Spatial patterns formed by growing TEOS polymers
B. Cabane, M. Dubois, R. Duplessix

To cite this version:

HAL Id: jpa-00210662
https://hal.archives-ouvertes.fr/jpa-00210662
Submitted on 1 Jan 1987

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Spatial patterns formed by growing TEOS polymers (*)

B. Cabane (1), M. Dubois (1) and R. Duplessix (2)
(1) DPC-SCM-UA331, CEN Saclay, 91191 Gif-sur-Yvette, France
(2) Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg, France

(Réçu le 3 juillet 1987, révisé le 17 août 1987, accepté le 27 août 1987)

Abstract. — Silicon tetraethoxyde (TEOS) monomers are dissolved in a water/ethanol mixture. Through hydrolysis and condensation they aggregate to form branched siloxane polymers; in a few hours these polymers build a gel throughout the solution. The patterns formed by the growing polymers are studied through small angle neutron scattering. In the reaction bath, these patterns result from repulsive interactions, whose range is controlled by the smaller polymers of the bath. In diluted solutions, the patterns give the size of the largest polymers, which limits the connectivity of the reaction bath. As the polymers recombine, the connectivity length diverges, whereas the interaction length remains microscopic and keeps growing regardless of the gel point. This growth leaves the network with a set of selfsimilar heterogeneities similar to those found in many other gels.

1. Introduction.

A polymer gel is an infinite network which is swollen by a solvent. The canonical gel has a set functionality at each junction and regular chain lengths between junctions [1-5]; it should appear uniform at scales well beyond the unit cell and should contain no voids. We do not know of any such gels: most gels, when examined through scattering or microscopy, appear inhomogeneous [6-12], i.e. regions of higher polymer density coexist with regions of lower polymer density; the growth of such irregularities appears to be an intrinsic part of the gelation process [13-16]. This is especially true for those gels which are prepared through the spontaneous condensation of monomeric units dissolved in a solvent: there the mechanisms which cause the aggregation of the monomers may also produce a spatial distribution with lumps and voids at all scales. Because such heterogeneities are omnipresent, they are at the same time a major nuisance and an interesting problem.

In this communication we present the spatial patterns formed by dissolved monomers of silicon tetraethoxide (TEOS) as they condense to form a polysiloxane gel. Oxide gels of this type are used as intermediates in the manufacture of glass ceramics through the sol-gel-glass process [17-26]. This manufacture involves transformations far from equilibrium such as drying and viscous sintering, where spatial variations in the original network may have catastrophic consequences on the distribution of stress within the final product. Thus it is of interest to understand and learn to control the growth of heterogeneities in the spatial distribution of the polymers.

(*) This work used the neutron beams of ILL in Grenoble and LLB in Saclay, France.
2. Polymerization of TEOS in water/ethanol mixtures.

When silicon tetraethoxide Si(OC₂H₅)₄ is dissolved in a water/ethanol mixture, its ethoxy groups are hydrolyzed into silanols (Si-O-H), which then condense to form siloxane bridges (Si-O-Si) [17-31]. This results in the formation of siloxane polymers, which are more or less branched according to the extent of the condensation: full condensation would yield SiO₂ particles, incomplete condensation will produce polymers with a siloxane backbone and silanol sidegroups. In fact, the growth of the polymers is controlled by the amount of water available for hydrolysis and by the nature of the catalyst. With large excesses of water and base catalysis, the fastest growing species are large, highly condensed clusters which grow mainly by addition of monomers. With moderate amounts of water and acid catalysis, the branching is less frequent and the dispersion of polymer sizes is smaller [19-22].

In our experiments we perform the initial hydrolysis in an emulsion stage, then proceed with the condensation when the reaction bath has turned into a homogeneous solution [32, 33]. A cold mixture of water (5.76 g) and HCl (0.056 g) is added dropwise to a cold mixture of TEOS (8.32 g) and ethanol (1.16 g), under strong agitation. At the outset, the amount of ethanol is not sufficient to cosolubilize the TEOS and water; therefore the hydrolysis occurs at the water/TEOS interface. When enough ethoxy groups have been hydrolyzed into silanols, the solution becomes clear; it is agitated until the heat of hydrolysis has been evacuated. Then it is placed in an oven at 50 °C; this time is taken as the starting point of the gelation process (t = 0). After 9 hours the solution will no longer flow; this time is taken as the gel point.

