Size Distribution of Polymers in Sol-Gel Condensation

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ABSTRACT: Silicon tetraethoxide (TEOS) monomers have been dissolved in ethanolic solutions and hydrolyzed to form reactive, multifunctional monomers. These monomers polymerize spontaneously; they form a collection of branched polymers which overlap each other and entrap the solvent into a macroscopic gel. At various times during the reaction, individual polymers have been extracted from the reaction bath and their size distribution has been examined through size-exclusion chromatography coupled with low-angle light scattering. We report results from the early times in the reaction, before the polymers have overlapped. The number distribution of polymers with mass M can be approximated by a power law $n(M) \approx M^{-\tau}$ with $\tau = 2$ and cutoffs at the lowest and highest mass. As the reaction time increases, the distribution shifts as a whole to higher mass, and both cutoffs remain proportional to each other. The growth of the average mass with reaction time is exponential. These features are in general agreement with predictions from kinetic models where the polymers diffuse through the solvent and recombine with a low reaction probability.

Introduction

Inorganic gels can be made through the spontaneous polymerization of organometallic precursors dissolved in an alcoholic solvent.[1-3] The reaction proceeds as follows: the precursors are hydrolyzed into reactive monomers; these are allowed to diffuse through the solvent and react upon collision to form oligomers. In turn oligomers recombine with each other or with unreacted monomers to form larger polymers; gels are formed when some polymers reach a macroscopic size. Beyond this point there is a long ripening stage where the remaining free polymers recombine with each other or with the macroscopic polymer. If there is no reverse reactions, the growth and ripening processes end when all polymers are either bound or unable to react.

Various reaction conditions yield gels with different structures: with the same monomers, some conditions produce transparent gels, some give turbid ones, and some result in precipitates. This is expected; indeed the structure of a gel depends not only on how many links are made but also on the relative locations of these links and on the topology of the network. The conditions which specify the type of growth are listed below:

(a) The *concentration* of monomers determines whether they will bind right where they are or whether they will have to segregate in order to bind to each other. In the latter case, the rules for interdiffusion and interpenetration of polymers will influence the course of growth.

(b) When monomers or polymers bind, they may have a *chemical preference* for highly condensed regions or for uncondensed branches. In the former case the polymers will grow as dense, compact particles; in the latter one they will expand as tenuous or bushy structures.

(c) The occurrence of *reverse reactions* determines whether the network of bonds is frozen in the configuration where it was formed or whether rearrangements are possible during the growth of the ripening of the gel.

Here we choose to study a generic gel, where a concentration is in the upper part of the usual range, there is no difference in reactivity between highly condensed and poorly condensed species, and there are few reverse reactions on the time scale of gelation. Each of these points represents an important choice for the type of growth and the structure of the final material; they are established as follows.

(d) For silica polymers the *range of concentrations* where gels can be made extends from a volume fraction $\phi = 0.004$ to $\phi = 0.1$. At concentrations much below the lower limit the structures are not strong enough to make real gels; it may also be that reverse reactions prevent complete gelation (see below). The upper limit is imposed by the volume of the precursor, which is much larger than that of the silica monomer. Within this range of concentrations the gelation rate $1/t_g$ varies as $\phi^{2.5}$ and the mesh sizes ξ of the resulting gels scale as $\phi^{-1.4}$.[4-6]

(e) *Chemical preferences* occur if a monomer which has already reacted one or two functions becomes more or less reactive for further condensation. This may occur because the partial charges carried by metal and oxygen atoms in the monomer will vary when it is bridged to other monomers. When the precursors are transition-metal oxides, this effect is so strong that it can change the growth mode from the recombination of bushy polymers to the precipitation of dense clusters.[7,8] For silica at neutral to acidic pH, this effect is weaker[1] and precipitation is never observed.

(f) The siloxane bonds which are formed, although strong, can be broken by water; indeed it is well-known that silica has a limited solubility in water.[9] For the growth of oxide polymers, the question is whether such *reverse reactions* are frequent or rare compared to forward reactions. This is governed by pH: at pH > 9 dissolution of silica proceeds quickly, and isolated briges are broken sooner or later; as a result the growing objects are dense, as in the Stöber process.[9] In water at pH < 6 these reverse reactions become rare;[9] in sol-gel processes this is confirmed by the fact that gels made in 350 h at pH 4 and $\phi = 0.004$ grow similarly to gels made in 1.5 h at $\phi = 0.04$.[5,6] Since the rate of reverse reactions does not depend on concentration, this implies such reactions are unimportant on a time scale of 350 h. In the present work the gels were made at pH 2, near the isoelectric point of silica; in such conditions reverse reactions in the reaction bath are expected to be even less common.

