Supporting Information

Effect of pH on molecular structures and network of glycol chitosan

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[**Content**]

I. Detail of energy profiles

We analyze the energy profiles of glycol chitosan hydrogel models at different protonation percentages. The Van der Waals energy (E_{vdw}) and the intermolecular electrostatic energy (E_{coul}) of glycol chitosan chains are shown in Figure S1. Figure S1A shows the Van der Waals energy and the results indicate that the aggregation of glycol chitosan chains could lower the Van der Waals energy by about 2000KJ/mol. Therefore, when the protonation percentage is low, the polymer chains tend to aggregate together to lower the Van der Waals energy.

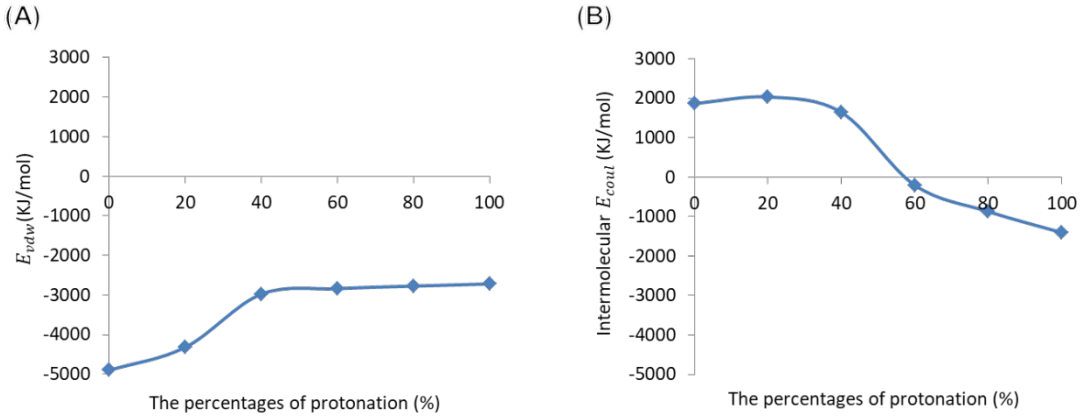

Figure S1. (A) The Van der Waals energy of glycol chitosan chains versus the protonation percentages. (B) The intermolecular electrostatic energy of glycol chitosan versus the protonation percentages.

Figure S1B shows the intermolecular electrostatic energy. When the protonation percentage is below 40%, there is no significant change on the intermolecular electrostatic energy while when the protonation percentage is larger than 40%, the polymer chains tend to disperse and could lower the intermolecular electrostatic energy by about 3300 KJ/mol. In summary, the Van der Waals interaction is dominant at low

protonation percentages while the intermolecular electrostatic energy is dominant at higher protonation percentages.

To estimate the dependence of conformational entropy of glycol chitosan chains on the protonation percentage, we firstly calculate the end to end distance of the five glycol chitosan chains in the hydrogel models. The conformational entropy of glycol chitosan chains is then calculated with the equation of conformational entropy of an ideal chain[1] as shown in Eq 1, where k is Boltzmann constant, $\vec{R}$ is the end to end distance of each glycol chitosan chain, N is the number of monomers of each glycol chitosan chain and b is the monomer size of glycol chitosan monomer.

$$\mathrm{S}(N,\overrightarrow{R}) = -\frac{3}{2}k\frac{\vec{R}^2}{Nb^2} + \mathrm{S}(N,0) \quad (1)$$

The monomer size of glycol chitosan monomer b is ~5.5 Å based on our simulation results. The results are shown in Figure S2. Figure S2A shows the results of end to end distance at different protonation percentage. It shows that the end to end distance is not affected by the protonation percentages. Figure S2B shows the conformational entropy at different protonation percentages. These results suggest that the conformational entropy does not play a significant role in the glycol chitosan hydrogel for our simulations because the molecular structure of each glycol chitosan chain remains similar at different protonation percentage. The major differences at different protonation percentage are the intra- and inter- molecular interactions including the

aggregation behavior and the hydrogen bond conformations.

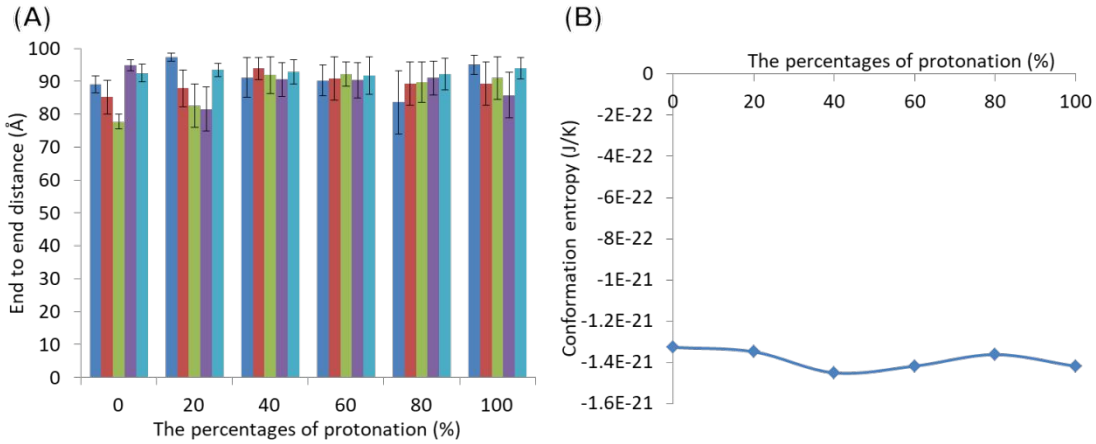

Figure S2. (A) The end to end distance of each of five glycol chitosan chains at different protonation percentages (B) The conformational entropy of glycol chitosan chains at different protonation percentages.

Reference

1. Rubinstein, M.; Colby, R. H. Polymer Physics; Oxford University Press: Oxford, U.K., **2003**.