Fractal Geometry of Silica Condensation Polymers

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The fractal dimension, D, of branched silica polymers is measured by small-angle x-ray scattering. D is independent of branching ratio and does not change during the course of polymerization to a gel.

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The concept of fractal geometry provides a new description of the structure of random systems.[1,2] Basically, the fractal dimension, D, quantifies the manner in which the mass, N, of an object increases with length R:

$$N \sim R^D. \tag{1}$$

Objects generated by different growth processes (e.g., diffusion-limited aggregation,[3,4] percolation[5]) may differ in D, so that D contains information about the growth process. Although D has been determined for an enormous number of computer-generated objects, no measurement of D of branched polymers has been reported. Here we report such a measurement on branched silica polymers produced by condensation polymerization.

The fractal dimension is measured from the power-law decay of the static structure factor in the Porod region[6] determined by small-angle x-ray scattering. We find that the fractal structure is independent of the degree of branching and does not change during growth. We suggest that these polymers are realizations of lattice animals.[7]

Silicate polymers are formed by the polymerization of silanol molecules in nonaqueous solvents[8]:

$$2(R\mathrm{O})_3\mathrm{SiOH} \rightarrow (R\mathrm{O})_3\mathrm{SiOSi}(\mathrm{O}R)_3 + \mathrm{H_2O}, \tag{2}$$

where R is a proton, or an alkyl, or silicate group. The silanols are formed by acid- or base-catalyzed hydrolysis of silicon tetraethoxide (TEOS), $\mathrm{Si(OC_2H_5)_4}$.

When the reactions are acid catalyzed, chemical arguments[9] indicate that the resulting polymers are weakly branched. This prejudice toward linear chains arises because, under acidic conditions, monomers and end groups on chains are more readily hydrolyzed than potential branch points. If condensation commences before the hydrolysis reaction is complete, branching is inhibited. In base-catalyzed systems, highly branched chains are expected. In this situation, partially hydrolyzed monomers hydrolyze more readily than unhydrolyzed monomers; hence upon condensation, branch points are introduced. Branching is also enhanced at high $\mathrm{H_2O/Si}$ ratios. In fact, dense colloidal particles can result if the reaction is carried out in base with excess $\mathrm{H_2O}$.

To avoid colloid formation and precipitation, the common practice is to carry out the reaction in two stages.[8] The first stage is acid catalyzed at a 1:1 $\mathrm{H_2O/SiO_2}$ ratio and probably generates clusters of about four units. In the second stage, more $\mathrm{H_2O}$ is added and these units are polymerized in either acidic or basic solution. The two-stage procedure is used here.

Fractal objects are self-similar structures whose geometric properties are scale invariant.[3] That is, the pair correlation function $\langle \rho(\vec{r}_1)\rho(\vec{r}_2)\rangle$ is homogeneous, so that under a scale change λ

$$\langle \rho(\lambda \vec{r}_1)\rho(\lambda \vec{r}_2)\rangle = \lambda^{-A}\langle \rho(\vec{r}_1)\rho(\vec{r}_2)\rangle, \tag{3}$$

where $\rho(r)$ is the concentration of monomers at position r. This property implies a power-law correlation function: $\langle \rho(\vec{r}_1)\rho(\vec{r}_2)\rangle \sim (r_2 - r_1)^{-A}$. The exponent A is related to D defined in (1). If $N(R)$ is the number of monomers within radius R, then

$$N(R) = \int_0^R d^3r \langle \rho(0)\rho(r)\rangle / \langle \rho \rangle \sim R^{d-A} = R^D, \tag{4}$$

and so $D = d - A$, where d is the dimension of space. Equation (4) applies only for distances small compared to R_g, the radius of gyration of the fractal, and large compared to the persistence length, a, which defines the local stiffness of the backbone.

The static structure factor, $S(K)$, is just the Fourier transform of the pair correlation function so that

$$S(K) \sim K^{-D}, \quad KR_g \gg 1 \gg Ka, \tag{5}$$

where K is conjugate to r. We exploit this simple relationship to measure D from the power-law decay of the structure factor in the so-called Porod regime[6] $KR_g \gg 1 \gg Ka$. Porod-region scattering contrasts with Guinier-region scattering ($KR_g \sim 1$) where Gaussian decay is expected. From the Guinier data we are able to assess the degree of

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overlap and interaction between polymer clusters.

