

Nanostructures of the Electrostatic Complexes of Poly(amidoamine) G4 Dendrimer and Sodium Dodecyl Sulfate

Yu-Fan Chang(張于凡)¹、Yu-Hsiang Chen(陳育祥)^{1,2}、Chun-Yu Chen(陳軍佑)³、Hsin-Lung Chen(陳信龍)^{1*}

¹Department of Chemical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

² Material and Chemical Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 300, Taiwan

³National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

hlchen@che.nthu.edu.tw

Abstract

The complexation of polymer with amphiphilic surfactants offers a facile route to construct long-range ordered nanostructures via microphase separation between the polar (composed of the polymer backbone and surfactant headgroup) and the nonpolar (surfactant alkyl tail) components. Previous studies on the type of supramolecule, have been centered on the complexes of surfactants with linear polymers, where the lamellar structure with flat interface had been predominantly observed. In this study, we demonstrate that the electrostatic complexation of a surfactant with an oppositely charged 3D polymer, dendrimer, yielded the long-range ordered columnar nanostructures with undulated interface, where the nonzero interfacial curvature was imparted by the geometric feature of the dendrimer. Here the anionic sodium dodecyl sulfate (SDS) surfactant was complexed with protonated poly(amidoamine) (PAMAM) G4 dendrimer whose positive charge density was presented by degree of protonation (dp). The actual binding fraction (x_a) of the SDS to the dendrimer measured by NMR spectroscopy revealed that the electrostatic binding between two components occurred cooperatively. The SAXS results revealed the transition of the self-assembled structure of the complex with respect to the increase of surfactant actual binding ratio (x_a), where the structure transformed from the body-centered cubic phase (BCC) to the hexagonal columnar phase (Col_h), and then to the centered rectangular columnar phase (Col_{cr}). When the actual binding fraction reached nearly the stoichiometric value, i.e., $x_a \cong 1.0$, an oblique columnar phase (Col_{ob}) was formed. Cryo-TEM observation revealed that the interface of the columnar formed by SDS was undulated. The present study has demonstrated the power of dendrimer as the supramolecular building block for constructing columnar mesophase with various space symmetries and further conferring undulated interface to the columnar composed of the surfactant.

Keywords - dendrimer, surfactant, electrostatic complex, undulated columnar phase