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## COMMUNICATION

## Supracolloidal Polymer Chains of Diblock Copolymer Micelles

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**Directional attraction with lateral repulsion between colloidal nanoparticles can create their supracolloidal chains. Here, we demonstrate supracolloidal polymers of diblock copolymer micelles which were polymerized by adjusting the polarity of the solvent. We also synthesized supracolloidal random and block copolymer chains.**

Colloidal nanoparticles such as spherical gold nanoparticles and one-dimensional gold nanorods self-assemble into various superstructures from aggregated clusters to organized superlattices.<sup>1-3</sup> Self-organized superstructures of colloidal nanoparticles depend on attraction and repulsion between colloidal building blocks.<sup>4-6</sup> For example, non-directional attraction induces aggregated clusters of nanoparticles whereas strong repulsive interaction makes colloidal nanoparticles stable in solution without forming a superstructure. In particular, directional attraction between nanoparticles with orthogonal repulsion to the attraction can produce a chain-like supracolloidal polymer. A representative example in this situation is a supracolloidal polymer chain of gold nanorods, which were mainly stabilized by polar surfactants, with their two ends selectively covered by non-polar polymers.<sup>7,8</sup> By increasing the polarity of the solvent around the gold nanorods, attraction between the non-polar polymers at the ends of neighbouring nanorods was generated due to unfavourable contacts of the polymer with the solvent. However, the lateral sides of gold nanorods were stabilized by polar surfactants so that gold nanorods were connected linearly to form a supracolloidal polymer chain. The strategy of balancing attraction and repulsion to guide a linear superstructure was recently applied to spherical gold nanoparticles to produce their supracolloidal polymer chains.<sup>9,10</sup>

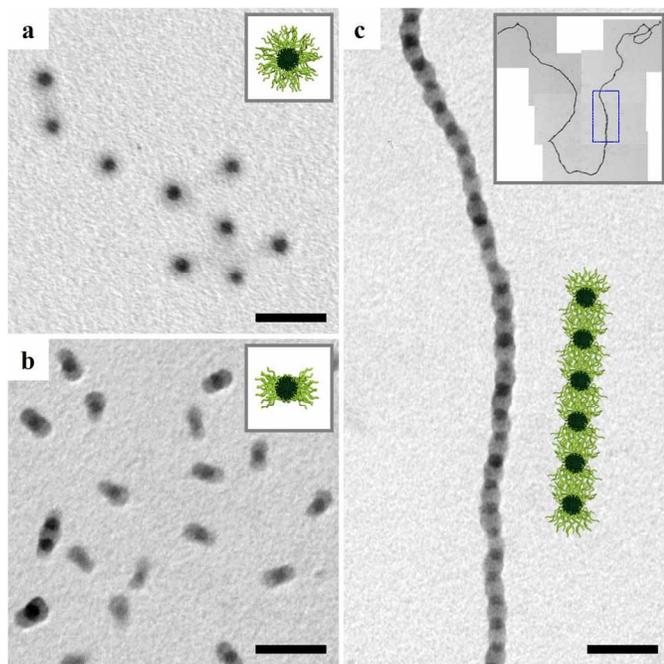
With polymeric colloidal nanoparticles including polymerization-induced self-assemblies,<sup>11-14</sup> various superstructures such as chains, ribbons, and worms have been reported.<sup>11-20</sup> Especially, by controlling attraction and repulsion of spherical micelles of triblock copolymers, hierarchically co-assembled suprachains as well as supracolloidal polymer chains were demonstrated.<sup>21,22</sup> In a non-solvent for the central block, triblock

copolymers formed spherical micelles that consisted of the insoluble core and the compartmentalized corona with polar patches and non-polar patches. By increasing the polarity of the solvent, the non-polar compartments in the corona generated attraction between the micelles but the polar compartments produced repulsion to avoid non-directional aggregation so that the micelles organized into a linear supracolloidal chain. The approach with triblock copolymers enabled the precise controllability on the nanoscale compartments in the corona of the micelles, although the synthesis of triblock copolymers would not be trivial.

