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RHEOLOGY OF THE GELATION PROCESS OF SILICA GEL

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The rheology of silica sols prepared from mixtures of tetramethoxysilane (TMOS)–methanol–water under basic neutral conditions has been studied at 25, 40 and 60 °C during the gelation process. The sols show non-Newtonian pseudoplastic behavior from the time of preparation with the appearance of yield stress near the gelation point. The results are analysed using rheological equations of state and the concept of the point of gelation is discussed. For neutral sols an apparent activation energy of 10 Kcal/mol is attributed to the process of polymerization. Qualitative determination of the gelation time for sols prepared under acidic, neutral and basic conditions is also reported at 25 °C and as a function of the water content.

1. Introduction

The preparation of silica via silicon alkoxides has been the subject of a large number of recent investigations. However, the process of gelation, i.e., the transformation of sol into a wet gel, is still not very well understood. The formation of such oxide gels occurs through hydrolysis and polycondensation. Both reactions are extremely complex and they usually occur at the same time, each one having a rate constant depending drastically on the pH, composition, and temperature of the sols. Earlier studies have shown that the gelation time [1–4] (often chosen arbitrarily as the time when the sol apparent viscosity reaches ~ 10² or 10³ P), as well as the pore size distribution [5], are highly dependent on temperature and pH. In very acidic sols (0 < pH < 3) the time of gelling (t_{gel}) of silicic acid increases with increasing pH values; it then decreases to a stable minimum for values 6 < pH < 8 and then increases again for pH > 9. As a function of temperature t_{gel} was found to follow an Arrhenius behavior. More recently Sakka et al. [6,7] studied in detail the rheological properties of Si(OC₂H₅)₂/ethanol/water sols. They showed particularly that sols which contain HCl as a catalyst undergo gelation in longer times than sols containing NH₄OH. The apparent and intrinsic

viscosity of the acidic sols prepared with a low water content increase gradually with time whole for sols prepared with a large water content or NH₄OH catalysed, both the viscosity, η, and the intrinsic viscosity, $[\eta]$, remain almost constant for $t/t_{gel} < 0.6$ and increase abruptly as the gelling time is approached. Based on these observations the authors suggested that the low water acid sols catalysed by HCl exhibiting spinnability, are formed by linear polymers while the others which do not show spinnability but gel into elastic bulk masses have non-linear or a network, colloidal polymer structure. The role of the starting components [8], of the catalyst [9], and of the temperature [10] on the sol–gel processing of silica was also recently studied by Mackenzie's group in great detail. Raman spectroscopy, ²⁹Si NMR, and the molybdenum chemical technique are also powerful microscopic tools to study the polymerization process. Qualitative correlation between the rate of hydrolysis and size of the resulting polymeric particles has been proposed [11] and the presence of organic additives has been shown to affect the mechanism of particle aggregation and the extent of the polymeric network [12]. In all these studies the definition of the point of gelation was somewhat arbitrary and qualitative, and no dynamic flow properties were reported. Klein and

Garry [13] have measured Brookfield viscosities at 50 rpm and proposed that the sol–gel transition is at 2000 mPas; Akhtar [14] has observed a maximum in the Brookfield viscosity and proposed that the time at which this maximum occurs corresponds to the point of gelation. However, in both cases the shear rates were not well defined and thus these proposals do not have a strong physical support. Recently Sacks and Sheu [15] published a systematic and careful study of the rheological properties of the silica sols having a composition similar to those studied by Sakka et al. [6,7] using dynamic and steady shear flow measurements. During the sol–gel transition, the sols exhibit transition from Newtonian to shear thinning to thixotropic flow behavior, and yield stresses have also been observed during the later stages of aging. These results have been corroborated by measurements of storage and loss moduli showing that elastic interaction becomes important during the shear thinning and thixotropic periods. The authors have also suggested that the gelling point could be better defined by a value of the loss tangent when determined under well-defined measuring conditions.

In this paper we study the rheology of silica sols as a function of temperature during the transformation of the sol into gel by measuring the viscosity of the solution with a concentric rotating cylinder viscosimeter. The sols are shown to exhibit, as a function of time, transition from Newtonian to shear thinning to thixotropic behavior. A model is proposed to explain the results and the concept of the point of gelation is discussed.