Thus the reacting species must diffuse and collide in order to bind, and when they do collide, permanent links are formed at random with no chemical preference for either dense regions or for the tips of chains. In such

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nonequilibrium conditions we have demonstrated that the polymers grow as *fractal objects*; as they recombine they form larger and larger voids and trap more and more solvent instead of forming a dense precipitate.[4-6]

An essential feature of these recombination processes is that they generate a *distribution of polymer sizes*, with a large number of small polymers, which carry most of the mass, and a small number of larger ones, which occupy most of the volume. As the reaction progresses, the larger polymers take an even larger volume because they grow as fractal objects. Since the reaction bath is at a finite concentration, the reaction arrives at a point where the smaller polymers are trapped within the mesh formed by the larger ones. This interpenetration is important, because it determines the spatial patterns formed by the polymers as they connect to each other.[5]

So what are the central questions in gel formation? They are of two types: (i) Which polymers bind to which other ones? This determines the *connectivity* of the gel and hence its mechanical properties. (ii) In which configuration do they connect? This determines the structure of the resulting polymer, and the *density correlations* throughout the material. In previous work we have measured these correlations through light scattering and neutron scattering experiments on the reaction bath; the results reflect the interpenetration of large polymers with smaller ones.[4-6] In the present work we return to the first question and try to determine whether the preferred reactions are between small polymers, between small and large ones, or between large ones.

The effects of such reactions can be observed in the size distribution of the reacting polymers. For instance, if the growth proceeds through percolation, large polymers should grow faster because their large surface allows them to capture more small ones. As a result, the distribution would become quite polydisperse, and the largest polymers would become macroscopic at a stage where most others are still quite small.[10,11] On the other hand, when growth occurs in a solution, the smaller polymers have a better chance to react because they diffuse faster; this would compensate for their smaller cross section, and the resulting distribution ought to become less polydisperse;[12] interpenetration would then be considerably more difficult.[13]

A formal analysis of such a process can be obtained from the Smoluchowski equation; this analysis is presented next. Then the method for growing inorganic polymers and measuring their size distributions is described. Next the measured distributions are presented, and finally the implications of such distributions for the growth processes are discussed.

Theoretical Background

Smoluchowski Equation.[12] The spontaneous recombination of subunits to form larger objects is described through a set of rate equations written 70 years ago by Von Smoluchowski. Accordingly, the number n_k of k-mers (polymers of k subunits) increases when i-mers recombine with j-mers to form k-mers, and it decreases when k-mers recombine with other polymers for form larger ones:

$$2\mathrm{d}n_k/\mathrm{d}t = \sum_{i+j=k} K_{i,j} n_i n_j - \sum_i K_{i,k} n_i n_k$$

In this set of equations the main assumption is that reactivity is controlled by polymer size. Other assumptions are as follows: (i) there are no backward reactions; (ii) structural features are ignored: all different ways of attaching an i-mer to a j-mer are lumped into a single rate constant; (iii) concentration effects are ignored: the rates are the same whether the polymers are isolated or surrounded by others. These assumptions correspond to points d–f in the Introduction.

Homogeneous Kernels. The evolution of the system is governed by the set of rate constants $K_{i,j}$, and it may be quite complex. However, for gelation it may be sufficient to know which reactions are dominant: those between small polymers, between small ones and large ones, or between large ones. This can be done in the theory of homogeneous kernels, where reactivity vs polymer size is a power law.[14,15] The analysis is based on the use of two exponents λ and ν, which describe the relative rates of large–large and small–large reactions.

The exponent λ describes the recombination of large polymers with polymers of comparable sizes (large–large): $K_{j,j} \approx j^{\lambda}$.

The exponent ν describes the capture of small polymers by much larger ones (small–large): $K_{1,j} \approx j^{\nu}$.