This method of polymerization is remarkable because of the small amount of ethanol which is used as a cosolvent; consequently the average separation of the reacting species is small, and the volume fraction of SiO₂ in the final gel is large, in our case 0.073; the corresponding weight fraction is 0.16. The other conditions which are important for the course of the reactions are: the amount of water available for hydrolysis (in our case there are 8 molecules of water per TEOS monomer, i.e. more than enough); the nature and concentration of catalysts (here the added HCl brings the pH down to 1); and the temperature, which is 50 °C.

3. Scattering from the reaction bath.

Small angle neutron scattering experiments were performed on the instruments D11 at ILL and PACE at LLB. The acquisition of one spectrum takes 15 to 30 minutes, which is short compared with the gel time (9 hours). Figure 1 shows the scattering curves taken at regular time intervals and plotted on Log scales. From the outset, the intensity has a peak at $2 \times 10^{-2}$ Å⁻¹; as the polymerization progresses, this peak grows and shifts to lower Q values. Thus the main structural effect is the growth of microscopic units, whose distances rise from 200 to 600 Å during the time range of the experiment. At larger distances (smaller Q), we presume that the solution is homogeneous. At smaller distances (higher Q), the intensities are stable after about 8 hours, presumably because by that time all the monomers have been incorporated into the polymers; after 26 hours the high Q behaviour has become a power law with the exponent −1.73, and at very long times this exponent tends to −2.2.

Remarkably, the rise of the peak and its shift to larger correlation distances appear to follow the same laws after the gel point t_g as before t_g. Figure 2 shows the peak position plotted against reaction time; the accuracy on these values is poor, at short times because of a low S/N ratio, and at long times because of a low resolution in Q values.

A better accuracy is achieved for the magnitude of the peak, which is plotted against reaction time in figure 3 (semi log scales), and in figure 4 (log-log scales). These plots show an induction regime where the growth may be exponential, followed by a regime of self similar, power law growth.

For other compositions of the ternary system we do not see a peak but a Guinier law. This defines a size and a mass for the heterogeneities, which again grow as power laws of time with no singularity at t_g. Thus the general behaviour is the growth of a microscopic distance (peak) or size (Guinier law) which does not seem to care about the gel point.
Fig. 2. — Position $Q$ of the peak in the scattering curves vs. reaction time $t$. At short times ($t = 2$ h) the peak position corresponds to a correlation distance of 200 Å; at the end of the experiment ($t = 26$ h) this distance has risen to 600 Å.

Fig. 3. — Reaction bath: Intensity at the peak of $I(Q)$ as a function of time (hours), in semilog scales; the early rise of the peak may be exponential.

Still, because we are at high concentration, this dimension may not be the « size » of the individual polymers. The proper way to measure the sizes and interactions of the growing units is through a dilution experiment. This is presented next.

4. Scattering by individual aggregates.

When the reacting mixture is diluted with ethanol, all distinct polymers are separated from each other according to the dilution ratio. This has two effects. First, the reaction is slowed down considerably, and even quenched if the dilution ratio is larger than 10. Second, because of the larger separations, the correlations between the locations of the distinct polymers are lost, and in the scattering pattern all interferences between them average out. This is seen in figure 5, where the scattering from three successive dilutions is compared with that of the reaction bath from which they were extracted. This comparison suggests that the « peak » in the reaction bath scattering curve is not a Bragg peak but rather the result of a depression in the intensities at low $Q$. The depression disappears when the bath is diluted; there-

Fig. 4. — Reaction bath: Intensity at the peak in full log scales; at long times the peak grows as a power of reaction time.

Fig. 5. — Dilutions at $t = 7.75$ h, about 1 h before the gel point. Filled lozanges: reaction bath. Squares: dilution 1/3. Filled squares: 1/10. Triangles: 1/30. The curves are scaled to match at high $Q$, yielding the intensity divided by concentration.
Therefore it is caused by correlations between the growing polymers rather than within their internal structure.

