Small Angle X-ray and Neutron Scattering Study on Hierarchical Superstructures of Multicomponent 1D Colloids

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1. Introduction

Fabrication of multicomponent nanoparticle superstructures that can exhibit emerging properties through synergetic coupling between different types of nanoparticles is of great interest because of its scientific merits as well as its broad potential application.[1] While there have been a few studies on the binary or multicomponent superstructures of spherical nanoparticles, multicomponent superlattice of one-dimensional (1D) nanoparticles have remained in the early stages.[2,3] Here, we investigate how three kinds of 1D colloids of different diameters are self-assembled when mixed in an aqueous solution using small angle X-ray and neutron scattering (SAXS and SANS).

2. Experimental Methods

2.1. Synthesis of 1D Colloids (p-C_nTVB)

p-C_nTVBs were prepared as described elsewhere.[4] *n*-alkyltrimethylammonium hydroxide (C_nTAOH, n = 8, 10, 12, 14, and 16) was synthesized by replacing Br^- in C_nTAB with OH^- via anion exchange resin. *n*-alkyltrimethylammonium 4-vinylbenzoate (C_nTVB) was synthesized by a neutralization of C_nTAOH with same stoichiometric amount of VBA. *p*-C_nTVB was synthesized through in-situ polymerization of the caunterions (VB-) of C_nTVB which forms cylindrical micelles in aqueous solution.

2.2. Preparation of Multicomponent Mixtures of 1D Colloids (p-C_nTVB/p-C_mTVB/$C_{12}E_5$/water)

p-C_nTVB/*p*-C_mTVB/$C_{12}E_5$/water samples with different mixing ratios (5/5/45/55, 5/10/45/55, *and 10/5/45/55)* were prepared by adding different amounts of *p*-C_nTVB and *p*-C_mTVB into $C_{12}E_5$/water (45/55_ solution. For homogeneous mixing, the mixtures of *p*-C_nTVB/*p*-C_mTVB/$C_{12}E_5$/water samples were vortex-mixed and then centrifuged more than 100 times in alternating directions. All the mixing was done at room temperature where $C_{12}E_5$/water sample (45/55) is in isotropic phase followed by placing the sample at room temperature for a few days to ensure sufficient stabilization.

2.3. SANS Measurements

SANS measurements were performed at HANARO (40 m SANS instrument), KAERI. Neutrons of a wavelength (λ) of 0.6 nm with a wavelength spread ($\Delta\lambda/\lambda$) of 0.12 were used. The sample-to-detector distance of 2.5 and 15.89 m was used to cover the q range of 0.04 nm^{-1} < q < 4 nm^{-1}, where $q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector and θ is the scattering angle. Background and empty cell scattering were subtracted from the sample scattering and the sensitivity of individual detector pixels was corrected followed by the absolute scaling using the direct beam flux method. All the SANS measurements were carried out using quartz cells of 1 and 4 mm path length. Temperature was controlled by using a circulation bath (Neslab RTE 740, USA)

2.4. SAXS Measurements

SAXS measurements were performed at the Pohang Accelerator Laboratory (beamline 4C). X-rays of λ of 0.12 nm with $\Delta\lambda/\lambda$ of 2×10^{-4} were used and collected with a 2D CCD camera (SX165; Mar USA, Inc. CCD 165). The sample-to-detector distance of 1 m was used to cover the q range of 0.4 nm^{-1} < q < 3.7 nm^{-1}. Temperature was controlled by using a water circulation bath (Lauda, Germany). All the samples were equilibrated for at least 10 min at each temperature to ensure sufficient stabilization and then measured.

3. Results

3.1. Characterization of 1D Colloids

One type of 1D colloids is $C_{12}E_5$ cylindrical micelles. When $C_{12}E_5$/water are mixed (45/55), $C_{12}E_5$ shows isotropic phase at room temperature and hexagonal phase at low temperature at which the diameter of C12E5 cylindrical micelles are 4.3 nm.[5] Another type of 1D colloids is *p*-C_nTVB. In the synthesis of *p*-C_nTVB, *n*, the number of carbon in alkyl chain, is varied from 8 to 16, leading to controlled diameter. The shape and size of *p*-C_nTVB were characterized by the SANS form factor analysis (Fig. 1 and Table I).[3] As n increases from 8 to 16, the diameter of *p*-C_nTVB linearly increases from 2.1 to 4.0 nm. This allows us to systematically investigate the diameter effects of three types of 1D colloids in a multicomponent self-assembled structure.

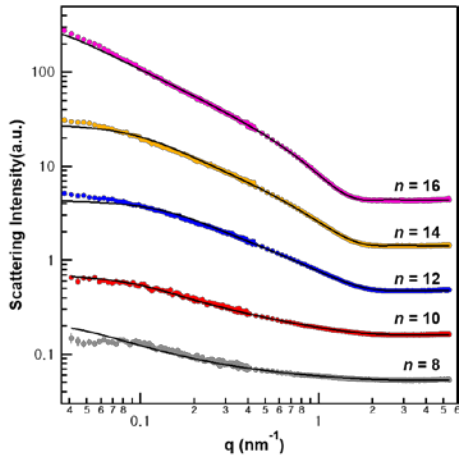

Fig. 1. SANS intensities of 0.1 wt % *p*-C$_n$TVB in D_2O for *n* = 8, 10, 12, 14, and 16 (color line). 10mM NaCl is dissolved in D_2O to minimize electrostatic interaction between *p*-C$_n$TVBs. The black lines are model fits using a cylindrical particle form factor. The SANS intensities are shifted vertically for visual clarity.

