# *Comments*

## Comments on “Chitosan-Catalyzed Aggregation during the Biomimetic Synthesis of Silica Nanoparticles”

Chang and co-workers present a detailed study of the effects of chitosan on different stages of silica polymerization.[1] The precursor used was sodium silicate, and the reactions were carried out at pH 4−5.6. Extensive characterization of polymerization kinetics and the materials formed have been reported. The authors reach following main conclusions: (1) silica polymerization follows a fourth-order kinetics over a long period of time (up to 800 min), (2) chitosan does not affect silicic acid polymerization kinetics, and (3) chitosan mainly affects the aggregation of silica particles. We disagree with conclusions 1 and 2 drawn from the kinetics data presented and part of the materials characterization and present an alternative interpretation.

We find that the method for interpreting the kinetics data is inappropriate. It appears that the authors have used the “minimum $R^2$” for the linear fits as their only criterion. This is incorrect analysis especially for such a long period of silica polymerization because it is known that there exist different stages of polymerization that dominate over distinct time durations.[2−4] This has also been proved with extensive mathematical analysis of molybdosilicate data.[5−8] The plots provided by the authors in their Supporting Information, Figure S1a for example, quite clearly support our model that there are at least two distinctly different regimes of silica polymerization, which in addition is also supported by our data.[5−8] Furthermore, the authors do not comment on the physical significance of the so-called fourth-order kinetics, as the notion of fourth-order kinetics for silica polymerization is confusing. Does it means that over a wide range of time, only tetramers are being formed which is contradictory not only to the well-known literature[2,9] but also to their own data wherein they show the formation of particles (and not tetramers!)? Or does it mean that tetramers are the dominating reactive species? We also disagree with the authors that silicic acid species up to tetramers could be detected by their molybdosilicate method. They follow a previously reported method,[10] where the molybdosilicate complex is allowed to form for 10 min. According to Iler[2] and our experience, only monomers and dimers form a molybdosilicate complex in 10 min.

The authors add chitosan to the silicate solution after 10 min of condensation time. By this time, from our data,[6−8] the initial fast condensation stage, which is usually affected by the presence of additives, will be over. Thus, the addition of chitosan thereafter will not significantly affect the kinetics of silica polymerization. Hence, the conclusion drawn by the authors that chitosan does not affect silicic acid polymerization kinetics is unsupported.

Furthermore, the infrared spectra appear to be mislabeled—the chitosan−silica and silica being swapped. The spectrum labeled silica−chitosan has been analyzed as if it were that but is a typical spectrum of silica particles formed in the presence of water, and that labeled pure silica has many of the chitosan bands. It does not look as if the amounts used were the same, and if they were why should the Si—O intensity drop so sharply on addition of chitosan? The CH stretch region of the chitosan is very strange, and there are some negative peaks, which are unexplained. We are mostly concerned about the analysis of the peak at 950 $cm^{-1}$. The peak probably appears in two spectra, but it is not possible to tell which two from the figure; it is likely to either be C—OH or be Si—OH, depending upon in which two spectra it appears. The authors state that it is only present in the silica−chitosan spectrum and is Si—OH; this would suggest that the silica without chitosan is free from these groups, a very unlikely state for silica formed in water, particularly with the large O—H band that is present at about 3500 $cm^{-1}$. The authors suggest that the O−H band is due to the presence of $OH^-$, which is highly unlikely. The source of the band is more likely to be hydrogen bonded silanol groups and adsorbed water. The silica should be negatively charged at the pH used and so would not be likely to be associated with hydroxide. Their evidence for Si—O—N bonding in the spectra is questionable; peaks around 1640 $cm^{-1}$ are usually due to usually C═O or amide functionality, very likely in chitosan. The sharp band observed in the presence of silica (or in the pure silica spectrum) appears to be a subtraction artifact as is the bizarre shape of the CH stretch bands and the negative peaks, probably because of mismatched backgrounds. As the authors write, the interaction between the silica and the chitosan is likely to be ionic in nature so the presence of Si—O—N bonding would be surprising.

The atomic mass composition was assessed by measuring C, H, and N from combustion gases and assuming the rest was $SiO_2$. This is not a very good assumption as the massive O—H band in the infrared spectra indicate the presence of considerably more oxygen than would be predicted in this way. The hydrogen in the silica will not usually be measured correctly as some of it will not be released during heating (as a result of pore closure on heating); with the mixed samples

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it is also quite possible that some chitosan will be entrapped and not observed. The data are described as quantitatively showing that the particles are 10% chitosan; however, the values for C and H suggest closer to 20%. The error limits of 0.3 wt % are very high compared to the N concentration of 0.75 wt %, suggesting that the C and H data are more accurate, so we would like to know why the N concentration was used to estimate the chitosan concentration. We are unsure why this analytical method was used at all; the scanning electron microscope could have been used to take an energy-dispersive X-ray analysis, and although this is also inaccurate (and does not measure H), it can measure Si and O and measures solid samples.

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