

Self-Organized Polyelectrolyte End-Grafted Layers Under Nanoconfinement

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Layers of end-grafted weak polyelectrolytes in poor solvent self-organize into a rich variety of structures due to the subtle competition among hydrophobic, electrostatic and steric interactions and the chemical acid–based equilibria of the weak polyelectrolyte. In this work, a molecular theory has been used to systematically study how nanoconfinement modulates the competition among these interactions and, therefore, dictates the morphology of the self-assembled layer. Two different types of confinement were considered and compared: (i) soft lateral confinement due to increasing surface coverage in a planar polyelectrolyte brush and (ii) hard vertical confinement due to the interaction of a planar polyelectrolyte brush with an opposing surface, as typically found in AFM-colloidal-tip and surface-force-apparatus experiments. It is shown that increasing the surface coverage (soft lateral confinement) or compressing the layer with an opposing wall (hard vertical confinement) have a similar qualitative effect on the morphology of the

system: both types of nanoconfinement increase the stability of morphologies that extend in one or two dimensions (such as the homogeneous brush, holes and stripes) over nonextended aggregates (such as hemispherical micelles).

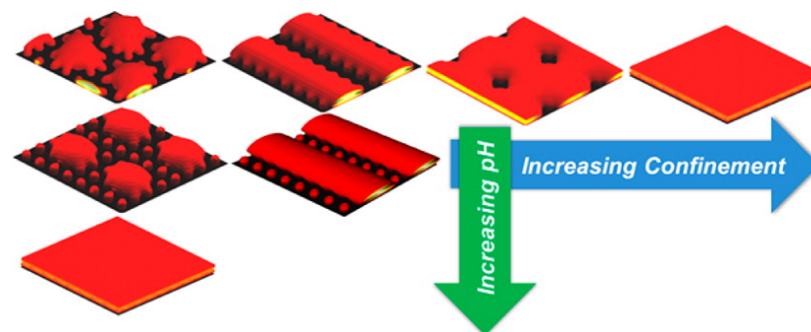


Fig. Morphologies predicted by the molecular theory for the one-wall system shown as isodensity surfaces. These morphologies are HB (homogeneous brush), H (holes), M (micelles), S (stripes), M+NA (micelles coexisting with nonaggregated chains) and S+NA (stripes coexisting with nonaggregated chains).

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