

Fabrication of nanoaggregates of *triple hydrophilic block copolymers* by binding of ionic surfactants

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Introduction

In the past decades, extensive attention has been paid to preparation of micelles from block copolymers. The polymeric micelles have wide applications in drug delivery systems and separation techniques etc. On dissolving the amphiphilic block copolymer into water, its self-assembly occurs to form the polymeric micelles having a hydrophobic core and a hydrophilic corona. Although the micelles of amphiphilic block copolymers have various advantages compared to the micelles of low molecular-weight surfactants, there is a drawback that they cannot incorporate ionic species into the core because the core is hydrophobic in nature.

Recently, steadily increasing attention has been paid to the *double hydrophilic copolymers* (DHBCs) because they have a unique self assembling property [1, 2]. The DHBC cannot form the micelle by itself on dissolving it into water. However, when one block of it is insolubilized with a suitable counterion such as a surfactant, metal ion or polyion, it forms a micelle having a core of the insolubilized block. The electrostatic interaction (or coordinate bond in some cases) between the added counterion and one block of the DHBC plays a primary role in the micellization process. For example, poly(ethylene oxide)-*b*-polymethacrylic acid (PEO-*b*-PMAA) can form micelles when the anionic PMAA block is insolubilized with a counterion such as poly-L-lysine (PLS) [3].

A few works have been reported so far by considering *triple hydrophilic block copolymers* although they may form more complex nanostructures with surfactant, drug etc. The nanostructures may break a fresh ground of nano-science as found in other nano-structured particles.

In this respect, we tried to fabricate the nanoaggregates using dodecyltrimethylammonium chloride (DTAC) and *triple hydrophilic block copolymers* comprised of poly(ethylene oxide), poly(sodium 2-acrylamido)-2-methylpropane sulfonate), and poly(methacrylic acid) (PEO-PAMPS-PMAA). DTAC is cationic surfactant and thus may bind to the anionic PAMPS and PMAA blocks of PEO-PAMPS-PMAA by electrostatic interaction, resulting in insolubilization of the both anionic blocks. Binding of DTAC in PEO-PAMPS-PMAA is confirmed by electrophoresis measurements while formation of nanoaggregates of DTAC and PEO-PAMPS-PMAA is observed by dynamic light scattering (DLS) measurements.

Experimental

Materials. DTAC was purchased from TCI. The procedure of the synthesis of PEO-PAMPS-PMAA and homopolymer, PAMPS, will be reported in future. The degree of polymerization of the PEO, PAMPS and PMAA blocks is 17, 260 and 49 respectively.

Preparation of Nanoaggregates. A known amount of PEO-PAMPS-PMAA stock solution (1g/L) was titrated with a solution of DTAC. The amount of added DTAC is expressed by an *apparent degree of neutralization (DN)*, which is defined as:

$$DN(\%) = \frac{\text{Amounts of DTAC in molar unit} \times 100}{\text{Amount of SO}_3\text{Na groups in base mole unit}}$$

Required amount of hydrochloric acid and sodium hydroxide was added into the nanoaggregates solution of DTAC/ PEO-PAMPS-PMAA to get desired pH.

Results and Discussion

DLS Measurements. It should be noted here that DTAC does not form its own micelles because the concentration of DTAC is much

lower than its CMC (20 mM) even for the sample with the highest *DN*.

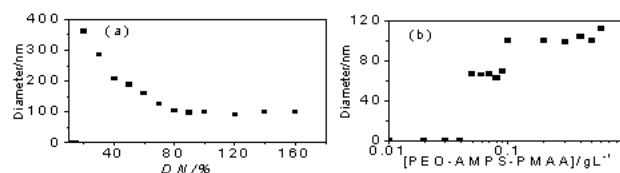


Figure 1. Hydrodynamic diameter of DTCA/PEO-PAMPS-PMAA nanoaggregates at pH 9 as a function of (a) *DN* (concentration of PEO-PAMPS-PMAA: 0.3 g/L) and (b) the polymer concentration at 100% *DN*.

Figure 1 shows the hydrodynamic diameter of DTCA/PEO-PAMPS-PMAA nanoaggregates at pH 9. In Figure 1a, the hydrodynamic diameter rises at 20% *DN*, indicating nanoaggregate formation. Afterwards, the hydrodynamic diameter decreases continuously with increasing *DN*. The hydrodynamic diameter decreases from 369 nm to 100 nm when *DN* is increased from 20% to 90%. This seems to be due to the fact that, at lower *DN*, there is still repulsive force in the PAMPS and PMAA block because both anionic blocks of PEO-PAMPS-PMAA is partially neutralized by cationic DTAC. Consequently, the core of DTAC/ PAMPS/PMAA will be swollen with water. On increasing the *DN*, the repulsive force in both anionic blocks of PEO-PAMPS-PMAA decreases continuously due to the electrical neutralization process, and this directs the cores of complexes to become more hydrophobic and compact.

From Figure 1b, it is found that there is a sharp increase in the diameter within the range of 0.05 g/L to 0.06 g/L, indicating nanoaggregate formation. On increasing the polymer concentration from 0.09 g/L to 0.1 g/L, the diameter of the nanoaggregates abruptly increases from 67 nm to 100 nm.

Zeta-potential Measurements. We carried out the zeta-potential measurements in order to confirm the binding of DTAC to the anionic blocks of PEO-PAMPS-PMAA polymer. Figure 2a shows the zeta-potential of nanoaggregates of DTAC/ PEO-PAMPS-PMAA as a function of *DN*. The increase in *DN* results in a steady increase in zeta-potential. At 100% *DN*, the zeta-potential is close to -49 mV indicating that non stoichiometric binding of DTAC to the sulfonate unit of the PAMPS block although at pH 9 both DTAC and PAMPS block are fully ionized. From Figure 2b, the nanoaggregates of DTAC/ PEO-PAMPS-PMAA show negative charge at 100% *DN* regardless of polymer concentration indicating that all added DTAC are not bound to the polymer.

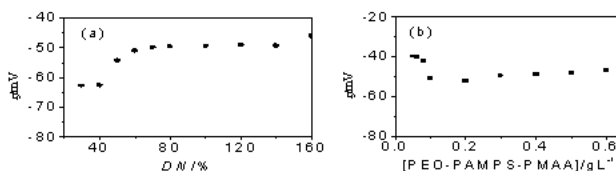


Figure 2. The zeta-potential of DTAC/PEO-PAMPS-PMAA nanoaggregates at pH 9 as a function of (a) *DN* at constant polymer concentration (0.3 g/L) and (b) the polymer concentration at fixed *DN* (100%).

Conclusions

We have fabricated the nanoaggregates of PEO-PAMPS-PMAA by insolubilizing the anionic PAMPS and PMAA block with a cationic DTAC. The formation of nanoaggregates was detected by DLS measurements. Binding of DTAC to the anionic block of polymer was confirmed by electrophoresis measurements.

References

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