

Importance of Cyclization during the Condensation of Hydrolyzed Alkoxysilanes

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In the majority of papers addressing the hydrolytic polycondensation of alkoxysilanes (e.g., refs 1–8), the authors neglect cyclization reactions. However, there is substantial evidence from vibrational^{9,10} and nuclear magnetic resonance (NMR)^{6,11–13} spectroscopy for three- and four-silicon cycles in siloxane polycondensation products (and there may well be larger cycles). There is also reason to believe that polycyclic structures (e.g., cages) exist.

The neglect of cyclization allows the use of classical polycondensation models (e.g., Flory–Stockmayer random branching theory¹⁴). Such models frequently work well for organic systems, particularly when the monomer is large compared to the smallest unstrained (i.e., easiest to form) cycle from the polymer backbone and when that backbone is stiff.¹⁵ However, silanes are small enough and siloxane bonds are flexible enough that small cycles form easily during ordinary alkoxysilane polycondensation.

We^{5,16} and others^{17–19} have discussed the need to account for cyclization in order to predict the gelation behavior of multifunctional silanes. The gelation conversion of hydrolyzed tetraethoxysilane (TEOS) is much higher than site-level models (where the system's evolution is approximated by reactions between independent sites; Flory–Stockmayer theory is the simplest of these

models) can predict. Despite this, many investigators have fit low-conversion site distributions using site-level models with first-shell (i.e., nearest neighbor) substitution effects (FSSE) alone, neglecting cyclization.^{8,20} This may seem puzzling, but it should be noted that these fits are obtained either by (1) using incorrect peak assignments (i.e., mistaking cyclic X_2 sites for X_1 sites, where X_i denotes a silicon site with i siloxane bonds attached) or (2) making the assignments correctly but lumping sites of the same connectivity (i.e., counting cyclic and noncyclic X_2 as kinetically indistinguishable).

With either approach, though, the fits fail after sufficient conversion that substantial branching is present.²¹ For instance, Vainrub et al.⁸ were able to fit ²⁹Si NMR transients up to gelation only by introducing an arbitrary time-dependent multiplier to the rate coefficients. This function may mimic the effects of polycondensation nonidealities but has no deliberate physical significance.

In this paper we examine whether the set of rate constants—particularly, the FSSE pattern—suggested by noncyclization models is correct. We do this by treating one set of experiments with two model, one accounting for cyclization and the other neglecting it. Figure 1 illustrates the full model appropriate for early-conversion, homogeneous alkoxysilane polycondensation. It has three parts.

First, hydrolysis and reesterification reactions are represented in the upper left corner. Often (especially for alkyl-substituted systems), the time scale for these reactions is so much shorter than that of condensation that these reactions are able to reach pseudoequilibrium.^{22,23} In those cases, hydrolysis is modeled with algebraic equations and has little impact on the structure of the oligomers formed.^{21,24}

Second, bimolecular site-level condensation reactions are represented in the upper right corner of Figure 1. A FSSE is allowed by defining different rate coefficients for reactions between differently connected sites. This is equivalent to the approach of Kay and Assink,³ when hydrolysis pseudoequilibrium is operative.²¹

Third, cyclization is treated by the “quasimolecular scheme” represented at the bottom of Figure 1. The dark arrows represent specific reactions for conversion between oligomers. One need only write expressions for the specific paths by which these species are created. These oligomers are consumed by reaction with any other site in the reaction mixture (the open-ended

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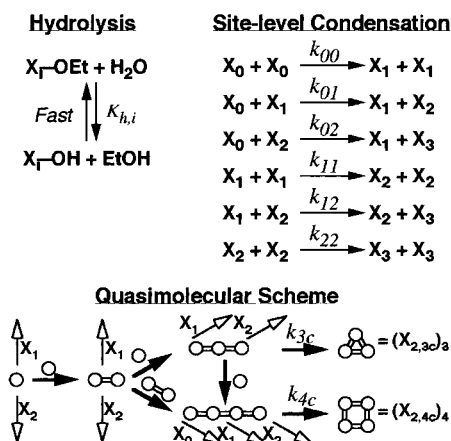


Figure 1. Scheme for ethoxysilane hydrolytic polycondensation. Hydrolysis (upper left corner) and its reverse occur quickly enough to reach pseudoequilibrium. Bimolecular condensation reactions between each pair of sites (upper right corner) X_i and X_j (subscript denotes degree of connectivity) allows for FSSE. The set of quasimolecular reactions at the bottom of the figure (which occur in parallel with the bimolecular reactions) account for three- and four-silicon ring formation.

arrows). Three- and four-silicon cycles (the species detectable by ^{29}Si NMR) form by unimolecular reactions (for details on the set of differential equations required, see Rankin et al.²⁵). The fate of the rings in Figure 1 is left in question for the moment. These reactions are sufficient to model condensation before there is substantial branching. (Below, though, we will discuss cyclization in branched systems.)