In this Communication, we demonstrated supracolloidal polymer chains of diblock copolymer micelles. With a diblock copolymer composed of a polar block and a non-polar block, typical spherical micelles were first obtained in a selective solvent for the non-polar block. Since diblock copolymer micelles have a simple nanostructure of the core and the corona, prediction of the size of micelles depending on the molecular weights is rather straightforward and there are many choices for a micelle-forming solvent. With diblock copolymer micelles, we cross-linked the polar core and then made the solvent preferable to the core block but still compatible with the corona block. The cross-linked core was not dissolved by the favourable solvent but it was exposed to the solvent by rearranging the corona into two separated patches. In other words, usual spherical micelles were converted to colloidal micelles with the corona reorganized into two non-polar patches and the central core that was directly exposed to the solvent. With the reorganized micelles as colloidal monomers, we were able to polymerize their linear supracolloidal chains by increasing the polarity of the solvent. Furthermore, we applied the same protocol to diblock copolymers having a lower molecular weight and produced small colloidal monomers which were then combined with large colloidal monomers for the synthesis of supracolloidal random and block copolymers.

We selected a diblock copolymer of polystyrene-poly(4-vinylpyridine) (PS-P4VP) which consists of a non-polar PS block and a polar P4VP block that can be effectively cross-linked with 1,4-dibromobutane (DBB).<sup>23,24</sup> First, a PS(51)-P4VP(18) micelle with

the PS corona and the P4VP core was obtained in toluene which is a selective solvent for the PS block.<sup>25</sup> The number in the parenthesis is a number average molecular weight in kg/mol. The P4VP core was fully cross-linked with a molar ratio of DBB to 4VP equal to 0.5. Quaternization of the 4VP units was confirmed by decrease of the 4VP band at 1600  $\text{cm}^{-1}$  and increase of the quaternized 4VP band at 1643  $\text{cm}^{-1}$  (Supporting Information Figure S1).<sup>26</sup> The P4VP core was also stained with  $\text{I}_2$  for TEM. In Figure 1a, a spherical micelle of the dark P4VP core with the grey PS corona is visible. Since the core is clearly discernible in the image, we obtained the average core diameter of 16.5 nm ( $\pm 2.7$  nm) over a larger area than this image.



**Figure 1.** TEM images: (a) spherical micelles of PS(51)-P4VP(18); (b) micellar colloidal monomers; (c) a supracolloidal polymer chain. All scale bars are 100 nm. The image in (c) corresponds to the marked area in the inset ( $3 \mu\text{m} \times 3 \mu\text{m}$ ) which shows a whole chain.

The solubility parameter of DMF ( $24.8 \text{ MPa}^{1/2}$ ) is close to that of P4VP ( $22.2 \text{ MPa}^{1/2}$ ) but somewhat larger than that of PS ( $18.6 \text{ MPa}^{1/2}$ ),<sup>27,28</sup> indicating that DMF is a good solvent for P4VP but a poor solvent for PS. That is, after the addition of DMF, the solvent around PS-P4VP micelles became preferable to the P4VP core. After changing the polarity of the solvent, as shown in the TEM image of Figure 1b, a spherical micelle was changed to a micelle with two separated patches of the PS block and the central P4VP core exposed to the solvent. With this micellar structure, the P4VP core can directly contact with the solvent. The diameter of the P4VP core was basically unchanged. We note that the rearranged micellar structure was not much affected with different amounts of cross-linking agents (the molar ratio of DBB to 4VP = 0.2~1.0).

Since the P4VP core was cross-linked, it was not dissolved by a favourable solvent of DMF. However, the P4VP core was exposed to DMF by rearranging the PS corona into two separated patches, i.e., by a popup structure of the P4VP core over the divided PS corona. Segregation of the PS corona initiated by the P4VP core can depend on the portion of the corona block to the total copolymer<sup>22</sup> which was 0.74 in terms of the molecular weight for PS(51)-P4VP(18). In a higher portion of the corona, the core would not be able to divide the corona. With a lower portion of the corona, more than two patches in the corona would be induced by the core. We are currently

investigating the patch formation in the corona depending on the portion of the corona block.