Class I: $\nu < \lambda < 1$. The reactions of large polymers with other large ones dominate ($\nu < \lambda$), but they do not lead to runaway growth ($\lambda < 1$). Hence, large polymers are used up while many small ones are left behind. The mass distribution for large polymers is a power law between cutoffs $i_{\min}$ and $i_{\max}$: $n_i \approx n_0 i^{-\tau}$ where $n_0 = 1/\sum_i n_i$; the exponent τ is equal to $1 + \lambda$, and it is smaller than 2. Because the total mass is constant, the numbers of smaller polymers must decrease when the cutoff $i_{\max}$ is pushed to larger mass; for $\tau < 2$ this decrease is significant, i.e., large polymers cannot grow unless all other populations (n_0) are depleted in the same way. Finally the average polymer mass grows as a power law t^z with $z = 1/(1 - \lambda)$; this is a comparatively slow growth process.

Class I′: $\nu < 1 < \lambda < 2$. The reactions of large polymers with other large ones dominate ($\nu < \lambda$), and they do lead to runaway growth ($\lambda > 1$). The mass distribution for large polymers is still a power law $n_i \approx n_0 i^{-\tau}$, but τ equals $(\lambda + 3)/2$ and remains larger than 2. In this case there are so few large polymers that their growth does not significantly deplete the populations of smaller polymers: n_0 no longer depends on $i_{\max}$. Hence, the size of the largest polymers diverges in a finite time t_g, while all other polymers remain finite; at t_g the system forms a gel where all finite polymers (most of the mass) are trapped by the infinite polymer (almost no mass). The averge mass diverges as $(t_g - t)^{-1/s}$ where $s = (\lambda - 1)/2$.

Class III: $\lambda < \nu < 1$. Large polymers react preferentially with much smaller ones ($\nu > \lambda$). Thus small polymers are consumed, and the mass distribution has a broad maximum with a sharp decay at high mass. As the reaction progresses, this distribution shifts as a whole toward higher masses. As in class I, the average polymer mass grows as a power law t^z with $z = 1/(1 - \lambda)$; this growth is slow because all polymers must grow together.

Class II: $\lambda = \nu = 1$. All reactions are equally probable. The mass distribution for large polymers is a power law $n_0 i^{-\tau}$, and τ is somewhere between 1.5 and 2. The situation with $\tau = 2$ is the threshold to runaway growth; indeed the populations of smaller polymers must still decrease when $i_{\max}$ rises, but the decrease is only logarithmic: $n_0 \approx 1/\log(i_{\max}/i_{\min})$. Also the average polymer mass grows exponentially with time. Hence, the system could easily cross over to a gelling regime if large polymers became more reactive than the rest.

Kinetic Analysis According to the Mass Distribution of Polymers. What the theory of homogeneous kernels tells us is the following: growth processes can be divided into discrete classes according to some general

Table I
Compositions of Reaction Baths

sample	monomer, mol	water, mol	ethanol, mol	pH	silica vol. fraction	gel time at 50 °C, h
P89	1	8	8.8	2.2	0.04	185
C90	1	4	0	2.6	0.10	90

criteria for the relative rates of large–large and small–large recombination processes. For each class, specific predictions can be made concerning the distribution of polymers which result from such processes. Conversely, if the distributions can be measured, then the balance of recombination processes will be determined, and the growth mode can be identified.

The *polymer mass distribution* can be obtained from scattering experiments where small and large polymers are physically separated from each other. For organic polymers in organic solvents, this separation is commonly performed through size-exclusion chromatography, where the larger polymers are eluted from the columns before the smaller ones; refractometry is used to measure the concentration of the eluted polymers and light scattering at a very small angle (LALLS) to measure their mass. The application of this method to inorganic polymers grown through sol–gel processes is now presented.

Polymerization Reactions

Silicon tetraethoxide monomers (TEOS) can be polymerized in a two-step process: first the ethoxy groups are hydrolyzed and replaced with silanols; then the silanols condense to form siloxane bridges.[16,17] We use conditions where hydrolysis is fast and complete, whereas condensation is slow and incomplete.

The rate and extent of hydrolysis are determined by the amount of water and by the concentration of H^+ ions. Complete hydrolysis of TEOS into $Si(OH)_4$ requires 4 mol of water, and some of this water is released on condensation; we used either 4 or 8 mol of water per monomer. H^+ ions were used to catalyze the hydrolysis; NMR experiments have shown that with excess water and acidic pH this hydrolysis is complete.[18] Detailed compositions are shown in Table I; a typical recipe is as follows. A cold solution of freshly distilled monomer (1 mol) in ethanol (4.8 mol) is added dropwise to a cold water (8 mol)/HCl (0.01 mol)/ethanol (4 mol) mixture under slow agitation. The hydrolysis is exothermal and brings the temperature of the mixture back to room temperature; it is complete in less than 1 h. Alternatively the hydrolysis may be performed without added ethanol, starting with an emulsion of monomer in water. If it is properly conducted,[19] this emulsion polymerization quickly generates enough alcohol to solubilize the remaining monomer, and the reactions continue as in the recipes with added ethanol.