Previously, we used a site model without cyclization (identical to the model in Figure 1 without the cyclization reactions: $k_{3c} = k_{4c} = 0$) to fit data for ethyl-substituted ethoxysilane polycondensation.²¹ More recently, we used the full model to fit data for methyl-substituted ethoxysilane polycondensation.²⁵ To see the importance of cyclization, we now compare the results of fitting the data reported in each of those references with both models. Since the model with cyclization is only strictly applicable until branching is observed, data beyond such times are not considered yet.

The fits of both models to the experimental data shown in Figure 2 are reasonable (with the obvious and important exception that the model without cyclization cannot fit the individual cyclic species concentrations). The new fits are consistent with the old data: the site model fits the overall site concentrations of the methylethoxysilane systems and the quasimolecular model fits the detailed concentrations of the ethylethoxysilane systems (with a marginally improved match to the experimental data).

Table 1 lists the sets of rate coefficients providing the best fits in Figure 2, along with error estimates (using standard techniques of error analysis for nonlinear least-squares fitting). The coefficients reported are water-producing condensation rate coefficients. In determining these numbers, we assumed that condensation proceeds primarily by a water-producing route.²⁴ In all cases, cyclization does not alter our estimate of k_{00} . This is not surprising, since the monomer is not

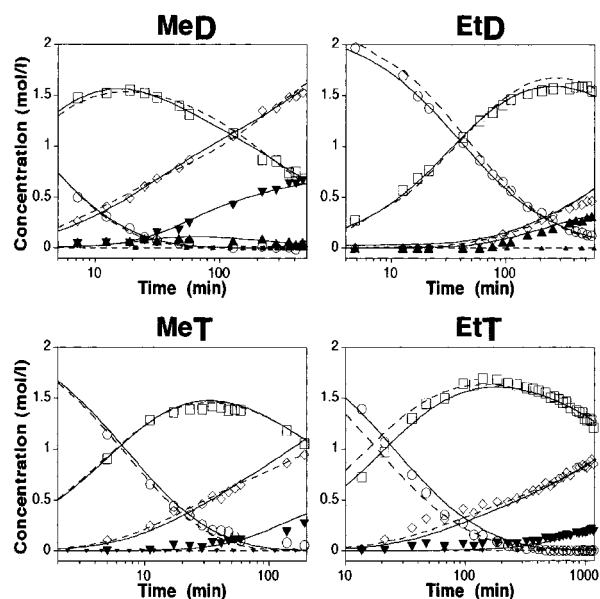


Figure 2. Least-squares fits of numerical solution of the model from Figure 1 with (solid lines) and without (dashed lines) cyclization to the indicated data. Points represent lumped (over all degrees of hydrolysis) concentration data from ^{29}Si NMR spectra. Monomers for the experiments are dimethyldiethoxysilane²⁵ (MeD), methyltriethoxysilane²⁵ (MeT), diethyldiethoxysilane²¹ (EtD), and ethyltriethoxysilane²¹ (EtT). Symbols represent X_0 (\circ), X_1 (\square), X_2 (\diamond), $X_{2,3c}$ (\blacktriangle), and $X_{2,4c}$ (\blacktriangledown).

directly involved in cyclization. However, reactions of chain ends (X_1) clearly are affected by cyclization reactions, as reflected in the coefficients in Table 1.

To clarify this effect, Figure 3 shows a comparison of the FSSE (as measured by k_{01}/k_{00} and k_{11}/k_{00}) estimated from models with and without cyclization. When we account for cyclization, these ratios are significantly smaller than when we do not; i.e., it becomes clear that the negative substitution effect for bimolecular reactions is more severe than previously thought. Also, accounting for cyclization shows a different trend in FSSE as organic groups are added. For instance, k_{01}/k_{00} with the noncyclization model passes through a maximum as methyl groups are added. Such a trend is difficult to rationalize with expected inductive effects. However, when we account for cyclization, k_{01}/k_{00} decreases monotonically. We cannot use the FSSE-only model as an approximation for the full model, even early in reaction—the parameters and trends are not similar to the true values.