2. Experimental

Silica sols were prepared by mixing first tetramethoxysilane (TMOS, Fluka) and anhydrous methanol (Merck) in the volume ratio 1:1. To this mixture was slowly added under vigorous stirring 4 mol of doubly distilled water without catalyst (pH ~ 5.7) for each mol of TMOS, resulting in sols having a time $t = 0$ the following molar proportion: TMOS : methanol : $H_2O \equiv 1 : 3.6 : 4$. Other sols have been prepared under basic and acid conditions modifying the pH of the water by

addition of either NH_4OH and HCl. The stirring of the sol was continued during approximately 50 min. The dynamic viscosity of the sol during the transformation of the sol into a wet gel was studied with a concentric rotating cylinder viscosimeter (model Rheotest 2, VEB Prüfgerate, Werk Medingen, RDA) at 25, 40 and 60°C. We used a configuration of cylinders having a very small gap (diameter ratio of 1.02) such that the values of the shear rates, $\dot{\gamma}$ (s⁻¹), and the shear stresses, τ (N/m²), in the liquid are uniform and well defined. The relative errors of the measurements of the viscosity η is of the order of 3–4%. Measurements were made as a function of the time of gelation for a given shear rate $\dot{\gamma}$ and as a function of the shear rate for given times of gelation. The viscosity is defined as

$$\eta = \tau_r/\dot{\gamma} \quad (\text{Pas}). \quad (1)$$

Results obtained using a Höppler-type viscosimeter were not found reliable, especially at high viscosity.

The gelation times were also qualitatively determined at room temperature by visual inspection (time at which the sols did not flow under gravity). These determinations were done for sols having the same TMOS/methanol ratio (50 vol%) but different molar ratio $r = [H_2O]/[TMOS]$ and prepared under acidic (addition of HCl, pH ~ 2.7, neutral (pH ~ 5.7) and basic (addition of NH_4OH, pH ~ 9) conditions.

3. Results and discussion

The time, t^*, for which the sols, measured at $T = 23°C$, do not flow under gravity, is shown in fig. 1 for sols prepared under acidic, neutral and basic conditions as a function of the molar ratio $r = [H_2O]/[TMOS]$. These values which can be taken as approximate values of the time of gelation, t_g, are found to decrease as a function of the molar ratio $r = [H_2O]/[TMOS]$ and are always found in the sequence $t^*(\text{acid}) > t^*(\text{neutral}) > t^*$

Fig. 1. Plot of gelation time, t^*, versus the molar ratio $r = [H_2O]/[TMOS]$ measured at 23°C for sols having TMOS:methanol ratio 50 vol% under acidic (pH ~ 2.7), neutral (pH ~ 5.5) and basic (pH ~ 9.5) conditions.

sols prepared also under acidic conditions and appears strongly dependent of the [alcohol]/[alkoxide] molar ratio. As this ratio decreases, the minimum of t^* shifts towards lower values of r and the overall values of t^* also decrease. Klein also found that, for a given r value, t^* increases linearly with the [ethanol]/[TEOS] ratio, the sols with $r = 1$ or 2 showing a stronger dependence on dilution than the sols with $r > 4$. This linear increase is thought to come from liquid diffusion. On the other hand, according to le Chatelier's principle [17], the condensation process should slow down when excess water is present since water is the product of the condensation reaction. We can therefore understand, at least qualitatively, the t^* behavior presented in fig. 1 for acidic sols for a given [methanol]/[TMOS] ratio (50 vol%). At very low r value the hydrolysis phenomenon is slow and far from being finished and r^* is large. As r increases, the hydrolysis rate increases and r^* diminishes. But since the water content increases, from r and from the condensation reaction, the condensation rate decreases according to the le Chatelier's principle and consequently the variation of r^* versus r decreases. Therefore r^* will tend to a minimum value and eventually increase again for high water content as it is observed in fig. 1 for $r > 8$. For a lower [alcohol]/[alkoxide] ratio, the curve for the acidic sol presents in our case a minimum for $r \sim 8$. Such a behavior has already been reported without explanation by Klein [16] for TEOS/ethanol/water
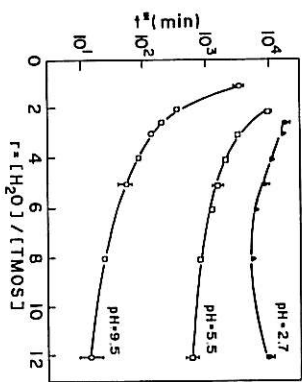
alkoxide concentrated sol, the hydrolysis rate will be faster since the liquid diffusion is easier. Consequently the condensation rate will be faster and

