Polymerization Kinetics of Multi-functional Silica Precursor Studied Using a Novel Monte Carlo Simulation Technique

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S1 Estimation of reaction cut-off

We perform an elementary calculation to estimate the reaction cut-off. We have taken two fully relaxed $Si(OH)_4$ molecules such that the distance between two vertices of the same tetrahedron $(|\mathbf{r}_m^i - \mathbf{r}_n^i|, m = 1 - 4, n = m + 1)$ is equal to equilibrium bond length, r_0 . The initial distance between reactive OH of two respective silicic acid $(|\mathbf{r}_{OH}^i - \mathbf{r}_{OH}^j|)$ is recorded, and the condensation reaction is preformed by replacing the two *OH* groups with a bridging oxygen (-O-) at their geometric center. The new configuration creates distortion in both tetrahedrons, i.e., change in $|\mathbf{r}_m^i - \mathbf{r}_n^i|$ values. The change in energy $\Delta U = U_{new} - U_{old}$ is evaluated for these old and new configurations (U_{old} and U_{new} , respectively). The similar procedure is repeated for various values of $|\mathbf{r}_{OH}^i - \mathbf{r}_{OH}^j|$, and observed trend for ΔU is shown in Fig. S1. The values of ΔU for non-relaxed silica tetrahedrons. Based on these calculations, we find that the Boltzmann factor, $e^{-\beta\Delta U}$ ($\beta = 1/k_BT$, k_B - Boltzmann constant, T - temperature), and hence reaction probability, is very low even for the case when two *OH* groups are separated by 3 Å. However, at the concentrations we have taken, even single OH group is not present within the vicinity of 3 Å region. Therefore, we have used 6 Å as our reaction cut-off.



Figure S1: Variation in the change in energy ($\Delta U = U_{new} - U_{old}$) of two $Si(OH)_4$ molecules when the reaction is performed, with respect to the initial distance between reacting OH groups, $|\mathbf{r}_{OH}^i - \mathbf{r}_{OH}^i|$. Inset illustrates the configuration of silica tetrahedron before and after the condensation reaction is performed for $|\mathbf{r}_{OH}^i - \mathbf{r}_{OH}^i| = 3$ Å. The configurational energy (U_{old} or U_{new}) is evaluated using the formula given in inset. Distances are in Å, the spring constants are $K_B = 425.5$ kJ mol⁻¹Å⁻² and $K_A = 113.37$ kJ mol⁻¹ and the equilibrium values are $r_0 = 1.6$ Å and $\theta_0 = 155$ degrees.

S2 Details of relaxation scheme performed during condensation reaction

During the condensation reaction move, the two *OH* groups are replaced by a -O- at their geometric center, which creates a significant distortion in the cluster. At any instance, the probability of accepting the reaction (P_{cond}) move depends on the change in the energy (ΔU) of the cluster and concentration of the species present in the system as,

$$P_{cond} = K_{eq} \quad \frac{N_{OH} \left(N_{OH} - 1\right)}{\left(N_{BO} + 1\right) \left(N_{H_2O} + 1\right)} \quad e^{\frac{-\Delta U}{k_B T}} \quad (correction \ factors), \tag{S1}$$

where, K_{eq} is equilibrium constant, and N_{OH} , N_{BO} and N_{H_2O} are the instantaneous number of OH, -Oand water species, respectively. The concentration of the species changes according to the degree of condensation (DOC = $2N_{BO} / \sum_{i=1}^{4} N_{f_i} \times i_{f_i}$, where N_{f_i} is the number of f_i functional silica precursors) of the system. So for a given DOC, the ΔU that would give rise to the probability of acceptance can be estimated from the above equation. We have estimated the ΔU for f_4 silica precursor system as shown in Fig. S2. Based on ΔU there are three zones where the condensation reaction will i) never be accepted (i.e., $P_{cond} \le 0.01$) ii) may be accepted ($0.01 \le P_{cond} \le 1$) and iii) always accepted ($P_{cond} \ge 1$). During the condensation MC moves, when the ΔU of the formed cluster has a probability of acceptance less than 0.01 then we invoke cluster relaxation scheme. For example, a system represented by point A in Fig. S2 has a given ΔU after replacing the OH group with bridging oxygen at specified DOC. When the chosen cluster is relaxed, the ΔU will decrease, represented by the straight line in the downward direction from point A. In principle, the cluster can be relaxed such that the final ΔU always gives rise to acceptance of condensation reaction (i.e., $P_{cond} \ge 1$), as represented by point C in Fig. S2. In actuality, reactions due to collisions events are stochastic in nature, however, this scheme of completely relaxing the cluster would lead to an unrealistic scenario where the condensation reaction is always accepted. This will introduce a bias in the condensation reaction probability. To maintain stochasticity in condensation reaction scheme, we randomly decide the condensation acceptance probability between $(P_{cond} =) 0.01 - 1$, based on which the target ΔU^t is estimated, as represented by point B in Fig. S2. The cluster is relaxed (from point A) by performing the displacement of all vertices of the cluster and if ΔU^t is reached than cluster relaxation step is stopped. In reality, this relaxation process would have occurred in considerable time (or MC steps), whereas we have performed this reaction in 1 MC step (condensation move) alone. Hence, we estimate the number of MC steps, $N_{MC,relax}$, that would be required to perform this relaxation move based on the net displacement and diffusivity of the vertices as,

$$N_{MC,relax} = \frac{\sum_{i=1}^{N_{ver}} |\mathbf{r}_i(a) - \mathbf{r}_i(b)|^2}{D_{ver}},$$
(S2)



