

論文の内容の要旨

論文題目 Self-Assembly of Silica Nanospheres Mediated by Block Copolymers
(ブロックコポリマーによるシリカナノ粒子の自己集合)

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This thesis describes the self-assembly of silica nanospheres (SNSs) of ten-nanometer scale in the liquid phase into one-dimensional (1D) chain-like, ring-like, and three-dimensional (3D) hollow nanostructures using different block copolymers (BCPs) as the mediators. This research is based on the findings by Fukao et al. (J. Am. Chem. Soc. 2009) that SNSs undergo 1D assembly in the liquid phase in the presence of F127, a PEO-PPO-PEO (PEO: poly(ethylene oxide); PPO: poly(propylene oxide)) BCP. Although the effects of F127 were not clarified at that stage, their findings suggest that BCPs provide a powerful self-assembly strategy towards novel assembled nanostructures. The overview of self-assembly, the properties of BCPs and silica nanoparticles, and the background of this thesis are described in Chapter 1. Chapter 2 presents the investigations conducted for further clarifying the polymers' effects on 1D assembly of SNSs. The effects of several PEO-PPO-PEO BCPs with different PEO and PPO segment lengths are examined. In Chapter 3, the effects of lysine, an organic small molecule contained in the F127-SNS 1D assembly system, are examined. In Chapter 4, the EOVE-MOVE (EOVE: ethoxyethyl vinyl ether; MOVE: methoxyethyl vinyl ether) BCPs are employed as the mediators for the self-assembly of SNSs. Ring and chain-like nanostructures are obtained with SNSs of different sizes. In Chapter 5, the PPO-PEO-PPO BCPs are used and vesicles composed of a monolayer of SNSs are obtained under hydrothermal conditions. Different surface topographies of the vesicles can be obtained in the presence of polymer. Finally, conclusions and perspective of the thesis are given in Chapter 6.

Self-assembly of nanoparticles (NPs) is essential for the development of advanced technologies. Polymers, as a particular class of soft materials, provide a powerful self-assembly strategy for fabricating nanostructures. Polymers in colloidal systems induce a wealth of interactions, which can be manipulated to assemble the colloidal NPs. The surface chemistry of silica NPs has been well studied. Facile methods have been developed by Yokoi et al. (J. Am. Chem. Soc. 2009)

and Snyder et al. (Langmuir 2007) to synthesize stable colloidal suspensions of silica nanospheres (SNSs) with controllable nano-scaled sizes. Such SNSs have great potentials as ideal building blocks for self-assembly to diverse nanostructures. Fukao et al. (J. Am. Chem. Soc. 2009) found that the SNSs assemble in the liquid phase to form chain-like nanostructures in the presence of F127. The SNSs are typical isotropic particles lacking obvious anisotropic interactions. It was supposed that synergistic effects between F127 and SNSs might lead to the 1D assembly of SNSs; however, the details were unknown. The F127-SNS 1D assembly system provides an ideal model for the study of polymer-mediated self-assembly. One of the outstanding advantages of this system is that F127 and SNSs associate with each other through surface adsorption, which means that synthetically-challenging procedures such as surface modifications are not necessary. Therefore, the self-assembly principles obtained from the current system can be transferred to other polymer-NP systems. In addition, the PEO-PPO-PEO BCPs with different PEO and PPO segment lengths are commercially available, which enables us to perform detailed investigations into the polymers' effect practically. This thesis has two objectives: to elucidate the effects of BCPs on the self-assembly of NPs and to explore novel assembled nanostructures through the BCP-mediated NP assembly approach. SNSs developed by Yokoi et al. (J. Am. Chem. Soc. 2006) are employed as the model NPs, and different classes of BCPs are used to mediate the self-assembly of SNSs.

In Chapter 2, the effects of PEO-PPO-PEO BCPs on 1D assembly were investigated to further clarify the mechanisms of 1D assembly. The F127-mediated 1D assembly of SNSs was found to be pH-sensitive and the optimal pH of 1D assembly ($\text{pH}_{1\text{D}}$) in the presence of F127 is around 7.5. pH should have significant effects on SNSs which are charged, whereas it should have little effect on F127 which is nonionic. 1D assembly of NPs is generally a result of delicate balance of attractive and repulsive interactions. Here, $\text{pH}_{1\text{D}}$ may serve as an index of such balance of interactions. To clarify the effects of F127 on the 1D assembly of SNSs, different PEO-PPO-PEO BCPs, P123, L64, P65, and F68, were employed to mediate the assembly of SNSs. All the investigated polymers lead to 1D assembly of SNSs; however, different $\text{pH}_{1\text{D}}$ is observed for different polymers. It is found that $\text{pH}_{1\text{D}}$ shifts from ~ 9.4 to ~ 7.5 with increasing hydrophilic-lipophilic balances (HLBs) of the polymers. The HLB value is a measure of the polymers' relative hydrophilicity. Therefore, the balance of interaction is affected by the relative hydrophilicity of the polymer. Relationships between $\text{pH}_{1\text{D}}$ and the polymers' number of N_{EO} and N_{PO} units further suggest that the polymers may contribute steric and hydrophobic interactions to the 1D assembly of SNSs. Finally, a model is proposed to explain the 1D assembly of SNSs mediated by the PEO-PPO-PEO BCPs.