Table I. Fitted diameters and lengths of *p*-C$_n$TVB

n	Diameter (nm)	Length (nm)
8	2.1	69.3
10	2.5	33.0
12	3.0	21.9
14	3.4	31.8
16	4.0	107.7

3.2. SAXS Measurements of Multicomponent Mixtures

To understand the self-assembling behavior of multicomponent 1D colloids with different diameters, *p*-C$_n$TVB and *p*-C$_m$TVB were mixed with $C_{12}E_5$/water (45/55) at room temperature. Here, the mixing ratio of *p*-C$_n$TVB/*p*-C$_m$TVB are varied with 5/5, 5/10, and 10/5 followed by adding into the fixed concentration of $C_{12}E_5$/water (45/55), resulting in the presence of three different types of 1D colloids (*p*-C$_n$TVB, *p*-C$_m$TVB, and $C_{12}E_5$ cylindrical micelle) in the mixture.

The SAXS intensity measured at 12 °C (Fig. 2) shows that $C_{12}E_5$/water (45/55) forms hexagonal structure of cylindrical micelles as indicated by the peak position ratio of 1:√3:2. The center-to-center distance between the nearest neighboring $C_{12}E_5$ cylindrical micelles ($d=4\pi/\sqrt{3}q_1$, where q_1 is the first order hexagonal peak) are estimated to be ca. 5.7 nm. As the mixtures of *p*-C_{10}TVB/*p*-C_{16}TVB (as a representative data set) with different mixing ratio are added to $C_{12}E_5$/water (45/55), different behaviors are observed. For the case of *p*-C_{10}TVB/*p*-C_{16}TVB/$C_{12}E_5$/water (5/5/45/55), new peak appears at lower *q* region, indicating that a new structure with larger lattice parameter than that of $C_{12}E_5$/water (45/55). The peak position ratio of new peak to 1st order hexagonal peak of $C_{12}E_5$/water is 1:√3. This indicates that the hierarchical superstructure is formed with addition of *p*-C_{10}TVB/*p*-C_{16}TVB. In the previous studies, the combination of SAXS and contrast matched SANS have shown that this relation can be attributed to the AB_2 type superlattice of 1D colloids.[2,3] For the case of *p*-C_{10}TVB/*p*-C_{16}TVB/$C_{12}E_5$/water (5/10/45/55), no new peak appears while the peak position is slightly shifted to higher q region, which can be explained by the increased concentration by the addition of *p*-C$_n$TVBs. Interestingly, for the case of *p*-C_{10}TVB/*p*-C_{16}TVB/$C_{12}E_5$/water (10/5/45/55), new multi peaks are observed. It should be noted that this SAXS intensity is rarely observed for other superstructure or any other ordered colloidal system. This clearly indicates that highly ordered new-type hierarchical superstructure of multicomponent 1D colloids are formed. A simple analysis of this SAXS intensity can be expected to reveal a tilted hexagonal structure although the detailed study is required. The detailed study can be done through the SANS measurement, which can selectively measure the certain colloid in the multicomponent system by the contrast matching technique.

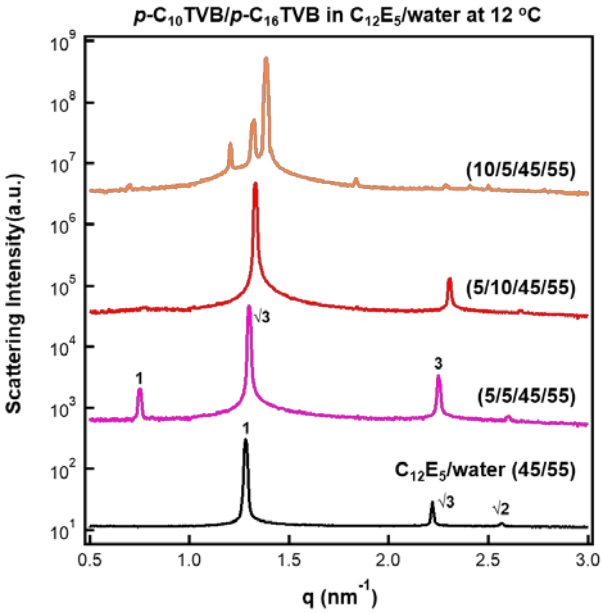

Fig. 2. SAXS intensities of $C_{12}E_5$/water (45/55) and *p*-C_{10}TVB/*p*-C_{16}TVB/$C_{12}E_5$/water with different mixing ratios at 12 °C. Scattering intensities are shifted vertically for visual clarity.

4. Conclusion

We investigated a highly ordered hierarchical superstructure of ternary 1D colloids. The shape and dimensions of nanoparticle were in-situ characterized using the SANS measurements. The superstructure of multicomponent 1D colloids in aqueous solution were in-situ characterized using the SAXS measurements. Therefore, the SAXS and SANS measurements are very

powerful tool to study the structural characterization of nanoscale system.

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