In the rearranged micellar structure shown in Figure 1b, two non-polar PS patches emanated from the core can act as attractive parts whereas the polar P4VP core, directly exposed to the solvent between two patches, can work as a repulsive part when the solvent becomes more polar by addition of water. We can consider this rearranged micellar structure an analogue of a polar-surfactant-stabilized Au nanorod with non-polar polymers attached to two ends<sup>7</sup> or a spherical triblock copolymer micelle having a divided corona with polar and non-polar compartments.<sup>22</sup> That is, the micelle with the non-polar patched corona and the polar core directly exposed to the solvent can be a colloidal monomer.

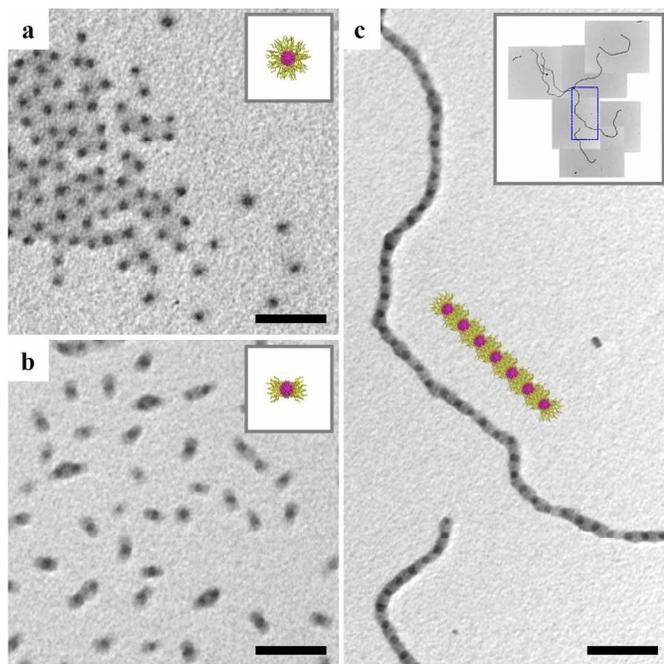
To increase the polarity of the solvent, we added water, which was diluted with DMF, to these colloidal monomers of the rearranged micelles of PS(51)-P4VP(18). As shown in Figure 1c, a supracolloidal polymer chain was successfully synthesized. The image clearly shows alternating colloidal monomer units of PS(51)-P4VP(18) micelles. The inset in Figure 1c shows a representative chain of a whole polymer, which is  $\sim 8.9 \mu\text{m}$  long. The boxed area in the inset is the image shown in Figure 1c. A fully enlarged image of the inset is also given in Supporting Information Figure S2. By dynamic light scattering (DLS) measurements (Supporting Information Figure S3), we also observed the increase of the average diameter as the reaction proceeded, although DLS gives a spherical-averaged diameter that is equal to neither the chain length nor the chain width.<sup>29</sup> It is noted that we did not observe individual colloidal monomers which were not incorporated into supracolloidal chains. Several defects of joining more than two colloidal monomers can be found in the whole chain.

By addition of water, the non-polar patches of the PS block in the colloidal monomer became unfavourable to the contact with water so that attraction between the PS patches of neighbouring colloidal monomers was exerted, leading to the reaction between the colloidal monomers. Simultaneously, the exposed P4VP core became more favourable to the contact with the solvent containing water so that lateral aggregation of the colloidal monomers was effectively prevented by the P4VP core exposed to the solvent. Thus, we effectively polymerized the colloidal monomers of the reorganized PS-P4VP micelles to a supracolloidal polymer chain.

