

A Small Angle Neutron Scattering Study of Cylindrical nanoparticle with Controlled Surface Charge Density

Tae-Hwan Kim^a, Steven R. Kline^b, Sung-Min Choi^{a*}

^a Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon, 305-701, sungmin@kaist.ac.kr

^b NIST Center for Neutron Research, Gaithersburg, Maryland 20899-8562, USA

1. Introduction

Surfactant molecules in aqueous solution self assemble into various micellar structures such as sphere, rod, vesicle, and lamellar, above critical micelle concentration (CMC) [1, 2]. Self-assembled surfactants systems, therefore, have been very popular as templates for preparing various nanostructured materials [3, 4]. Due to their dynamic nature, however, micellar structures are very susceptible to solution conditions such as temperature, concentration, pH and pressure [5, 6], limiting their applications.

In this study, we have developed rigid rod-like nanoparticles with controlled surface charge density by the free radical polymerization of cationic surfactants with polymerizable counterions, cetyltrimethylammonium 4-vinylbenzoate (CTVB), with varying concentration of sodium styrenesulfonate (NaSS). The structure and surface charge density of the nanoparticles were characterized by small angle neutron scattering (SANS) and zeta potential measurements

2. Experimental Section

Cetyltrimethylammonium 4-vinylbenzoate (CTVB) was synthesized by neutralization of 4-vinylbenzoic acid (VBA) in the presence of a slight stoichiometric excess of CTAOH followed by repeated crystallization. The detailed procedure is described elsewhere [7, 8]. For the counterion polymerization of CTVB, the 1wt% CTVB solution was prepared using water in which oxygen was removed by bubbling with ultra-high purity nitrogen, which is free-radically polymerized by injecting of initiator (VA-044, 5 mol% relative to the CTVB concentration). To control the surface density of the polymerized CTVB particles, various concentrations of NaSS (0, 5, 10, 40, 50, 60 mol% relative to the CTVB concentration) which has a polymerizable counterion, SS⁻, was dissolved into the CTVB solution before injecting the initiator. The schematics of polymerization process and the resulting particle structures are depicted in Figure 1.

Neutron scattering experiments were carried out on 9m SANS instruments at the HANARO in Korea Atomic Energy Research Institute (KAERI), Daejeon and on the NG3 30m SANS instruments at the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA. In the experiments at HANARO, neutrons of wavelength $\lambda = 5.08\text{\AA}$ with full width half maximum of $\Delta\lambda/\lambda=11.8\%$ were used.

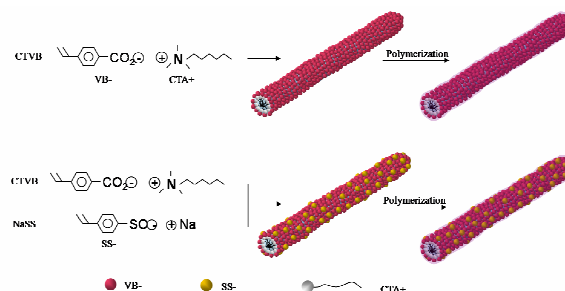


Figure 1. The schematic of surface charge control for polymerized CTVB nanoparticle

The scattered intensities were measured by a 2-dimensional 64 cm x 64 cm ³He detector. Two different sample to detector distance (2 m and 4.6 m) were used to get an overall q range of $0.009\text{ \AA}^{-1} < q < 0.3351\text{ \AA}^{-1}$, where $q=(4\pi/\lambda)\sin(\theta/2)$ and θ is the scattering angle. In the experiments at NIST, neutrons of wavelength $\lambda=6.5\text{\AA}$ with full width half maximum of $\Delta\lambda/\lambda=10\%$ were used. Two different sample to detector distances (1.3 m and 13 m) were used to cover the overall q range of $0.004\text{ \AA}^{-1} < q < 0.4\text{ \AA}^{-1}$. In very dilute system, SANS data sets were analyzed by two methods; Guinier fitting and rigid cylindrical form factor fitting [9, 10].

The surface charge density of polymerized CTVB with and without NaSS was characterized by zeta potential measurements using a Zeta Plus instrument (Brookhaven Instruments Corporation).

To confirm the polymerization of counterions, VB- and SS-, NMR measurement was conducted on a Bruker FT-500 MHz NMR spectrometer. All the measurements were carried out in D₂O

3. Result and Discussion

A polymerizable surfactant CTVB forms worm-like micelles in aqueous solution and 1 wt % CTVB in water was very viscoelastic. Upon the counterion polymerization of VB- and SS- around worm-like micelle, the viscosity of the solution was dramatically reduced which became fluidic like water. The conversion of counterions to polymer was verified by NMR measurements. The NMR peaks arising from vinyl group and aromatic group have completely disappeared upon polymerization, indicating the nearly perfect conversion to polymer.