Figure S2: The change in the system energy, ΔU required for probability of condensation, $P_{cond} = 0.01$ and 1 at various degree of condensation (DOC). The ΔU is calculated using Eq. S1 for a system of 1000 f_4 silica precursor having 6000 water molecules and temperature of 300 K using equilibrium constant of 500. The point A, B, and C represent system having ΔU at given DOC which has $P_{cond} \leq 0.01, 0.01 - 1$ and >1. The vertical line A to B represents the evolution of system due to cluster relaxation move.

where, \mathbf{r}_i is the coordinates of vertex before (b), and after (a) cluster relaxation, N_{ver} is the total number of vertices of the cluster and D_{ver} is vertex diffusivity. In an all-atom MD simulation, it was observed that diffusivity of silica precursor atoms decreases by around three (3) orders of magnitude due to polymerization.[1] Inspired by the MD results, in our simulation, we have also considered vertex diffusivity to be 3 orders of magnitude smaller than monomer diffusivity (D_{mono}) (i.e., $D_{ver} = 10^{-3} D_{mono}$). This $N_{MC,relax}$ is used to correct the probability of condensation (Eq. S1) due to relaxation move performed by multiplying factor of $1/N_{MC,relax}$.

S3 Sensitivity analysis of developed reaction algorithm

We have performed a comprehensive check of the developed algorithm by performing the sensitivity analysis of simulations parameters. We discuss the effect of each of these parameters in details below.



Figure S3: Evolution of degree of condensation (DOC) of various system having different probabilities to select second *OH* group within the reaction cut-off ($P_{rxn,vol}$). No significant difference is observed suggesting that the algorithm is not sensitive to the probability of selection.

S3.1 Effect of probability of reaction within cut-off region on polymerization kinetics

As discussed in the reaction scheme, we use the concept of reaction volume where higher preference (probability $P_{rxn,vol}$) is given to reactant present within the specified region as compared to others. We have performed a sensitivity analysis of this probability. We varied $P_{rxn,vol}$ in the range of 0.5 to 0.9, covering all possible scenario (i.e., 0.5 have no preference for selection and 1 have all the preference within reaction cut-off). For clarity, we are showing the DOC profile of all the systems and observed that variation due to the difference in probability of selecting second *OH* is insignificant (Fig. S3). Based on this analysis, we used the probability of 0.8 to select second *OH* in our reaction algorithm.

S3.2 Effect of number of cluster relaxation moves performed on polymerization kinetics

During the cluster relaxation process, the number of MC steps performed are crucial. For example, if the number of MC steps attempted during cluster relaxation steps are very low, then the transformation of the system from never accepted ($P_{cond} < 0.01$) region to may be accepted region ($0.01 \le P_{cond} \le 1$) will never occur (Fig. S2) and the simulation would require astronomically large computational time to observe the condensation reaction. Whereas, if the number of MC steps are too large than this transformation from point A to C of Fig. S2, will always occur and introduce a systematic bias in the condensation reaction. Hence, to introduce the stochastically and maintain uniformity across the cluster, we attempt 500 MC steps during cluster relaxation process. We performed the sensitivity test on the number of MC steps used during the relaxation process. We observed that the rate of evolution of silica species increases with increase in the number of relaxation MC steps used; however, the relative scale of all the simulations is same (Fig. S4), hence we decided to use 500 MC steps. The number of MC steps fixed at 500 is also helpful in cases when the cluster is compact, or system is at higher DOC, and the strain created in the cluster due to joining of two OH group is very high and requires an astronomically large number of relaxation steps. In such cases, the relaxation process will stop after the fixed number of relaxation steps, and the fate of reaction is decided based on the energy of (current and before reaction) system.



Figure S4: Evolution of mole fraction of Q_n species (silica monomer with *n* bridging oxygen) for system with (a) 500 (reference system), (b) 250, (c) 1000, and (d) 1500 MC cluster relaxation steps. Evolution is faster for a higher number of relaxation steps; however relative scale for the distribution of Q_n profiles for all the systems is similar.