the overall r^* values will be smaller. The minimum of t^* will also shift towards lower values since a higher water amount will be available from the condensation reaction in agreement with Klein's observation [16]. For very dilute sol, i.e. a high [alcohol/alkoxide] ratio, it is likely that the minimum of r^* will be shifted to high r values and that only a monotonic decrease of t^* versus r will be observed. This effect was indeed observed by Gottardi et al. for sols having a dilution of TEOS in ethanol around 5 wt% SiO_2 [18]. Comparing sols of the same composition the overall t^* values are smaller for higher pH and the r^* variation as a function of r presents only a monotonic decrease without showing a minimum. It is well known in these cases that hydrolysis is likely to be incomplete and that additional water may still be needed to complete it. Therefore the t^* values which are higher for low r values will gradually decrease as r increases in agreement with our observation (fig. 1).

Figure 2 shows the behavior of the viscosity as a function of the aging time measured for neutral sols at 25, 40 and 60°C for a shear rate $\dot{\gamma} = 87.5$ s⁻¹ (curves a, a', a'') as well as the change of viscosity measured at 25°C using three different shear rates (10 s⁻¹ (b), 87.5 s⁻¹ (a) and 750 s⁻¹ (c)). All curves present basically the same overall time dependence: first a slow increase of the viscosity as a function of the aging time due to the growth of SiO_2 clusters. When these aggregates are large enough, their clustering results in the formation of a SiO_2 skeleton which fills the measuring cell in a very short time; this process is accompanied by a rapid increase of the viscosity. Curves a, b and c show that the viscosity measured at 25°C is independent of the shear rates for aging time up to ~ 1020 min but becomes strongly dependent upon $\dot{\gamma}$ for longer times. These results illustrate well the ambiguity associated with the previous definitions of the gelling point. The saturation observed near the gelation point is not yet understood. However, similar observations have been reported by Akhtar [14] and others and attributed to artifacts in the measurements: a decrease of the measured torque due to the creation of a "hole" in the gel by the rotating spindle of the viscosimeter.
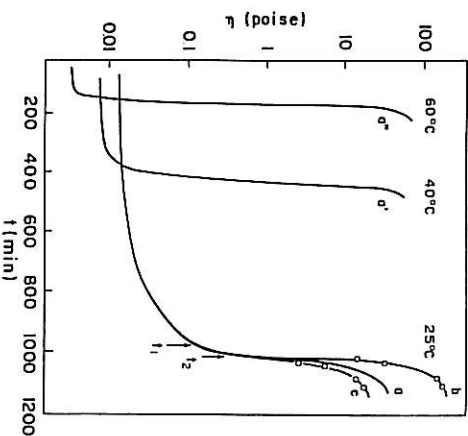
Fig. 2. Variation of the apparent viscosity, η, as a function of the time during the gelation process of neutral sols for $T = 25$, 40 and 60°C measured for $\dot{\gamma} = 87.5$ s^{-1} (curves a, a' and a'') and at $T = 25$°C for $\dot{\gamma} = 10$ s^{-1} (curve b), 87.5 s^{-1} (curve a) and 750 s^{-1} (curve c). The arrows indicate the reference time η (t_r) and the transition from Newtonian to pseudoplastic flow (t_1) and the appearance of yield stress (t_2) (see fig. 5).

Fig. 3. Arrhenius plot $\ln t_r$ vs $1/T$. The values of t_r is defined arbitrarily by $\eta(t_r) = 1$ Pas for $\dot{\gamma} = 87.5$ s^{-1} (neutral sol).

Curves a, a' and a'' show that the gelation time becomes shorter as the temperature increases and follow an Arrhenius behavior (fig. 3). A reference gelation time t_r was arbitrarily chosen in this case at the time when the solution viscosity reached a value η (t_4) = 1 Pas (i.e. 10 P) with $\dot{\gamma} = 87.5$ s^{-1}. At that time the sols are already transformed into

$$1/t_r = A \exp(-E^*/RT),$$ (2)

where E^* is an apparent activation energy whose value in our case is 10.2 Kcal/mol. This value is quite similar to the values obtained by Colby et al. [10] using sols of TMOS : methanol : H$_2$O : HX (X = Cl or F) having the molar ratio 1:4:4:0.5.

