Electronic Supplementary Information

Factors Affecting the Stability of Chitosan/Tripolyphosphate Micro- and Nanogels: Resolving the Opposing Findings

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A. pH Effects on Chitosan/TPP Binding. Fig. S1 compares the ITC data obtained by titrating 0.16 wt% TPP into 0.04 wt% 72% DD (M_v = 80 kDa) chitosan at pH 7.0 to that obtained at 4.0 (both with no NaCl). The continuous decrease in binding enthalpy at pH 7.0 indicated a weak “simple ion condensation-type” chitosan/TPP binding between chitosan and TPP, which was much weaker than the cooperative (ionic crosslinking) at pH 4.0.

![Fig. S1](image-url)  
**Fig. S1.** ITC data for the titration of 0.16 wt% TPP into 0.04 wt% chitosan (DD = 72%) solutions at (■) pH 7.0 and (●) pH 4.0. The solid curves are guides to the eye.
B. Supplementary Dissolution Stability Data. The dissolution stability of chitosan/TPP particles in pH 7.2 PBS was also characterized using higher molecular weight chitosan ($M_v = 260$ kDa) with a DD-value of 80%. The light scattering analysis in Fig. S2 revealed that, despite the much higher molecular weight, the particles rapidly dissolved upon their placement into PBS (even at the highest, $7.1 \times 10^{-2}$ wt% chitosan concentration, where the drop in scattering intensity corresponded to an $I/I_0$-value of around 0.1). After they dissolved, however, the chitosan molecules (which were insoluble in pH 7.2 PBS) precipitated again. This was similar to the behavior of particles formed from 80 kDa, 91% DD chitosan (see Fig. 5). The reprecipitation, however, occurred much more rapidly, with much of the increase in the light scattering intensity occurring within a minute of mixing (see inset in Fig. S2).

![Fig. S2](image-url)

**Fig. S2.** Derived light scattering intensity evolution upon placing chitosan/TPP particles into PBS (chitosan $M_v = 260$ kDa and DD = 80%). The shaded region marks the light scattering intensity prior to the mixing of the dispersion with PBS, while the inset captures the early stages of the reprecipitation process.