After the hydrolysis was completed, the reaction bath was placed in an oven at 50 °C; then the silanols condensed to form siloxane bridges between the silicon atoms and released some of the water used for hydrolysis. This reaction is fast when the silanols are ionized, either as $SiOH_2^+$ or as SiO^-, and it is slow near the isoelectric point of silica. Thus the concentration of H^+ is a controlling parameter, as shown in Figure 1. Moreover, gels made near the isoelectric point of silica are transparent, whereas those made at pH values between 4 and 6 are turbid.[5,6] We chose the former condition, as indicated in Table I.

In order to obtain reproducible size distributions and gel times, however, it is not enough to control the bulk conditions for hydrolysis and condensation; it is also necessary to prevent heterogeneous polymerization conditions. These may occur because the reaction rate varies greatly with the concentration of reacting monomers (approximately as the power 2.5 of concentration). Excess concentrations may occur during hydrolysis, if monomers are concentrated in water drops, or during condensation, if solvent evaporates at the free surface of the reaction baths. For this reason the reaction bath must be kept in a vessel which is never opened or in disposable containers such as syringes.

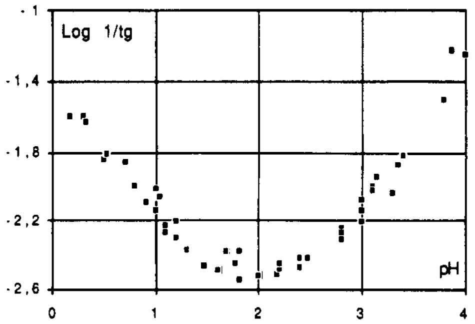

Figure 1. Gelation rates for reaction baths made at a volume fraction of silica $\phi = 0.04$ and kept at 50 °C. Vertical scale: inverse gel time, log scale. Horizontal scale: concentration of H^+ in the reaction bath, log scale.

Table II
Compositions of the Elution Mixture and of the Solutions Injected into the Columns, in Volume Fractions

	silica	water	alcohol	THF
elution mixture	0	0.025	0.181	0.794
reaction bath P89	0.007	0.025	0.181	0.787
reaction bath C90	0.01	0.025	0.179	0.785

Size-Exclusion Chromatography

In size-exclusion chromatography (SEC) polymer size must be the only factor that determines the behavior of the macromolecules in the columns. Hence, there must be no chemical or physical affinity of the macromolecules for the material in the columns. This condition is difficult to meet with polymers extracted from a reaction bath, which are always reactive. Inorganic polymers react through their hydroxyl groups; hence, it is essential that the columns carry no such groups. This condition is met with the cross-linked polystyrene gels which are commonly used for the separation of organic polymers.

The difficulty lies with finding an eluent which can dissolve inorganic polymers and carry them into all the pores of the columns. This eluent must be a good solvent of the polymers; it must also wet and swell the styrene gel which is packed inside the columns. The solvent of the polymerization reaction, which is an ethanol–water mixture, is not adequate, since it does not swell the polystyrene gel. We found that we could use tetrahydrofuran (THF): it is a good eluent for the styrene gel columns and it mixes in all proportions with the reaction bath. After dilution the pH of the solutions had risen from 2.2 to 3.

Individual polymers must be separated from each other before they are pushed through the columns. The separation is achieved by diluting the reaction bath; this has the added advantage of effectively stopping the polymerization. In order to minimize solvent peaks it is best to dilute the polymers with the eluent. The dilution is performed by adding pure THF to the reaction bath; then the solvent of the polymers is a mixture of THF, alcohol, and water; the composition of this mixture is indicated in Table II. Visual observation of the samples shows no turbidity during the dilution process; accordingly the mixture appears to be a good solvent for the polymers.

This was checked through light scattering experiments, where the same reaction bath was used to make dilutions in THF and in ethanol; both series of solutions gave similar values for the average molecular weight of the polymers.

