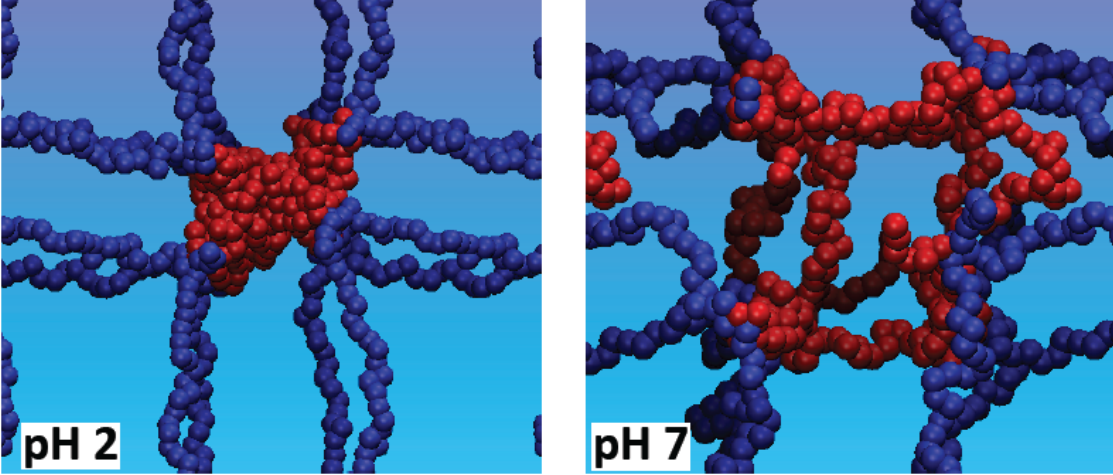


pH-Controlled Nano-Aggregation in Amphiphilic Polymer Conetworks

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We theoretically studied domain formation and control in pH-responsive amphiphilic polymer conetworks. Two different molecular architectures are considered, depending on whether the pH-sensitive motif is borne by the hydrophobic or the hydrophilic monomer.

- When the hydrophobic polymer contains acidic groups, such chains form nanometric aggregates at acidic conditions, but they are found in a swollen state at alkaline pH. At intermediate pH, the nano-aggregation behavior of the hydrophobic polymer depends critically on the environment salt concentration. Moreover, our results indicate the presence of microphase separation into domains of swollen and aggregated hydrophobic chains.
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- If the hydrophilic polymer is the ionizable component of the network, the nano-aggregation of hydrophobic monomers is weakly dependent on the pH and salt concentration, and except at very low volume fraction, the aggregate is the most probable conformation of the network in all the range of pH and salt concentration studied.
 - The two different hydrogels display quantitatively similar swelling transition and apparent pK_a , but at the nanoscale their behavior is qualitatively different.
 - The spatial distribution of electric charge on the network as well as the local density of the different chemical species within the hydrogel can be controlled, as a function of pH and salt concentration, by the molecular architecture of the polymer network.
 - These findings have relevance for applications in biomaterials and nanotechnology; in particular, in the design of oral delivery devices for the administration of hydrophobic drugs.