Figure 4 shows the variation of the coefficient of viscosity with the shear rate $\dot{\gamma}$ measured at 25°C for different times $t = 975$, 995, 1010, 1030, 1045 and 1090 min (see also fig. 2). Up to 975 min the sols show a Newtonian behavior because the viscosity is independent of the shear rate. It is followed, for times up to ~ 1020 min, by a period of shear thinning in which the sols present a non-Newtonian pseudoplastic behavior [19,20]; in

wet gels and present a solid aspect, since the values of η for $\dot{\gamma} = 0$ are much larger (figs. 2 and 4). As already observed for sols prepared from silicic acid [2–4] or sols prepared from TMOS or under acidic conditions [10], the plot is linear and follows the law:

$$\dot{\gamma} = k\tau^n$$ (3)

where $n = 1$: Newtonian behavior; $n > 1$: pseudoplastic behavior.

Figure 5 shows the variation of n as a function of the time of aging (upper scale) and t/t_r (lower scale). For $t < t_1$, = 970.6 min, $n = 1$ as it should be for a Newtonian flow. A sharp break occurs at $t = t_1$ and defines the time at which the flow changes from a Newtonian to a pseudoplastic non-Newtonian (shear thinning) behavior. This behavior is observed only during a very short period of time (~ 42 min). Figure 4 shows that already for a time equal or longer than 1010 min the simple relation (3) is not valid. Yield behavior and thixotropic loops similar to the one shown in fig. 6 are observed at all temperatures. An analytical method for describing the flow properties of compositions with a yield
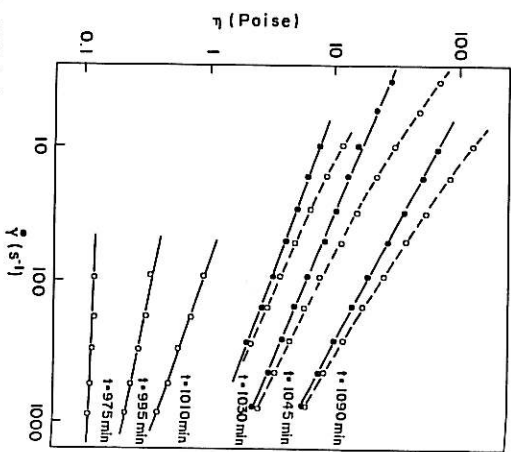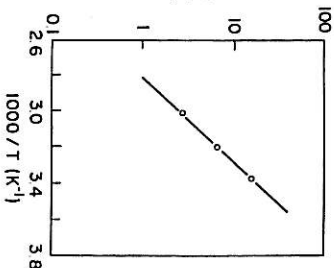
Fig. 4. Variation of the viscosity (P) with the shear rate $\dot{\gamma}$ (s^{-1}) measured for neutral sols at $T = 25$°C for $t = 975$, 995, 1010, 1030, 1045 and 1090 min (○) see also fig. 2). The full straight lines and dots (●) are calculated adjusting for each time the parameters n and τ_0 from relations 3 and 5.

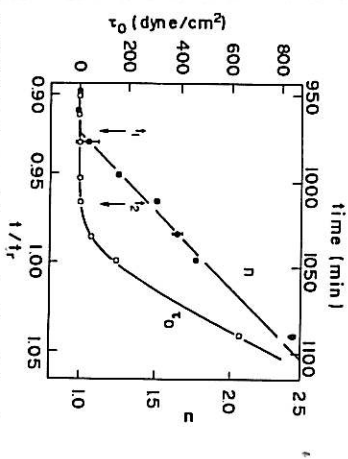Fig. 5. Variation of n and t_0 as a function of time (upper scale) and t/t_r (lower scale) for neutral sols. t_r is an arbitrary reference time for which $\eta = 10$ P at $\dot{\gamma} = 87.5$ s^{-1}. The values of n and τ_0 are adjusted for the data of fig. 4 in order to fit relations 3 and 5. t_1 and t_2 correspond to the transition from Newtonian to pseudoplastic (shear thinning) and the appearance of yield stress (shear thinning) respectively.

