Morphology and Dynamics of Polyelectrolyte Brush Condensates in Trivalent Counterion Solution

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Recent theories, experiments and simulations have shown that trivalent counterions induce collapse of flexible polyelectrolyte brushes, over a certain range of grafting density, polymer size, and ion concentration, into octopus-like surface micelles; however, if individual chains are rigid enough, the ion-mediated local nematic ordering assembles the brush chains into fractal-like dendritic condensates whose relaxation dynamics is significantly slower than that in the surface micelles. Notably, the trivalent ions condensed in the dendritic condensates are highly mobile displaying quasi-one-dimensional diffusion in parallel along the dendritic branches. Interplay between counterion-mediated interaction and stiffness inherent to polymer chain brings substantial complexity to the morphology and dynamics of polyelectrolyte brush condensates. Our findings in this study are potentially of great significance to understanding the response of cellular organization such as chromosomes and charged polysaccharides on membranes to the change in ionic environment.