We applied the same protocol to PS-P4VP having a lower molecular weight in order to obtain smaller colloidal monomers and their supracolloidal polymer chains. We selected PS(25)-P4VP(7) that has less than a half molecular weight of PS(51)-P4VP(18). However, the portion of the corona block to the total copolymer was similarly 0.78. Figure 2a shows smaller spherical micelles of the dark P4VP core ( $9.4 \text{ nm} \pm 1.7 \text{ nm}$  in diameter) with the grey PS corona. We note that Figure 1 and Figure 2 are in the same scale for good comparison. After the polarity of the solvent was changed with DMF, smaller patched micelles compared to those of PS(51)-P4VP(18) were obtained as shown in Figure 2b. Thus, we produced smaller colloidal monomers consisting of two non-polar PS patches in the corona and the central P4VP core directly exposed to the solvent.

To polymerize these colloidal monomers of PS(25)-P4VP(7), we further changed the polarity of the solvent by adding water as before. But more water was necessary for the polymerization of these smaller monomers. As shown in Figure 2c, a supracolloidal polymer chain with smaller colloidal monomers was again synthesized, which has alternating colloidal units of PS(25)-P4VP(7) micelles. Several polymer chains can be found in the inset of Figure 2c, which are clearly discernible in a fully enlarged image of Supporting Information Figure S4. The length of a whole polymer

chain was  $\sim 2.8 \mu\text{m}$ , which was shorter than that of PS(51)-P4VP(18).

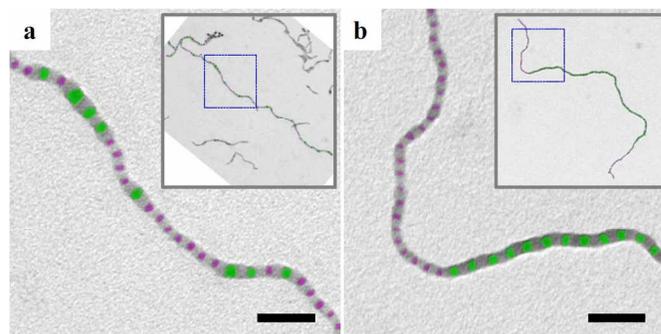


**Figure 2.** TEM images: (a) spherical micelles of PS(25)-P4VP(7); (b) colloidal monomers; (c) a supracolloidal polymer chain. All scale bars are 100 nm. The image in (c) corresponds to the marked area in the inset ( $3 \mu\text{m} \times 3 \mu\text{m}$ ) which shows several whole chains.

To obtain supracolloidal polymer chains of colloidal monomers of PS-P4VP after 48 hr polymerization (Figures 1c and 2c), 15 wt% water in the solution was needed for PS(25)-P4VP(7) whereas 10 wt% water was enough for PS(51)-P4VP(18). The non-polar PS patches in the colloidal monomer generate the attraction necessary for polymerization of the colloidal monomers, which is originated to avoid unfavourable contacts of the PS patches with the polar solvent containing water. Thus, a larger patch of the PS block can induce stronger attraction, i.e., higher reactivity of the colloidal monomer. Therefore, the colloidal monomer of PS(51)-P4VP(18) having larger PS patches can be polymerized with a lower content of water. In addition, the colloidal monomers of PS(51)-P4VP(18) produced a higher degree of polymerization (approximately 262 by dividing the chain length of  $\sim 8.9 \mu\text{m}$  with the monomer length of  $\sim 34 \text{ nm}$ ) than those of PS(25)-P4VP(7) ( $\sim 117$  by  $\sim 2.8 \mu\text{m} \div \sim 24 \text{ nm}$ ) after 48 hr polymerization (Supporting Information Figures S1 and S2), indicating faster polymerization with larger PS patches. It is noted that polymerization of colloidal monomers in the condition we used was relatively slow because 24 hr or longer polymerization was necessary to detect a supracolloidal chain with an appreciable length. We also note that aggregation of the colloidal monomers was observed in low contents of water after 48 hr, presumably because low contents of water would not generate enough repulsion between the P4VP cores, which were directly exposed to the solvent, to avoid the lateral aggregation of colloidal monomers. A study on the detail of polymerization of colloidal monomers depending on water contents and non-polar patch sizes is in progress.

