Complexation of $\text{AB}^+$, $\text{AB}^+\text{C}$, $\text{ACB}^+$, and $\text{A(B}^+\text{-stat-C)}$ block copolymer micelles with poly(styrene sulfonate) as models for tunable gene delivery vectors

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— We investigate the complexation of poly(styrene sulfonate) with micelles with mixed cationic/hydrophilic coronas as models for tunable gene delivery vectors. The micelles are self-assembled from $\text{AB}^+$, $\text{AB}^+\text{C}$, $\text{ACB}^+$, and $\text{A(B}^+\text{-stat-C)}$ block polymer architectures, where the hydrophobic A blocks (poly(styrene)) form the micelle cores, and the cationic B blocks (poly(dimethylamino ethyl methacrylate)) and hydrophilic, nonionic C blocks (poly(poly(ethylene glycol) methyl ether methacrylate)) form the coronas. We find that hydrophilic units do not change the colloidal stability of the complexes, and complexes based on all four micelle architectures form broad, multimodal size distributions. While complexes based on the $\text{AB}^+$, $\text{AB}^+\text{C}$, and $\text{ACB}^+$ polymer architectures are kinetically trapped at low ionic strength, however, those based on the $\text{A(B}^+\text{-stat-C)}$ architecture rapidly rearrange into single-micelle complexes when the linear polyanion is in excess. This suggests that the randomly-placed hydrophilic units break up the ion pairing between the cationic and anionic chains and promote formation of over-charged complexes. Design of the micelle architecture may thus provide a powerful way control the structure and stability of micelle-polyelectrolyte complexes for gene delivery applications.

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