Still it is necessary to check that dilution in THF does not change the size distribution of the polymers extracted from the reaction bath. For this purpose size distributions were measured immediately after extraction and dilution by THF and then again after equilibration in THF for different lengths of time. For equilibration times of a few hours we found that the distributions remained stable; hence, polymerization was very much slowed down by dilution and reverse reactions were not significant. Over a period of 1 month we found that the distribution had shifted to larger sizes; the shift for most populations was a factor of 1.5 in mass; for the largest populations the shift was slightly less, and this may be taken as an indication of reverse reactions. We concluded that dilution in THF is quite safe for silica polymers at short times; it may not be so at very long times, and it is not so for other inorganic polymers. Also the effect of reverse reactions is easily identified as a limitation to the growth of very large polymers.

Since the reaction solvent (ethanol + water) is injected in the columns together with the polymers, it is necessary to examine its effect on the size-exclusion process. There are two possible problems: osmotic instability of the columns and solvent peaks in the detected signals. The instability can be prevented by using columns which are strongly cross-linked; we use PL 10-μm gel columns[20] with the exclusion limits of 10^6, 10^5, 10^4, 10^3, and 10^2 Å and found them to be adequate. The solvent peaks can be minimized by using an eluent which has the same composition as the solution to be injected for analysis. We found that PL gel columns will function adequately with eluents which contain up to 10% of water, ethanol, or both. The short-term stability is good, as shown by the stability of the pressure and of the refractometer base line; on the other hand, there is a slow increase in the overall pore volume which becomes noticeable over a period of weeks. The compositions of the eluents used in our experiments are given in Table II.

After elution through the columns the concentrations and molar mass of polymers in the eluted liquid were analyzed on line with two detectors: a refractometer and a low-angle light scattering instrument.[21] The differential refractometer compares the refractive index of the eluted fractions with that of a cell containing the original eluent; when a single species is dissolved in the fractions the difference signal is proportional to its concentration. The light scattering instrument (Chromatix CMX 100) measures the intensity scattered by the fractions as they flow through a small scattering cell; the volume of the scattering cell was 10 μL, and the scattering volume was 0.04 μL. The scattering angle was 6°; at this angle all the rays scattered by a macromolecules are in-phase and the scattered intensity is proportional to the number of macromolecules multiplied by the square of their molar mass; this is more conveniently expressed as the product of molar mass by concentration.

The two signals were discretized into "fractions", stored, and treated according to standard procedures.[22] First the base line was determined, and the range of useful data was determined to include all elution volumes for which both signals are significant, excluding the solvent peaks. The refractive index increment of the polymers in the eluent was determined separately: it is $dn/dc = 0.05$ cm^3/g; this value was used to calculate the concentration of polymer in each fraction according to the refractometer signal. The product of mass times concentration was calculated from the light scattering signal according to the instrument constant and to the square of the refractive index increment. Finally both quantities were compared to extract the concentration and the molar mass in each fraction.

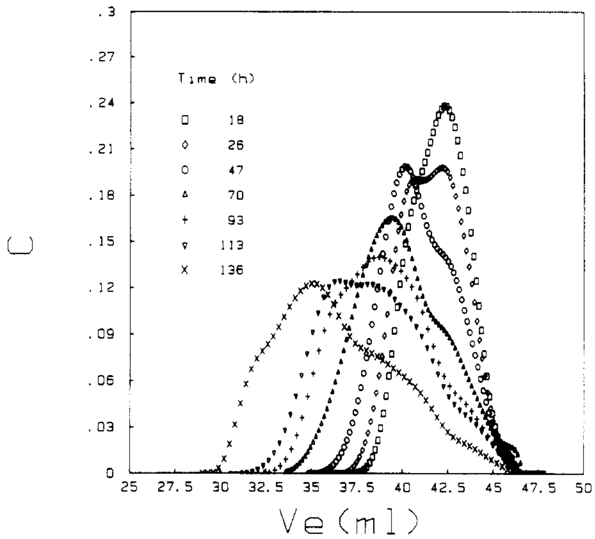

Figure 2. Refractometer trace for solutions extracted at different times from a reaction bath at volume fraction 0.04. The horizontal scale is the elution volume, and the vertical scale is proportional to the concentration of polymer eluted at this elution volume.

