + KG(1 - G)$$

where f_g is the free volume fraction of the gel and K is a constant characteristic of the interaction between the two components. K, f_g, and f_p are assumed to be independent of the gel fraction G. The two first terms represent the free volumes brought by the free chains and the gel, respectively. The third one is added to take into account the possible interaction between the two components: if $K > 0$, it is an extra free volume, i.e., the two species do not pack in a compact manner; on the contrary, if $K < 0$, the two components pile up so that the final free volume is decreased. It represents the fractional volume change during the mixing.

Introducing $\Delta f = f_p - f_g$, one finds

$$f = f_p - \Delta f{*}G + K{*}G{*}(1 - G) \qquad (1)$$

To fit with the experimental data, f_p/B was set equal to 0.223[10] and $\Delta f/B$ and K/B were adjusted by a least-mean-square routine. The solid lines in Figure 6 represent theoretical variations determined from the fitting procedure. The computed values of $\Delta f/B$ and K/B are reported in Table II. It is interesting to note that $K > 0$ in the three gel systems investigated. But it is worth pointing out that the maximum value of the third term in relation (1) is 0.005, that is, 2.5% of the total free volume fraction. This term is a small correction to the whole free volume.

(c) Correlation between Free Volume and the Maximum Swelling. The computed value of the free volume fraction f_g/B of the gel is plotted as a function of its swelling degree $\langle Q_m V_c \rangle$ in Figure 7. As can be seen, the free volume fraction in the gel is an increasing function of the swelling degree; in other words, it is a decreasing function of the cross-link density. This is consistent with the assumption made in the previous paragraph: the more cross-links, the less free volume.

A more direct correlation was also found between the statistical structure of the gel, characterized by the swelling ratio Q_m, and the dynamics of the free chains that determine the value of the shift factor: S is represented versus $1/Q_m$ in Figure 8. From this plot it appears that the three systems have the same behavior: they seem to obey the same relation between S and $1/Q_m$. The dynamics of the free chains in the reaction bath, after the cross-linking process, is related to the maximum swelling effect of the obtained gel; the state of maximum swelling is induced by the presence of a good solvent after eliminating all chains that do not belong to the gel structure. Also, if one considered the same gel swollen at a variable amount

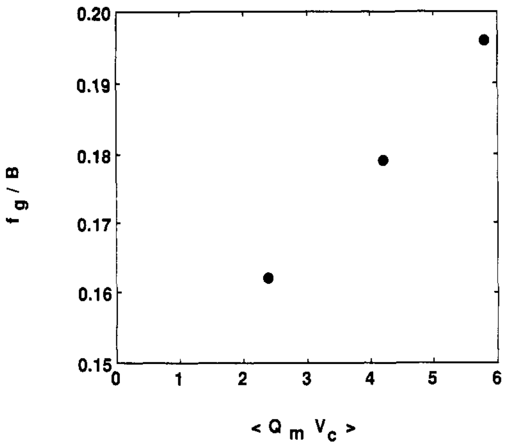

Figure 7. Volume fraction of free volume in the gel, as a function of the equilibrium swelling constant $\langle Q_m V_c \rangle$.

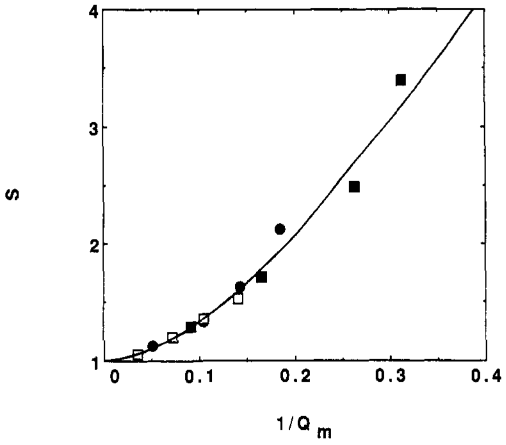

Figure 8. Shift factor variations with the inverse of the equilibrium swelling degree. Gel series A (●), B (□), and C (■).

of free chains, this relation would not hold: the free-chain dynamics would be dependent on the free-chain content, and the equilibrium swelling degree in solvent would be a constant. The correlation between the shift factor S and the swelling ratio Q_m shows that a relation exists between the free volume perceived by the free chains and the cross-link density of the surrounding gel.

VII. Conclusion

The dynamics of low molecular weight siloxane chains moving freely in siloxane gels was investigated from nuclear magnetic relaxation of protons attached to the free chains. They were added, at various contents, to functional chains in the reaction bath, in order to obtain a larger amount than would be obtained from polymer swelling after cross-linking. The variation of the relaxation rates of the free chains upon variation of the gel fraction was interpreted as a free volume decrease upon cross-linking. The volume fractions of free volume in the three gels studied here were deduced from this dependence. This parameter was related to equilibrium swelling degrees, and it was found that it was a decreasing function of the cross-link density.

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