The structures of polymerized CTVB particles with various amounts of NaSS were characterized by SANS

measurements. From SANS intensities of 0.1 wt % polymerized CTVB in D₂O, which are prepared with varying NaSS concentrations, we obtained the diameter and length of the polymerized particles. While the diameter of the particles is a constant of ~4 nm for all NaSS concentrations, the length is varied depending on the concentration of NaSS, 43.8 nm (0 mol %), 85 nm (5 mol %), 50.9 nm (10 mol %), 26 nm (25 mol %) and 20.4 nm (40 mol %). The SANS data were also analyzed with the Guinier model to estimate the radius of gyration of the particles. Using the radius of gyration, we estimated the length of the particles [9], which is consistent with the results of cylindrical model fitting.

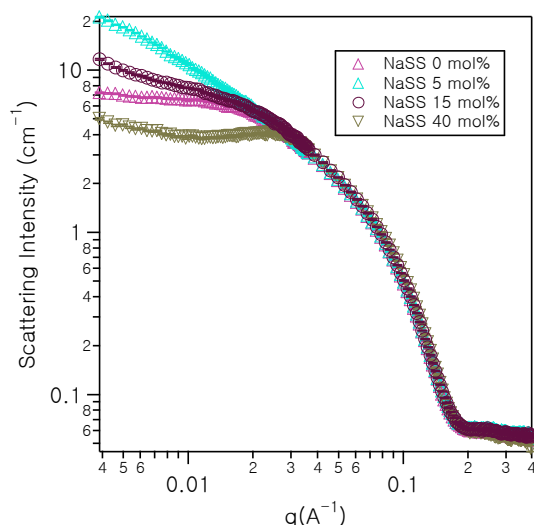


Figure 2. SANS intensities of 1 wt % polymerized CTVB in D₂O with varying NaSS concentrations.

The coulomb interactions between the polymerized cylindrical nanoparticles were characterized by SANS measurements for 1wt% the polymerized nanoparticle with different NaSS concentration as shown in Figure 2. It is clear that the appearance of interaction peaks is strongly dependent on the NaSS concentration. SANS intensity of polymerized CTVB without NaSS shows a Coulomb interaction peak at $\sim 0.015 \text{ \AA}^{-1}$. As the concentration of NaSS is increased to 5 mol %, the interaction peak disappears entirely. At 15 mol% NaSS concentration, the interaction peak is slightly appeared. When the NaSS concentration is further increased to 40 mol %, however, the interaction peak becomes strongly pronounced again ($\sim 0.03 \text{ \AA}^{-1}$). Since the NaSS provides SS⁻ counterions which are co-polymerized with VB-counterions, the results indicate that when there is no NaSS, the cylindrical particles are slightly positively charged and as the concentration of NaSS increases the particles become neutral and eventually become negatively charged.

To estimate the surface charge of the polymerized cylindrical nanoparticles, zeta potential measurements for various NaSS concentrations were performed. The zeta potential changes from +12.8 mV to -44.2 mV, as the concentration of NaSS is increased from 0 mol % to 40 mol %. The charge inversion from positive to

negative value occurred at ~ 7 mol % of NaSS concentration, which is consistent with the interpretation of the SANS measurements of 1 wt % samples. As the NaSS concentration is further increased, the zeta potential was saturated at nearly -50mV

3. Conclusion

Rod-like nanoparticles with controlled surface charge density have been developed by the free radical polymerization of cationic surfactants with polymerizable counterions, CTVB, with varying concentration of NaSS. SANS measurements showed that the diameter and length of the nanoparticles were 4nm and 20nm \sim 80nm, respectively, depending on the concentration of NaSS. The zeta potential measurements showed that the zeta potential of the nanoparticles is changed from positive to negative (+12.8 mV \sim -50 mV) as the concentration of NaSS is increased from 0 mol % to 60 mol %.

REFERENCES

- [1] J. N. Israelachvili, Intermolecular and Surface Forces, Academic Press, New York, 1992
- [2] P. C. Hiemenz, R. Rajagopalan, Principles of Colloid and Surface Chemistry 3rd Ed, Marcel Dekker, Inc. New York, 1997
- [3] C. M. Paleos, Polymerization in Organized Media; C. M. Paleos, Ed.; Gordon and Beach: Philadelphia 1992
- [4] G. Cao, Nanostructures and Nanomaterials, Imperial College Press, London 2004
- [5] P. A. Hassan, G. Fritz, E. W. Kaler, J. Colloid and Interface Science Vol. 57, p. 154, 2003
- [6] V. K. Aswal, P. S. Goyal, Chemical Physics Letters Vol. 364, p. 44, 2002
- [7] S.R. Kline, Langmuir Vol. 15, p. 2726, 1999
- [8] T. H. Kim, S. M. Choi, S. R. Kline, Langmuir Vol. 22 p. 2844, 2006
- [9] A. Guinier, and G. Fournet, "Small-Angle Scattering of X-Rays", John Wiley and Sons, New York, 1955
- [10] J. S. Higgins, H. C. Benoit, "Polymers and Neutron Scattering", Oxford University Press, New York, 1994