We are particularly interested in the effect of branching on the fractal structure. The silica system is ideal in this sense because it is possible to vary the degree of branching by choice of catalytic conditions. The compositions used in this study are given in the figure caption. Unfortunately, characterization of branching is a central unsolved problem in polymer science, and so we have only qualitative information on branching provided through chemical insights described above and from the concentration dependence of the structure factor in the Guinier regime.

Composition A2 is an acid-catalyzed system with low water content. Under these conditions we expect less branched structures compared to A3 and B2. System A3 has a high water content which favors hydrolysis, and therefore branching, despite the use of an acid catalyst. Finally, B2 is a base-catalyzed system in which multiply hydrolyzed monomers condense to produce highly branched clusters.

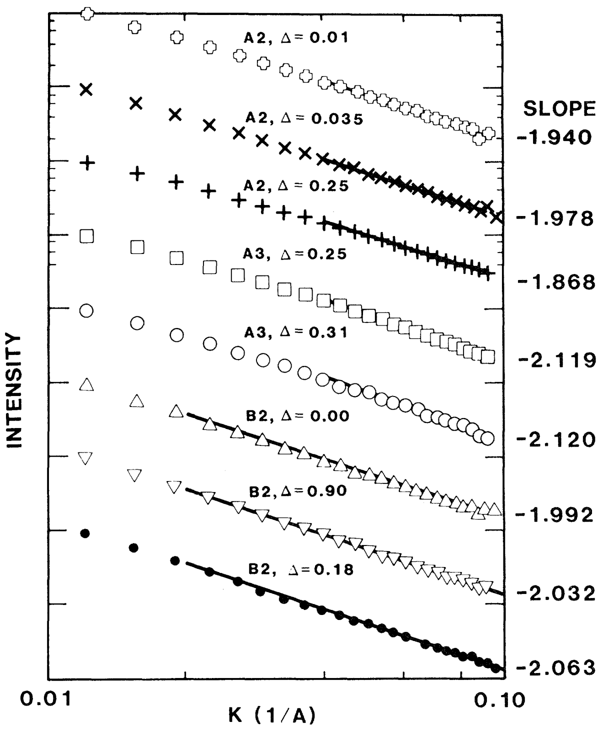

FIG. 1. Structure factor for diluted and quenched silica solutions polymerized under different catalytic conditions at 40 °C in propanol. A2: TEOS = 10.9 mol%, $p\mathrm{H}=0.8$, $\mathrm{H_2O/Si}=5.1$; A3: TEOS = 6.1 mol%, $p\mathrm{H}=3.1$, $\mathrm{H_2O/Si}=12.4$; B2: TEOS = 12.9 mol%, $p\mathrm{H}=8.2$, $\mathrm{H_2O/Si}=8.1$. pH is measured with a glass electrode. Backgrounds are subtracted, the backgrounds being identical unpolymerized solutions. Δ is the time increment to gelation: $\Delta=(t_{\mathrm{gel}}-t)/(t_{\mathrm{gel}}-t_0)$, where t_{gel} is the gel time, t_0 is the initiation time, and t is the observation time. Note that power-law behavior is found only at high K where $KR_g \gg 1$.

The scattering curves are shown in Fig. 1. These data are for samples diluted at least 10 to 1 in propanol and quenched to 7 °C. The Porod slopes $(=-D)$ are shown on the figure. The data indicate that $D=2.0\pm0.1$. This value is nearly independent of both the chemical conditions, which control branching, and the extent of reaction. No change in D is observed in the vicinity of the gel point $(\Delta=0)$.

Although Fig. 1 illustrates that the fractal structure of all three samples is similar, dilution studies show that the samples are topologically quite different. In the dilution studies, we measured the Guinier radius, R_G, from the initial curvature of the scattering curves. In dilute solution, R_G is the radius of gyration, R_g, of the clusters. In more concentrated solutions, R_G is not well defined but is a correlation range which decreases as clusters overlap or interact.[10]

Figures 2 and 3 show the effect of dilution on R_G for B2 and A2. In most cases, the samples were diluted 10:1. Near the gel point, however, dilutions of 20 to 1 and 50 to 1 were also studied to assure that the samples were in the dilute limit. Data for A3 are not shown but the results are intermediate between B2 which showed no change in R_G on dilution and A2 which showed considerable change.