S3.3 Effect of overall probabilities of various kinds of MC moves on polymerization kinetics

In our MC simulation, we have performed translational moves (for vertex, tetrahedron, and cluster), orientational moves (for tetrahedron and cluster) and reaction moves (condensation and hydrolysis). Every move is performed with pre-determined probabilities throughout the polymerization process. The pre-determined probabilities used in our simulations for the reference case (AR0) is listed in Table S1. We assumed that overall movements of the monomeric unit, i.e., tetrahedron, is important than the movement of individual vertices (or atoms) in the evolution of silica polymerization system. Hence based on this assumption, we decided the probabilities of AR0 system. In order to understand the effect of these probabilities on polymerization kinetics, we studied three other systems with a) equal probabilities of all non-reactive moves (AR1), b) higher probabilities of cluster moves as compared to tetrahedron move (AR2) and c) higher probability of reaction moves (AR3) as listed in Table S1. We find that qualitatively the kinetics of all the systems is similar, confirming that our simulations algorithm is robust with respect to probabilities of various moves. To make quantitative comparison, we compared the number of MC steps at which profile of Q_0 and Q_1 crosses for a given system with respect to reference system, i.e. $N_{MC,ratio} = N_{MC,Q_0=Q_1}(AR)/N_{MC,Q_0=Q_1}(AR0)$. We find that the $N_{MC,ratio}$ is around 1 for AR1 and AR2 system, indicating that not significant variation in the kinetics is observed with change in probabilities of non-reactive moves. It is understood that reaction kinetics would change only with attempting probabilities of reaction moves. Larger the reaction attempts faster would be the kinetics. Hence when the attempted probabilities of reaction was increased five times from 0.02 in AR0 to 0.1 in AR1, a similar magnitude of change of faster dynamics ($N_{MC,ratio} = 0.23 \sim 1/5$) is observed.

MC moves \ Systems		AR1	AR2	AR3
Vertex displacement		0.196	0.2	0.18
Tetrahedron displacement		0.196	0.1	0.18
Tetrahedron orientation		0.196	0.1	0.18
Cluster displacement		0.196	0.29	0.18
Cluster orientation		0.196	0.29	0.18
Reaction (condensation and hydrolysis)		0.02	0.02	0.10
$N_{MC,ratio} = \frac{\text{MC steps for crossing of } Q_0 \text{ and } Q_1}{\text{MC steps for crossing of } Q_0 \text{ and } Q_1 \text{ in AR0 system}}$	1.00	0.95	1.12	0.23

Table S1: Systems having different probabilities of various MC moves

* - Reference system



Figure S5: Profile of mole fraction Q_n species for various system (AR0-AR3) having different probabilities of various MC moves. Qualitatively, all the systems have similar polymerization kinetics.



Figure S6: Evolution of mole fraction of Q_n species with time for the system of 1000 to 20000 f_4 silica precursor. The excellent agreement of Q_n evolution for various system sizes confirms that the developed algorithm have no finite size effect on the polymerization process.

S3.4 Effect of system size on polymerization kinetics

To verify that the developed algorithm is finite size effect, we performed the simulation of 1000 to 20000 f_4 silica precursor. As the number of precursor molecules increases, the number of MC steps per cycle also increases. Hence, we normalized the number of MC step based on the system size, by taking the Q_0 and Q_1 crossing point as the common reference point and scale all the evolutions with respect to experimental time (i.e. time = 0.1 hr at mole fraction of $Q_0 = Q_1$) as shown in Figure S6. The trends of mole fractions of Q_n species for all systems overlap with each other, thereby confirming that the reaction algorithm is independent of system size.

S4 Figures for all *f*₃ systems



Figure S7: Evolution of shape factor of polymer in f_3 silica precursor system. The cluster evolves form linear polymer to ellipsoid shape cluster , which is closer to two dimensional (2D) ellipse.



Figure S8: Evolution of (1) average size of the cluster ($N_{cl,avg}$), (2) radius of gyration (R_g), (3) average ring size (H_{avg}), and (4) total number of rings (H_{total}) during polymerization of all f_3 silica precursor. The above evolution shows three stages of polymerization; oligomerization (0-76 hr), ring formation (76 - 1912 hr) and aging (> 1912 hr) for all f_3 silica system.



Figure S9: Occurrence of various kind of condensation and hydrolysis reactions during polymerization of all f_3 silica precursor system; (1.a) Ring formation, (2.a) oligomer - oligomer/polymer reaction, (3.a) polymer - polymer reactions, (#.b) is the backward of respective reactions due to hydrolysis. Also shown are the evolution of the (4) total number of oligomer (×10), (5) polymer, and (6) average polymer size.



Figure S10: Degree of condensation for linear and ring polymers (of size, N_{cl}) made of f_2 and f_4 precursors. The DOC of linear polymer for f_2 and f_4 precursor (DOC_{f2} = $\frac{N_{cl}-1}{N_{cl}}$, DOC_{f4} = $\frac{N_{cl}-1}{2 \times N_{cl}}$) increases asymptotically to 1 and 0.5, respectively. Whereas, ring polymers of f_2 and f_4 precursor have DOC equals to 1 and 0.5 for all polymer sizes.

References

[1] Bhattacharya, S. and Kieffer, J. Molecular dynamics simulation study of growth regimes during polycondensation of silicic acid from silica nanoparticles to porous gels. J. Phys. Chem. C, 112(6):1764-1771, 2008.