

## STRUCTURES OF POLYSACCHARIDE POLYELECTROLYTE COMPLEXES

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Complexation between oppositely charged macromolecules driven by electrostatic interactions are important for numerous biological processes, e.g. organization of DNA to packed chromosomes or interactions between enzymes and charged ligands. Linear, negatively charged biopolymers, such as DNA, can undergo a transition from extended to a compact state driven by intersegment attraction mediated by oppositely charged ions. The formation of the polyanion-polycation (polyelectrolyte) complexes is mainly driven by an electrostatic mechanism, where the exchange reaction of counter-ions with different valence is important. Here, the compacted structures of semiflexible anionic (alginate, acetan, xanthan) and cationic (chitosan) polysaccharides were studied. The analysis of the atomic force (AFM) topographs included application of quantitative image analysis. The observed polyelectrolyte complexes were identified and a shape factor was calculated for each of these structures to be used as a basis for constructing ensembles of morphologically linear, toroidal and globular species. Subsequent quantitative analysis of dimensions was obtained from each of these ensembles. The toroidal morphology was observed as a small fraction of the compacted polyanions with chitosan when the persistence length,  $L_p$ , of 30 nm (acetan) was reached. The toroidal family constituted a larger fraction of the complexed structures formed between DNA,  $L_p = 50$  nm, and xanthan,  $L_p = 120$  nm and the given chitosan at room temperature than observed for the more flexible polyanions. Chitosan induced complexation of high molecular weight xanthan did not reveal a significant fraction of the rodlike morphology. The average height of the compacted xanthan toroids was observed to  $\sim 2$  nm. Reducing the degree of polymerization of xanthan yielded a decrease in the fraction of toroids. Racquet type morphologies were identified as kinetically trapped states occurring on the folding path towards the energetically stable state of the toroids. Annealing at elevated temperature yielded a shift of the distribution of xanthan-chitosan morphologies towards this stable state. The mean height of the toroids, extracted from the ensembles, increased upon heating, with a selective increase in the height range above 2 nm. The high molecular weight fraction of xanthan is suggested to make up the metastable structures formed at room temperature. The compaction of xanthan by chitosan captures the system at various stages in the folding towards a low-energy state, and thus allows experimental analyses of these intermediates and their evolution, and may therefore serve as a model system for condensation of semiflexible polymers in general.