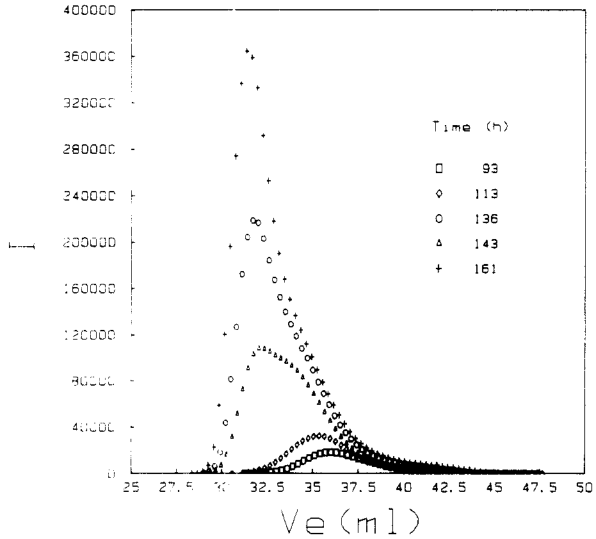

Figure 3. Intensity scattered by solutions extracted at different times from the same reaction bath as in Figure 2. The vertical scale is proportional to the product of mass times the concentration of polymer eluted at each elution volume.

Results

The *size distributions* are qualitatively similar to those found with solutions of branched polymers.[22] Figure 2 shows the evolution of the size distribution according to the refractometry signal. At short reaction times the distribution of concentration vs elution volumes is a symmetrical peak with sharp cutoffs; at longer reaction times this peak vanishes while a second peak and a tail grow on the high M side (low elution volumes).

Figure 3 shows the evolution of the distribution according to the light scattering signal: this yields the product molar mass times the concentration. At short times the signal is quite weak, owing to the low molar mass of the polymers. At longer times a very high peak

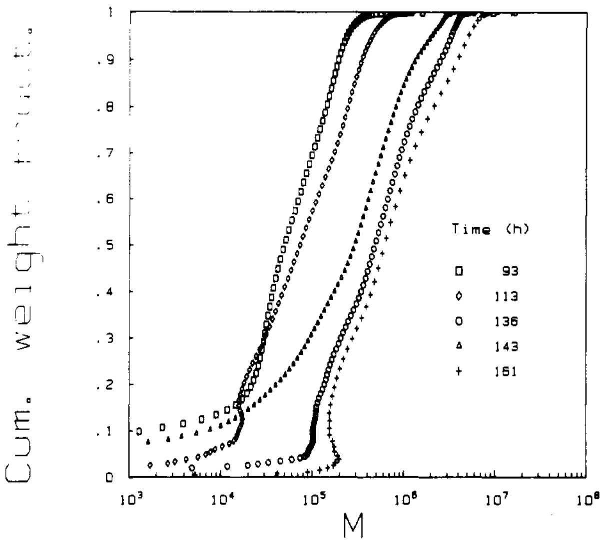

Figure 4. Cumulated distribution of concentration vs molar mass for a reaction bath at volume fraction 0.04.

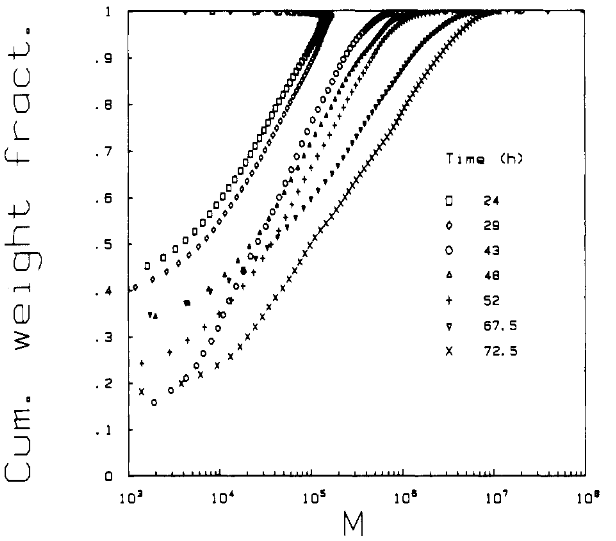

Figure 5. Cumulated distribution of concentration vs molar mass for the reaction bath at volume fraction 0.10.

grows in the high M side, corresponding to the tail at low elution volumes in the refractory curves. This peak is produced by a small concentration of polymers with very high molar mass. These large polymers are responsible for the gelation of the sample, while the smaller ones will be trapped in the mesh formed by larger ones.