The fact that R_G is independent of concentration for B2, is consistent with relatively compact

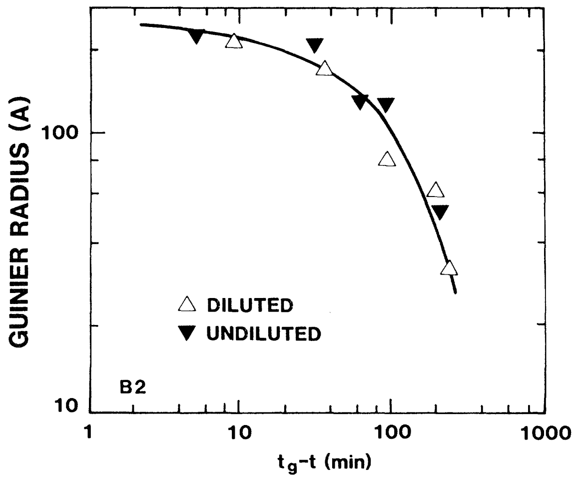

FIG. 2. Time and concentration dependence of the Guinier radius for B2. The data are characteristic of heavily branched clusters which do not interpenetrate. Porod slopes are unchanged by dilution.

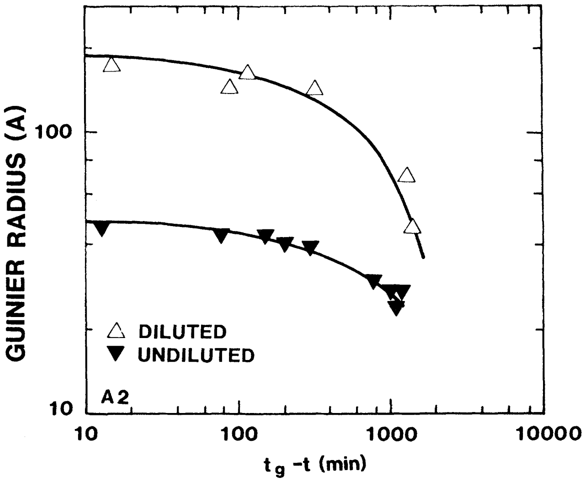

FIG. 3. Time and concentration dependence of the Guinier radius for A2. The data are characteristic of weakly branched chains which disentangle on dilution. The Porod region is limited for the undiluted system, but it appears that D is unchanged on dilution.

branched clusters which scatter independently right up to the gel point. In the case of A2, however, R_G is strongly dependent on concentration showing that the macromolecules strongly interact soon after condensation begins. This behavior is consistent with weakly branched chains which disentangle on dilution. The conclusion of the dilution studies is consistent with the chemistry described above. That is, branching is favored at high water ratio and under base-catalyzed conditions.

We draw three conclusions from this study. The first conclusion is that we have, in fact, generated fractal clusters. Fractal structures as opposed to dense colloids are unusual in the silica system. The observation of fractals here suggests that structures of low D are the key to the production of quality films via the sol-gel glass process. Empirically derived sol-gel procedures are explained by this observation. Techniques such as the two-stage hydrolysis and the use of mild catalytic conditions with limited water preclude colloid formation.

The second conclusion is that D is independent of the degree of branching. This result is consistent with the renormalization-group calculations of Family.[11] As long as K^{-1} is much larger than the distance between branch points, asymptotic exponents are observed regardless of the short-range chemical details.[11] Other interpretations are possible, however, because solvent quality may be different in acidic versus basic conditions.

Finally, although it is impossible to establish a definitive cluster geometry or a growth model from the measured fractal dimension, we suggest that the observation $D=2$ is due to structures called lattice animals.[12] This conclusion is reached by elimination of competing structures (linear chains and percolation clusters) which also give $D=2$.

Linear chains are not a viable structure because these systems form brittle gels which are characteristic of highly crosslinked polymers. Percolation clusters, however, are possible. For percolation the effective fractal dimension, D_{eff}, taken from the Porod slope, is not the D of an individual cluster ($D=2.5$ for percolation) but rather reflects an averaging over the power-law distribution of cluster sizes[13,14] with the result $D_{\mathrm{eff}}=2$. Although percolation cannot be excluded, we consider this model unlikely since the measured Porod slopes are unchanged during the polymerization even beyond the gel point. In the late stages of polymerization, deviations from a power-law cluster size distribution are expected as a result of exhaustion of the monomer.

Lattice animals are the randomly branched analogs of self-avoiding linear chains.[15] These structures give $D=2$ consistent with our observations.[10] Lattice animals are essentially percolation clusters whose distribution function is not weighted by the conditional probability that surface sites be unoccupied.[2] For polymerization in solution, this lack of surface sensitivity is reasonable since the clusters are mobile. At the very least, the coincidence of our observations with that expected for lattice animals is enticing and could have deeper meaning.

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