this range the viscosity decreases as a power law of the shear rate [20]. Using the relation

$$\eta = \frac{\tau}{\dot{\gamma}} = k' \dot{\gamma}^{(1/n-1)}$$ (4)

where $n = 1$: Newtonian behavior; $n > 1$: pseudoplastic behavior.

where $n = 1$: Newtonian behavior, and k and n are parameters to be adjusted, the viscosity is therefore given by

$$\dot{\gamma} = k\tau^n$$ (3)

where $n = 1$: Newtonian behavior; $n > 1$: pseudoplastic behavior.

value is the use of a rheological equation of state or a constitutive equation of the form:

$$\gamma = \begin{cases} 0 & \text{for } \tau < \tau_y, \\ k(\tau - \tau_0)^n & \text{for } \tau \geq \tau_y, \end{cases}$$ (5)

where k, n and τ_0 are parameters to be adjusted, τ_0 being in general not equal to the yield stress τ_y [20]. Measurements show that in our case both values of τ are practically identical. The experimental results of the three upper curves of fig. 4 have been used to adjust the parameters n and τ_0 according to relation (5) and the fit shown by the full curves is in good agreement. The time variation of n and τ_0 is shown in fig. 5. We observe that n continues to increase for time a Newtonian and a pseudoplastic sol, starts to increase for time $t_2 \geqslant 1014$ min. The knee of the curve is not as well marked as for the n plot. The times t_1 and t_2 which indicate the time of the transition from Newtonian to pseudoplastic and from pseudoplastic to pseudoplastic yield stress flow behavior, respectively, are also shown by arrows in fig. 2. It is interesting to note that the times t_1 and t_2 are defined from the parameters n and τ which are independent of the shear rate; in this way the ambiguity existing in the definition of the time of gelation, t_g, will be eliminated.

The dynamic viscosity measured for basic sol (pH = 9.5) at $T = 25$°C and $\dot{\gamma} = 87.5$ s^{-1} presents basically the same behavior as for neutral sols (fig. 7) although the transition is not quite as sudden. The data can be fitted by the constitutive equation
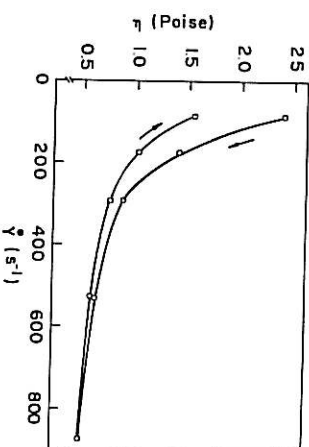

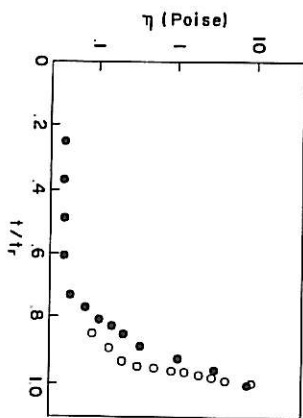Fig. 6. Example of thixotropic loop observed with neutral sols at $T = 40$°C and $t = 430$ min (see fig. 2).

Fig. 7. Variation of the apparent viscosity, η, as a function of the reduced time, t/t_1, measured at $T = 25°C$ and $\dot\gamma = 87.5$ s. (a) neutral sol (○), $t_1 = 1048$ min; (b) basic sol (●), pH = 9.5, $t_1 = 126$ min.

particles grow as a function of time the viscosity of the sol increases slowly. With further aging larger aggregates are formed and solid loading increases rapidly [21]. For $t \geqslant t_1$ the sol shows a shear thinning behavior; the viscosity are relatively high at low shear rate and the aggregates are partly broken as the shear rate increases and consequently the dynamic viscosity decreases. For longer aging a continuous three-dimensional network is formed through further polycondensation and agglomeration (clustering of clusters). The network acquires an elastic character which is observed by a yield stress for time $t > t_2$. As the yield stress is exceeded, a shear thinning behavior is observed and hysteresis is observed in the form of a thixotropic loops. Once again the network structure is broken as the shear rate increases. Saks et al. [15] have observed in the shear thinning regions ($t_1 < t < t_2$) an increase of the storage and loss moduli which reflect the increase of an extensive particle–particle interaction and in the effective solids loading as large-cluster formation occurs. At the onset of the thixotropic flow period, the storage modulus increases very rapidly but the loss modulus passes through a maximum at time t_2 and then sharply decreases. This decrease reflects a rapid development of a three-dimensional network gel structure. They suggest that an improved definition of the gelling point would involve specifying a value of the loss tangent determined under well-defined measuring conditions. We think that our results corroborate quite well their observations and that the time defined as t_2 and measured through dynamic viscosity methods could also be a better definition of the gelling point.