It is difficult to interpret these curves directly. For instance, the peak at large elution volumes in the refractometer signal is produced by very small polymers which are not detected by the light scattering instrument. Moreover, a peak in the distribution of concentration vs elution volume does not necessarily correspond to a peak in the *distribution of concentration vs molar mass*.[22] This last distribution, which is the really useful information, requires a comparison of both signals, which is possible only in the region where the high M tail of the refractometer signal overlaps with the low M tail of the light scattering signal.

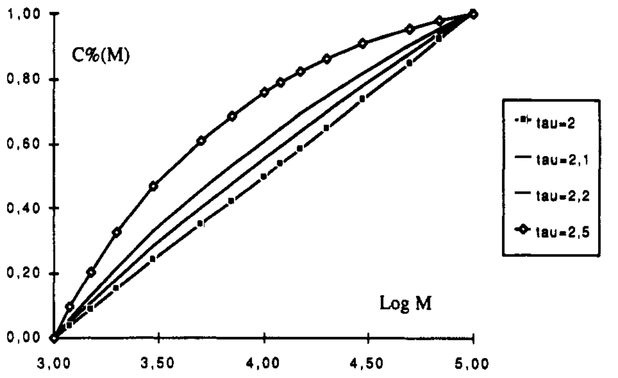

Figure 6. Cumulated distributions C % (M) according to population distributions of the form $n(M) = M^{-\tau}$ with cutoffs at $M_{\min} = 1000$ and $M_{\max} = 100\,000$. The distribution with $\tau = 2$ corresponds to the RLCA model and that with $\tau = 2.2$ to percolation.

The quantity which is best measured by the experiment is the cumulated amount C % (M) of polymers with a molar mass ranging from 0 to M; this is shown in Figures 4 and 5 for the reaction baths listed in Table I. The curves at short reaction times are incomplete since the polymers of lower mass are not detected by light scattering; complete distributions are obtained after $t/t_g \approx 0.2$. Each distribution starts with a trail at low M, then it is approximately linear in log M over 80% of the total amount of polymer, and finally it has a sharp cutoff at high M. We call $M_{\min}$ and $M_{\max}$ the cutoff values which are defined by the intersection of the linear fit with the limits at 0% and 100% of polymer.

First consider the shape of the individual distributions. The linear behavior with log M is in general agreement with a population distribution of the form

$$n(M) = n_0 M^{-\tau} h(M)$$

where the exponent τ is equal to 2 and $h(M)$ is a cutoff function which is zero for $M < M_{\min}$ or $M > M_{\max}$. Indeed the corresponding mass distribution will be

$$F(M) = n_0 M^{1-\tau} h'(M)$$

and for $\tau = 2$ the integral C % (M) will indeed be a linear function of log M.[23] Here the problem is to determine how precisely a cumulated distribution which appears linear implies that τ equals 2. For this purpose simulated distributions with τ values which differ from 2 have been presented in Figure 6. Comparison with the experimental data shows that distributions with $\tau > 2.2$ would have been recognized. Similar experiments have been performed with other reaction baths; none of them produced distributions where the exponent is significantly different from 2. Still this result is unsatisfactory since $\tau = 2$ and $\tau = 2.2$ correspond to very different growth modes (see Theoretical Background).

A better discrimination is provided by comparison of successive distributions. The remarkable feature is that the curves obtained at different reaction times are shifted parallel to each other; this indicates that the ratio of the largest mass $M_{\max}$ to the lowest mass $M_{\min}$ remains constant. For the reaction bath at volume fraction 0.04 (P89) this ratio is $M_{\max}/M_{\min} = 66$; it remains constant between $t/t_g = 0.3$ and $t/t_g = 0.8$. For the bath at volume fraction 0.10 (C90) this ratio equals 600, and near t_g it becomes even larger.

The fact that $M_{\max}/M_{\min}$ remains constant during the course of the reaction is in agreement with a growth mode at $\tau = 2$. Indeed for $\tau = 2$ the populations are all normalized by the ratio $M_{\max}/M_{\min}$:

$$\mathrm{C}\ \%\ (M) = \frac{\log (M/M_{\min})}{\log (M_{\max}/M_{\min})}$$

Hence, the total mass of each population only depends on $M/M_{\min}$. If a population is defined by an interval $\{M/M_{\min}, M/M_{\min} + \Delta(M/M_{\min})\}$, then the experimental result is that there is no net transfer of mass between populations.