Such depressions at low \( Q \) are commonly observed in solutions of particles which repel each other through steric forces; therefore it is useful to compare the behaviour observed here with that expected for repelling particles. This is best done by comparing the values of the intensity scattered at \( Q \rightarrow 0 \). For a dilute solution of « hard spheres », these intensities rise linearly with the concentration as in any solution of weakly interacting objects; they reach a maximum when the volume fraction of spheres is 0.12 and then decrease with concentration when the spheres become strongly correlated. The corresponding variation for the TEOS polymers is shown in figure 6. Remarkably, the location of the maximum shifts with reaction time; this has already been observed in other gelating systems [34].

The maximum occurs when the reaction bath has been diluted to the point where neighbouring TEOS polymers are no longer correlated with each other. Its shift with reaction time implies that, as the polymers grow bigger, they must be diluted to lower weight fractions before they become uncorrelated (\( \bar{c} \approx M/R_3 \)). This is a general feature of objects with a low fractal dimensionality (\( M \approx R^D \) with \( D < 3 \)). The same would occur with hollow spheres, rigid stars and crumpled sheets.

More interesting is the absolute value of \( \bar{c} \), which is \( 1.6 \times 10^{-2} \text{ g/cm}^3 \) for the dilutions taken from the reaction bath at \( t = 7.75 \text{ h} \). This is too low for hard spheres, where \( \bar{c} = 0.12 \times \text{ density} = 0.24 \text{ g/cm}^3 \) with a density of 2 g/cm\(^3\). However it is much too high for fractal objects which do not interpenetrate, where:

\[
\bar{c} = 0.12 \times (\text{density}) \times (a/R)^3 - D.
\]

Taking the monomer size \( a = 4 \text{ Å} \), \( R = 500 \text{ Å} \) and \( D = 2 \) (see below) for the dilution at \( t = 7.75 \text{ h} \), we obtain \( \bar{c} \approx 2 \times 10^{-3} \text{ g/cm}^3 \), an order of magnitude too low. This suggests that the polymers are largely interpenetrated.

At low concentrations the low \( Q \) limit of the scattering curves measures the overall parameters of the individual polymers. Figure 7 shows these scattering curves plotted in the Zimm representation for the dilution at 7.75 hours.

![Fig. 7. — Zimm plot for the dilute solutions extracted from the reaction bath at \( t = 7.75 \text{ h} \). Squares : 1/3. Diamonds : 1/10. Filled diamonds : 1/30.](image)

The individual radii (\( z \) averaged) and masses (weight averaged) which are extracted from these plots are listed in table I. Near the gel point the radii become much larger (\( \geq 1000 \text{ Å} \)) than the interaggregate distances measured in the reaction bath (\( \approx 400 \text{ Å} \)); however they are too large to be determined accurately in this range of \( Q \). The weight averaged masses \( M_w \) of the polymers are obtained with a better accuracy; here the main uncertainty lies in the scattering densities: we assume that the density of scattering length for a polymer is \( \rho_p = 2.5 \times 10^{10} \text{ cm}^{-2} \) and that for ethanol \( \rho_s = -0.35 \times 10^{10} \text{ cm}^{-2} \). Because the TEOS polymers are highly branched, these masses are much larger than those for linear polymers of comparable sizes (Tab. I).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( M_w )</th>
<th>( R_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution at ( t = 7.75 \text{ h} )</td>
<td>( 4 \times 10^6 )</td>
<td>( &gt; 500 \text{ Å} )</td>
</tr>
<tr>
<td>Dilution at ( t = 8.5 \text{ h} )</td>
<td>( &gt; 3 \times 10^7 )</td>
<td>( \approx 1000 \text{ Å} )</td>
</tr>
<tr>
<td>Poly(ethylene oxide) in water (35)</td>
<td>( 5 \times 10^5 )</td>
<td>( 500 \text{ Å} )</td>
</tr>
<tr>
<td>Poly(ethylene oxide) in water (35)</td>
<td>( 1.2 \times 10^6 )</td>
<td>( 1000 \text{ Å} )</td>
</tr>
</tbody>
</table>