Why does the neglect of cyclization lead one to underestimate the severity of the negative FSSE? Primarily because cyclization reactions are very fast compared to ordinary bimolecular condensation. Cyclization occurs between two end groups (X_1 sites), so if the model only accounts for bimolecular consumption of those sites, the rate coefficient appears to be too large. The high rate of cyclization and the severity of the negative FSSE may explain (1) why conversion rises quickly but suddenly slows its increase (once many cycles have formed) for tetrafunctional systems¹⁶ and (2) why an arbitrary time function would be required to fit transient connectivity distribution data⁸ (this function must compensate for the effects of cyclization).

Clearly, if one wants a predictive, quantitative model for alkoxy silane polycondensation, one must include

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Table 1. Rate Coefficients^a Found by Fitting Using a Model with or without Cyclization

sample	cyclization?	$k_{w(0,0)}$, L (mol SiOH) ⁻¹ h ⁻¹	$k_{w(0,1)}$, L (mol SiOH) ⁻¹ h ⁻¹	$k_{w(1,1)}$, L (mol SiOH) ⁻¹ h ⁻¹	$k_{w(3c)}$, h ⁻¹	$k_{w(4c)}$, h ⁻¹
MeD ^d	y	4.4 ± 3%	1.9 ± 4%	0.21 ± 3%	1.3 ± 23%	4.3 ± 6%
MeD	n	4.3 ± 4%	2.6 ± 5%	0.29 ± 3%	0 ^c	0 ^c
EtD	y	0.18 ± 5%	0.013 ± 6%	0.010 ± 8%	2.6 ± 56%	<i>b</i>
EtD ^e	n	0.15 ± 7%	0.032 ± 7%	0.012 ± 8%	0 ^c	0 ^c
MeT ^d	y	1.4 ± 3%	0.52 ± 5%	0.036 ± 12%	<i>b</i>	1.4 ± 12%
MeT	n	1.5 ± 3%	0.62 ± 4%	0.044 ± 4%	0 ^c	0 ^c
EtT	y	0.42 ± 2%	0.090 ± 4%	0.0045 ± 5%	<i>b</i>	0.031 ± 4%
EtT ^e	n	0.43 ± 4%	0.10 ± 5%	0.0056 ± 10%	0 ^c	0 ^c

^a The coefficients are averaged with respect to the hydrolysis state of each system (cf. ref 25). Figure 2 presents a comparison between fit curves and experiment. ^b Not measured. ^c Fixed a priori. ^d Rate coefficients from ref 25. ^e Rate coefficients from ref 21.

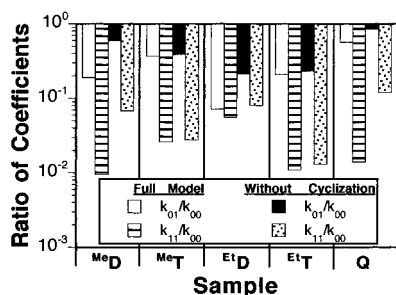


Figure 3. Ratios of rate coefficients (see Figure 1 for definitions) for indicated models. Both models feature hydrolysis pseudoequilibrium and FSSE, but only the full model also allows for cyclization. Q data are for the tetraethoxysilane system.²¹

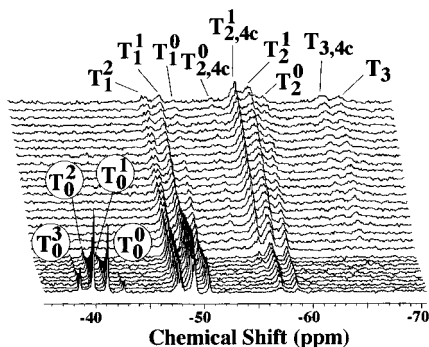


Figure 4. ²⁹Si NMR spectra of the MeT system ([Si] = 2.0 M; [H₂O]₀ = 4.0 M; [HCl] = 0.002 M; 1 wt % Cr(acac)₃ added to solvent ethanol). Notation is as in Figure 1, with added details: “T” denotes a trifunctional site, a superscript denotes the hydrolysis degree of the site and “4c” in the subscript indicates four-silicon cycle membership. Spectra were collected with a VXR-500 spectrometer with a broadband probe, using a 10 s delay between 60° pulses. The first spectrum was collected 5 min after mixing. Six minutes elapsed between the first nine spectra, and 32 transients were collected for each. One hour elapsed between the subsequent spectra and 72 transients were collected for each. All assignments match the literature^{13,25,30} with the exception of the distinction between T₃ and T_{3,4c}. This assignment is made by analogy with the separation between peaks from sites in and out of four-silicon cycles in di-,³¹ tri-,¹³ and tetrafunctional¹² systems.

cyclization reactions. As we have noted elsewhere,²⁵ the cyclization rate coefficients are so high in ethoxysilane systems that cyclization can never be neglected, even for polycondensation with continuous solvent removal!