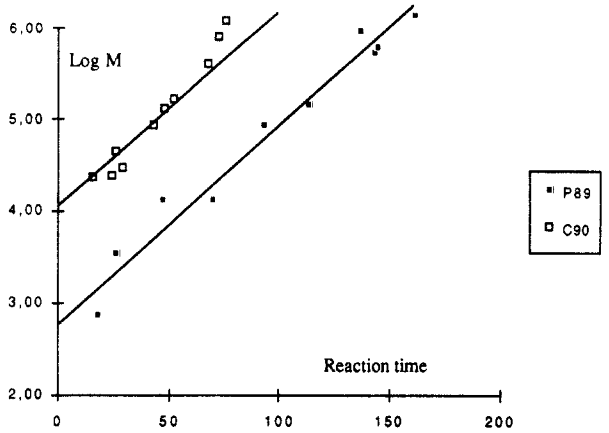

Figure 7. Growth of the average mass of the polymers in both reaction baths. P89 gelled at a time t_g = 185 h; the growth is exponential between $t/t_g = 0.2$ and $t/t_g = 0.9$.

Finally, since the distribution shifts as a whole, its evolution may be characterized by the variation of an average mass with reaction time. Figure 7 shows the evolution of M_w: it rises exponentially with reaction time up to $t/t_g = 0.8$. Beyond this time the polymers become so large that they no longer pass the filters which protect the light scattering instrument. This time is also close to the time where the polymers begin to overlap in the reaction bath.[5]

Discussion

Our aim was to find out which reactions dominate in the growth of inorganic polymers: those between small polymers, between small ones and large ones, or between large ones. This was done by observing how the distribution of concentration vs molar mass evolves with reaction time. The results can be summarized as follows.

(i) At each reaction time, up to $t/t_g = 0.5$, the number distribution is monotonically decreasing between cutoffs $M_{\min}$ and $M_{\max}$; it can be approximated by a power law $n(M) \approx M^{-\tau}$ with $\tau = 2 \pm 0.2$.

(ii) As the polymerization progresses the cutoffs, $M_{\min}$ and $M_{\max}$ remain proportional to each other. This is in agreement with a growth mode at $\tau = 2$ only.

(iii) The growth of the average mass with reaction time is exponential.

These results reflect a growth process where the distribution is made of many populations defined according to their value of $M/M_{\min}$, and the total mass of each population remains constant as it moves to higher molar mass. This could happen in two ways: either recombination reactions operate exclusively within individual populations (this would be a hierarchical growth process) or there are recombinations between different populations but the net balance is equilibrated.

According to the classification of van Dongen and Ernst,[14] this is a class II process. Such processes are expected when all reactions are equally probable, as in the reaction-limited aggregation of clusters (RLCA). The other classical growth models give predictions which are at variance with our results. The diffusion-limited aggregation of clusters (DLCA) gives distributions which are bell shaped, which is not observed here. The percolation model gives $n(M) \approx M^{-\tau}$ with $\tau = 2.2$, which would produce a significant curvature in the plot of the integrated distribution (Figure 6). Moreover, the percolation distribution is characterized by a much faster growth of the larger polymers, with the result that $M_{\max}/M_{\min}$ increases with time; this is not observed here.

The agreement with a RLCA process is not unexpected. Indeed the results have been obtained from early stages of the reaction, where the polymers must diffuse and collide in order to react; we also know that the reaction rate is slow and controlled by the catalyst of the reaction. These are the conditions for RLCA.

The next question is, what happens when the polymers become so large that they overlap? Light scattering experiments have shown that interpenetration occurs beyond $t/t_g = 0.5$;[5] beyond this stage the larger polymers are unable to move, but they may still bind small polymers which link them to each other. This resembles a percolation mechanism, and then the larger polymers would be expected to grow faster than the rest. Indirect evidence for this crossover is provided by dynamic light scattering experiments by Martin et al.[24,25]

In this respect it is interesting to compare both reaction baths. In the more dilute one (P89) the polymers are not expected to overlap until quite close to the gel point; we found that $M_{\max}/M_{\min}$ remains constant and small throughout this range of reaction times, in agreement with a kinetic aggregation process. In the more concentrated reaction bath (C90) overlap is expected sooner; this bath shows distributions which are more polydisperse, and this polydispersity appears to increase in the last two curves. Thus there may be a crossover from kinetic aggregation to percolation when the polymers begin to overlap.

References and Notes

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