

Electrostatic Self-Assembly of Neutral and Polyelectrolyte Block Copolymer and Oppositely Charged Surfactant

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Interactions between polyelectrolytes and oppositely charged amphiphiles have attracted a great deal of interest in the last decades, due to their importance both in fundamental polymer physics/biophysics and in biological and industrial applications. The interactions between polyelectrolytes and oppositely charged surfactants are quite strong and can induce a complex formation, often resulting in highly ordered structures. These well-defined supramolecular structures of the polyelectrolyte-surfactant complexes have unusual properties. We investigate the microscopic structure of colloidal complex made from poly(N-isopropylacrylamide)-block-poly(acrylic acid) (PNIPAM-b-PAA) (Fig. A) as thermosensitive neutral-anionic block copolymer and dodecyltrimethylammonium bromide (DTAB) as cationic surfactant under various conditions, specifically the effects of the DTAB concentration (surfactant-to-polymer charge ratio and temperature.

PNIPAM-b-PAA with low polydispersity was prepared by RAFT polymerization in methanol. SANS (Fig. B) clearly indicates that the aqueous solution of PNIPAM-b-PAA and DTAB associate into colloidal complexes. For low surfactant-to-polymer charge ratio $Z (= [S]/n[P], [S]: \text{DTAB conc.}, [P]: \text{PNIPAM-b-PAA conc.}, n: \text{degree of polym. of PAA block})$ lower than the critical value Z_c , the colloidal complexes are single DTAB micelles dressed by a few PNIPAM-b-PAA (Fig C-i). Above the critical value $Z_c \sim 0.7$, the colloidal complexes form a core-shell microstructure (Fig. C-ii). The core of the complex consists of densely packed surfactant micelles (DTA+), and PAA block chains bind to these micelles, displace their counteranions (Br-) and bridge them together. The core ra-

dius is ranging between 150-160 Å depending on the charge ratio and temperature, and the intermicellar distance of the DTA⁺ micelles is ~ 39 Å, which is independent of the charge ratio Z as well as temperature. The corona of the complex is constituted from the thermosensitive PNIPAM. The aggregation number expressed in terms of DTA⁺ micelles per complex is also determined using the analogy with the homopolyelectrolyte/surfactant system, and found to be 200-250 depending on the charge ratio and temperature.

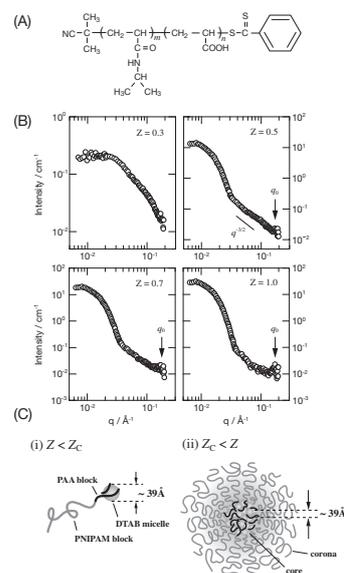


Fig. 1. (A) Chemical structure of PNIPAM-b-PAA. (B) SANS profiles for 0.4 wt% aqueous solutions of PNIPAM-b-PAA. (C) Schematic representation of complex (i) $Z < Z_c$, and (ii) $Z_c < Z$.