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Self-Assembly of Giant Gemini Surfactants Based on Polystyrene-Hydrophilic Polyhedral Oligomeric Silsesquioxane Shape Amphiphiles YI-WEN LI, ZHAO WANG, STEPHEN CHENG, Department of Polymer Science, The University of Akron, Akron, OH, 44325 — A series of giant gemini surfactants consisting of two hydrophilic carboxylic acid-functionalized polyhedral oligomeric silsesquioxane (APOSS) heads and two hydrophobic polystyrene (PS) tails covalently linked via rigid spacers (PS-$(APOSS)_2$-PS) was designed and synthesized Our current study revealed a morphological transition from vesicles to wormlike cylinders and further to spheres as the degree of ionization of the carboxylic acid groups on POSS heads increases in their micelle solutionPS tails were found to be less stretched in micellar cores of PS-$(APOSS)_2$-PS than those of the corresponding single-chained giant surfactant. It was also observed that the PS tail conformations in the micelles were also affected by the length of rigid spacers where the one with longer spacer exhibits more stretched PS chain conformation. Both findings could be explained by the topological constraint imposed by the short rigid spacer in giant gemini surfactants. This constraint effectively increases the local charge density and leads to an anisotropic head shape that requires a proper re-distribution of the APOSS heads on the micellar surface to minimize the total electrostatic repulsive free energy. Moreover, their supramolecular structures in bulk were also found to be strongly affected by rigid spacer effects. Our study has general implications in the basic physical principles underlying their self-assembly behaviors in solution and bulk states

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