We had two different colloidal monomers of PS(51)-P4VP(18) and PS(25)-P4VP(7) that were well discernible in TEM images due to their sizes. Thus, we demonstrated the synthesis of supracolloidal random and block copolymer chains. For random copolymerization, two colloidal monomers of PS(51)-P4VP(18) and PS(25)-P4VP(7)

after DMF addition were first mixed and then polymerized by water addition. Figure 3a shows a supracolloidal random copolymer consisting of the colloidal monomers of PS(51)-P4VP(18) and PS(25)-P4VP(7) whose cores are marked by green and pink false colours, respectively. A whole chain of the random copolymer is shown in the inset and clearly visible in an enlarged image of Supporting Information Figure S3. We mixed two colloidal monomers with the same weight so that the number of small colloidal monomers of PS(25)-P4VP(7) were 2.8 times more than that of large monomers of PS(51)-P4VP(18) in an initial monomer solution by considering the volume ratio of large to small micelles equal to 2.8 which was estimated from the TEM images. Although counting of the monomer units in the chain (Supporting Information Figure S5) was statistically insufficient, the small monomer units in the random copolymer were found 1.8 times more than the large monomer units. In addition, the chain length of random copolymers was similar to that of the homopolymer of small colloidal monomers, presumably because prevalent small colloidal monomers, which are less reactive, could govern the growth of the chain.



**Figure 3.** TEM images of supracolloidal copolymer chains; (a) random copolymer; (b) block copolymer. The scale bars are 100 nm. Each image corresponds to the marked area in the inset ( $2 \mu\text{m} \times 2 \mu\text{m}$ ). Green and pink false colours are applied to the cores of PS(51)-P4VP(18) and PS(25)-P4VP(7), respectively.

We also synthesized a supracolloidal block copolymer simply by mixing two pre-polymerized chains. We first synthesized two homopolymer chains of the colloidal monomers of PS(51)-P4VP(18) and PS(25)-P4VP(7) for 24 hr polymerization. Then, two homopolymers were mixed with the same weight for additional 24 hr. Figure 3b clearly shows a supracolloidal block copolymer chain consisting of two end blocks of PS(25)-P4VP(7) in pink colour and one middle block of PS(51)-P4VP(18) in green colour. An enlarged image is also given in Supporting Information Figure S6. We note that more homopolymer chains of PS(25)-P4VP(7) were added for block copolymerization because of mixing in the same weight of two pre-polymer chains. It is also noted that the length of each block in the block copolymer was relatively short because homopolymer chains were polymerized only for 24 hr.

## Conclusions

Based on the concept of directional attraction with orthogonal repulsion to the attraction between colloidal building blocks to achieve a linear assembly of colloidal nanoparticles, we accomplished supracolloidal polymerization of colloidal monomers of PS-P4VP diblock copolymers. We induced colloidal monomers of PS-P4VP micelles with the non-polar PS patches in the corona and the cross-linked P4VP core directly exposed to the solvent. During the polymerization of these colloidal monomers driven by increasing the polarity of the solvent, the non-polar PS patches worked as

attractive parts for the reaction whereas the exposed polar P4VP core acted as a repulsive part to limit non-directional aggregation so that a supracolloidal polymer was synthesized. Because the size of colloidal monomers was determined by the molecular weight of PS-P4VP, we were able to synthesize supracolloidal random and block copolymers consisting of large and small colloidal monomers. The strategy demonstrated here is applicable to various diblock copolymers which can form a micelle with a cross-linkable core so that we expect a variety of supracolloid polymer chains with diverse colloidal building blocks. In addition, encapsulation of functional materials such as quantum dots, metal nanoparticles, and fluorophores into the core of diblock copolymer micelles<sup>30</sup> is feasible so that supracolloidal polymers of diblock copolymer micelles can be further functionalized for numerous applications.

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### Notes and references

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