Cyclization modeling can be challenging, though. We have been careful to note that the model in Figure 1 is complete only when little branching is observed (i.e., at low conversion). Is it sufficient at higher conversions to model cyclization simply by allowing the cycles

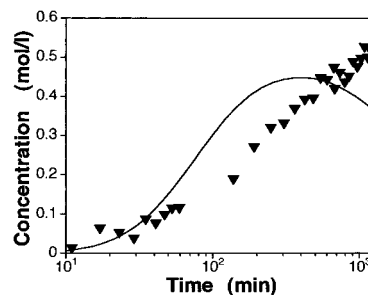
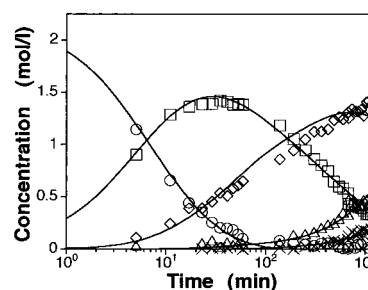
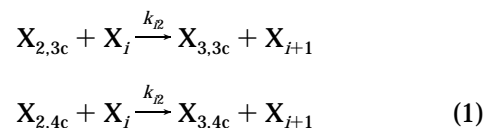


Figure 5. Best fit to the integrated MeT ²⁹Si NMR data (Figure 4) of the full quasimolecular model (Figure 1) with further condensation of cycles by eq 1. Points represent data, and lines are the calculated best fits. Symbols are as in Figure 2, with the addition of X₃ (Δ) and X_{3,4c} (×). The X_{2,4c} data and fit line are shown in the separate, lower plot for clarity.

formed in the scheme of Figure 1 to participate in branching by reactions such as eq 1? This is straightforward to do, but it implies stringent structural assumptions, namely, no back-biting or chain-pinching reactions, no cyclization within oligomers larger than tetramers, and polycyclic structure formation only from preexisting rings. We suspect that these assumptions should not be made.



To confirm our suspicion, we collected the ²⁹Si NMR spectra of hydrolyzed methyltriethoxysilane shown in Figure 4. Figure 5 shows the results of attempts to fit the integrated NMR data from Figure 4 with the model of Figure 1 and with the continued reaction of cycles by eq 1 (using numerical integration and nonlinear optimization routines from the IMSL Fortran library). The fit is acceptable for some sites but not for [T_{2,4c}] (doubly connected sites in four-silicon cycles). The predicted concentration peaks prematurely.²⁶ This failure is meaningful because it represents the first time this

modeling approach has been pushed beyond its ability to match experimental observations. The fitting subroutine gives rate coefficients which overestimate the rate of $T_{2,4c}$ formation. There is no other way to match the concentration of $T_{3,4c}$ sites when they are allowed to form only by eq 1. This suggests that there must be alternative pathways to form $T_{3,4c}$, namely, cyclization reactions between more highly connected sites than chain ends (e.g., back-biting of a linear pentamer to give a cyclic tetramer with one site protruding).

In terms of the large-scale structural features (molecular weight and gel point), we have already shown that, using parameters similar to experimentally measured ones and the model from Figure 1 and eq 1, gelation conversions approaching only about 53% can be predicted for tetrafunctional monomers,²⁷ well below the experimentally observed 82% for tetraethoxysilane.¹⁶ This supports the hypothesis that alternative pathways to cycle formation must be considered. To allow these pathways requires more detailed models and different techniques than those discussed here (Monte Carlo simulation²⁸ is most promising), and we have begun developing such a model.²⁹

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To conclude, we find cyclization to be an essential feature of ethoxysilane polycondensation models, even early in reaction. Models without cyclization may be capable of fitting lumped connectivity distribution data over a limited conversion range, but the parameters found may be misleading. The model in Figure 1 can be used instead to assess the importance of cyclization in systems without branched sites. Even more complex models allowing polycyclic species will be needed to quantitatively model cyclization in nonlinear alkoxy-polysiloxane systems.

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