Lysine, a basic amino acid as the catalyst for the synthesis of the SNSs, is contained in the F127-SNS assembly system. Lysine has $-\text{NH}_2$ and $-\text{OH}$ groups; therefore, it can interact with both F127 (EO units) and SNSs ($\equiv\text{SiOH}$ groups) via hydrogen bonding interactions. Lysine and SNSs also electrostatically interact through the NH_3^+ and SiO^- groups. Small molecules interacting with both the BCP and NPs have been reported to affect the self-assembly in BCP-NP nanocomposites. To further clarify the mechanism of 1D assembly, the F127-mediated assembly of SNSs in the absence and presence of lysine was examined in Chapter 3. The absence of lysine is realized by synthesizing SNSs using primary amines (*n*-butylamine, *n*-propylamine) or ammonia as the base catalysts. The F127-mediated 1D assembly of SNSs proceeds even in the absence of lysine, suggesting that lysine is not essential to 1D assembly. The presence of basic amino acids in the suspension tends to shift $\text{pH}_{1\text{D}}$ to higher values. The basic amino acids may increase interparticle attractions through electrostatic shielding effects.

In Chapter 4, a novel class of EOVE-MOVE BCPs developed by Aoshima and co-workers (J. Polym. Sci., Part A: Polym. Chem. 2008) were employed to mediate the self-assembly of SNSs. The EOVE and MOVE segments are thermoresponsive, having the lower critical solution temperature at 20 °C and 60 °C, respectively. The EOVE and MOVE segments carry ether oxygens; therefore, they should interact with the SNSs via hydrogen bonding interactions. It is found that the SNSs with a diameter of 15 nm assemble into ring nanostructures composed of 3–6 particles in the presence of the EOVE₁₀₀-*b*-MOVE₃₁₀ BCP at pH 7.8. Several BCPs with different EOVE and MOVE segment lengths also lead to the ring formation; however, an EOVE-MOVE random copolymer does not. Therefore molecular structure of the BCP is important for the ring assembly. SNSs with a diameter of 30 nm are found to assemble into 1D chain-like nanostructures in the presence of the EOVE₁₀₀-*b*-MOVE₃₁₀ BCP at pH 7.8. This gives important insights into the mechanisms of ring assembly: (1) the size of SNSs critically affects the mode of assembly, and (2) the ring assembly may be a particular case of 1D assembly.

In Chapter 5, the SNSs were found to assemble into vesicles composed of a monolayer of SNSs in the presence of 25R4, a PPO-PEO-PPO-type BCP. The assembly favorably proceeds in the presence of 1.8–2.2 wt% 25R4 under hydrothermal conditions (110–190 °C) at pH 8.8–9.4. The mode of assembly is strongly affected by the molecular structure of the BCP. The SNSs assemble into vesicles in the presence of 17R4, another PPO-PEO-PPO BCP, whereas they assemble into ill-defined spheres or aggregates in the presence of PEO-PPO-PEO-type BCPs (L121, P123, L64, P65, F127, and TR-704). 25R4 further mediates the anisotropic organization of SNSs confined in the surface of the vesicles. This anisotropic assembly along with the Gibbs-Thomson effect reconstructs the surface topography of the vesicles.

In this thesis, several BCPs were employed to mediate the self-assembly of SNSs. Chapters 2 and 3 provide insights into the mechanism of 1D assembly of SNSs mediated by PEO-PPO-PEO BCPs. In Chapter 4, the ring assembly of isotropic SNSs in the liquid phase is achieved for the first time. In Chapter 5, vesicles composed of a monolayer of NPs, which had been achieved only through complicated or synthetically challenging processing, are obtained with a relatively simple method. In addition, an usual assembly phenomenon, i.e. the anisotropic assembly of SNSs confined in the curved surface of the vesicles, is identified. This thesis revealed that the BCP-mediated self-assembly of SNSs is an effective route for fabricating novel assembled nanostructures. Because the SNSs and the BCPs associate with each other through surface adsorption (hydrogen bonding), the self-assembly principles may be transferred to other NP-polymer systems. Nowadays, synthetic polymers with a wide range of compositions, topologies, and functionalities are available. These polymers, including commercial or tailored-made, shall lead to many interesting nanostructures assembled from NPs of metal oxides, noble metals, semiconductors, and so on.