On the other hand the characterization of the evolution of the mechanical properties during or after the gelation process of silicon alkoxide solutions has also been attempted recently by the percolation theory; it is assumed that the viscosity η near the gelation point takes the form

$$\eta \propto \left(\frac{p_c - p}{p_c}\right)^{-k}, \qquad (6)$$

where p is the conversion factor which measures the degree of gelation and takes the value $p = p_c$

(5) and fig. 8 shows the time behavior of the parameters n and τ_0. We note however that the transition from Newtonian to shear thinning behavior defined by the time t_1 is observed on the relative scale t/t_1 at smaller values in agreement with Saks et al. [15]. Both observations suggest that in basic sols agglomerates and microgel regions form at relatively early stages of aging.

At the early time of aging the particles are small and their concentration is low; we observe Newtonian behavior since the particle interactions do not influence the flow behavior. As the SiO$_2$

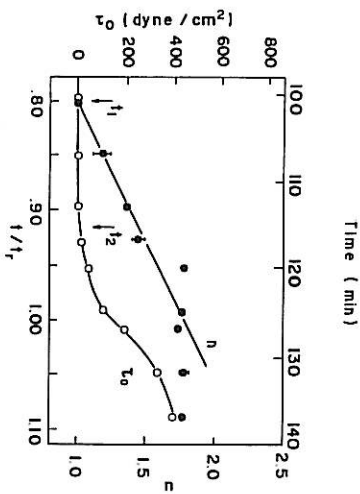Fig. 8. Variation of n and τ_0 as a function of time (upper scale) and t/t_1 (lower scale) for basic sol (pH = 9.5). t_1 is an arbitrary reference for which $\eta = 10$) at $\dot\gamma = 87.5$ s^{-1}. t_1 and t_2 correspond to the transition from Newtonian to shear thinning and the appearance of yield stress respectively.

at the gelation point [22,23] and k a critical exponent. For systems which are governed by a chemical reaction, i.e. gels in which the chemical bondings between the initial particles are large compared to the thermal agitation and which are consequently thermally irreversible, the conversion factor can be assimilated to the time of reaction. Therefore,

$$\eta \propto \left(\frac{t_g - t}{t_g}\right)^{-k}. \qquad (7)$$

Preliminary results show that the evolution of the viscosity measured for $\dot\gamma = 87.5$ s^{-1} can also be described by eq. (7) in the relative time interval $5 \times 10^{-2} < 1 - t/t_g < 5 \times 10^{-3}$ with a critical exponent $k = (0.9 \pm 0.1)$ and t_g values very close to the t_2 values. The value of the critical exponent is very similar to those obtained on radical copolymerization and polycondensation and of the superconductivity of a percolating random network of superconducting and normal bonds $k = 0.75 \pm 0.04$ [24]. We should note however that other k values have been recently reported for SiO$_2$ sols. Gauthier-Manuel [23] found a value $k = 1.1$ for a silica sol prepared with a 0.5 M NaCl aqueous solution and $k = 1.0$ for a silica sol prepared with pure water. Kozuka et al. [22], studying silica sols prepared in acid condition, found a dependence of the exponent value with the shear rate $\dot\gamma$ with values ranging from $k = 1.5$ for $\dot\gamma = 100$ s^{-1} to $k = 2.6$ for $\dot\gamma = 2$ s^{-1}. There is a great discrepancy between these results and more researchers are necessary to elucidate these divergences.

Work is presently under way in our laboratory in order to check the evolution of the viscosity in terms of the rheological equations of state and in terms of the percolation theory for sols prepared under various pH conditions and to corroborate the results with the evolution of the gel structure, determined by small angle X-ray scattering and static dynamic light scattering techniques.

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