This high degree of branching was expected from the chemistry of the reaction [27-31]. Here the surprising feature is that it shows up in the low \( Q \) limit of the intensities (mass vs. radius of the...
polymers) and not in the high $Q$ behaviour (internal structure). Indeed we would expect a fractal dimensionality of about 2 for randomly branched polymers, whereas the measured exponent for $I(Q)$ is 1.6 (Fig. 5). As noted earlier [38], the reason for this odd behaviour is that it integrates over the intensities scattered by all polymers, large or small, and the small ones give intensities which are not in the self similar range. Thus the measured exponent is a complicated function of the internal structure and of the distribution of polymer sizes; it is remarkable that the value found for TEOS polymers (1.6) is identical with that of a percolating system where the distribution of polymer sizes is presumably quite different [38].

Finally, in the high $Q$ limit, the absolute values of the scattered intensities measure the mass per unit length of the polymer. In this range we describe a polymer as a collection of $N$ units of size $a$ and mass $m$; these units form a structure of fractal dimensionality $D = 2$ and overall radius $R$. Then the scattering curve follows the Debye function:

$$P(Q) \approx \frac{2}{Q^2 R^2} \quad \text{with} \quad R^2 = Na^2$$

and the intensity scattered by the polymer on an absolute scale is:

$$\frac{I(Q)}{cV} = (\rho_p - \rho_s)^2 \frac{a^2}{Q^2} \frac{2}{m}.$$ 

The intensity measured at $Q = 0.0861 \text{Å}^{-1}$ is $I(Q) = 3.4 \text{cm}^3/\text{g}$; on an absolute scale this yields $I/cV = 0.28 \text{cm}^2/\text{g}$ [36]. If we choose the monomeric unit to be:

$$\begin{array}{c}
\text{OH} \\
\text{Si}
\end{array}$$

then its mass is $m = 62/N_{\text{Avog}}$; inserting this value into the expression for the intensity, we find that the unit size $a$ is equal to 4 Å. Hence the ratio $m/a^2$ measured by the experiment is compatible with the growth of single strand polymers, as opposed to fibers or films (for example in a system of films the film thickness would have to be as low as 1 Å in order to match the measured intensities).

5. Discussion.

We must account for the existence of two different lengths in this problem: an interaction distance $\xi$, and a connectivity length $R_c$. At first sight their behaviours seem to conflict with each other: on the one hand the reaction bath appears to be made of microscopic units ($\xi$), which keep growing beyond the gel point just as they did before the gel point; on the other hand the dilution experiments show that individual polymer sizes ($R_c$) are much larger, and do become macroscopic at the gel point.

Obviously this conflict cannot be resolved within a model where all the polymers have the same size. And indeed it is well known that the distribution of polymer sizes is an essential feature of a gelating system [34, 37-39]. Such a distribution may contain a majority of small, microscopic polymers and a minority of very large ones. Then the smaller, more numerous polymers control the local density of chain segments while the few larger ones are responsible for the gel point.

This spatial ordering can be analysed as a screening mechanism [2, 4, 40]: the polymers are fractal objects, and the larger ones have larger holes; thus the smaller polymers are denser, and they can penetrate them. If the polymers repel each other in most collisions [41], and stick only in a few rare events [42], then the smaller polymers will effectively screen all variations in the segment density which would be created by the larger polymers. Therefore the reaction bath will be homogeneous at all scales down to the size of the smaller, more numerous polymers (Fig. 8).

![Fig. 8. — Recombination of interpenetrated polymers. The polymers repel each other in most collisions, and bind in a few rare events. Because of these repulsions, the average density of monomers tends to be as uniform as possible; hence the sample appears uniform at scales shorter than $\xi$. In the reaction bath, screening is efficient, and $\xi$ is comparable to the sizes of the smaller polymers. As the polymers recombine, this screening length keeps growing until they all are bound.](image)

Still there must be a lower cutoff or a marked maximum in the distribution of polymer sizes, otherwise the density would be homogeneous all the way down to the average monomer separation, and there would be no small angle scattering. The observation of small angle scattering with a characteristic dimension $\xi$ implies that there is such a maximum. Because of this maximum the gel appears non uniform at all scales shorter than $\xi$, and we can observe the internal structure of the polymers in this range (Fig. 8). The growth of $\xi$ with reaction time indicates that the maximum shifts to larger polymers, presumably through recombination of the smaller ones.

We also know that the distribution of polymer
sizes must be quite wide, since the larger polymers are penetrated and screened very efficiently by the smaller ones. The fact that they are seen in the scattering from the diluted samples indicates that the dilution effectively separates all polymers; then the low $Q$ limit of the scattering is controlled by the $z$-average of the distribution, while the high $Q$ limit depends on its $n$-average [43, 44].

Now consider the consequences of the gelation process. As the reaction proceeds through the gel point and beyond, the free polymers keep moving until they find others to which they link; in this process some regions of the bath are depleted and can no longer be filled by the growing polymers; thus the continuous rise of $\xi$ implies that the gel becomes less and less uniform (and indeed the scattering at low $Q$ keeps rising). We believe that this rise of heterogeneities beyond the gel point is general for all gels which are made through aggregation of a finite number of monomers dispersed in a solvent; it is of course contrary to the behaviour described by the bond percolation model, where a growing number of bonds are placed on a fixed number of sites: that system must become homogeneous beyond the gel point, because all the sites will eventually be filled.

If we do understand how aggregation produces gels which are spatially non uniform, we may wish to control such heterogeneities. As shown in figure 8, the behaviour of the smaller polymers in the distribution of sizes is critical to the development of heterogeneities of the polymer density within the bath. This remark suggests a number of ways to test the screening mechanism by manipulating the distribution of polymer sizes: shorter polymers or even oligomers could be added at a given time during the reaction, or to the contrary, the reaction bath could be fractionated to eliminate either shorter polymers or larger ones; alternatively the catalysis could be changed (pH jump); finally dense silica particles could be dispersed in the reaction bath. These techniques are similar to well known methods used to improve the properties of gels made with organic polymers, which are also heterogeneous because regions of high polymer density and regions of low polymer density develop in the course of gelation; they follow the general principle that since we can't get rid of heterogeneities, we might as well learn to live with them.

6. Conclusion.

The spatial patterns formed by a collection of branched polymers in a solvent result from two basic ingredients: the distribution of polymer sizes, and the interactions between distinct polymers. In the acid catalysed growth of TEOS polymers, the distribution of sizes appears to be quite wide, and the interactions mostly repulsive. This leads to a remarkable situation where: (i) the repulsions keep trying to maintain a uniform segment density in the reaction bath, and they succeed at scales beyond the screening length $\xi$; (ii) the recombination of the polymers keeps pushing $\xi$ to larger dimensions, thereby increasing the scale within which the reaction bath appears non uniform.

The structure of the final gel is determined by the outcome of this competition. We find that the recombination of interpenetrated polymers produces objects with selfsimilar structures; conversely the reaction bath is gifted with a collection of depleted regions whose distribution is also selfsimilar. This is akin to the growth of heterogeneities in many other gels and particularly in gels of organic polymers. Hence it may be worth paying attention to systems such as this one where the growth of heterogeneities results from simple kinetic processes.

Acknowledgments.

This work originated from discussions with M. Adam, S. Alexander, M. Daoud, M. Delsanti, J. F. Joanny, M. Kolb and L. Leibler; it was made possible through the help of staff members of ILL and LLB, particularly J. P. Cotton, J. Teixeira and P. Timmins. We would also like to thank the referees for pointing out to us the importance of interactions in this problem.

References

We put the intensities on an absolute scale through a normalization with the incoherent scattering of water; here absolute intensities are obtained by dividing the measured intensities by a factor of 12.1 cm. The general procedure is described by Ragnetti, M., Geiser, D., Hocker, H., Oberthür, R. C., Makromol. Chem. 186 (1985) 1701.


Pouxvil, J. C., Boilot, J. P., to be published.


We put the intensities on an absolute scale through a normalization with the incoherent scattering of water; here absolute intensities are obtained by dividing the measured intensities by a factor of 12.1 cm. The general procedure is described by Ragnetti, M., Geiser, D., Hocker, H., Oberthür, R. C., Makromol. Chem. 186 (1985) 1701.