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# Formation of well-defined supramolecular microstructures consisting of $\gamma$ cyclodextrin and polyether -rods, cubes, plates, and nanosheets-guided by guest polymer structure



POLYMER

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### HIGHLIGHTS

·Well-defined microstructures were formed by complexation of  $\gamma$ -cyclodextrin. ·The microstructure morphologies were controlled by the axis polymer structure. Molecular weight, chemical property, and sequence of axis affects the morphologies.

#### ARTICLE INFO

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## ABSTRACT

To construct well-defined microstructures, strict controls of the temperature and sophisticated techniques are generally required because microstructure formation is usually based on crystallization, which easily results in a kinetic trap of disordered structures. Herein, we report the formation of various microstructures such as rods, cubes, plates, and nanosheets via supramolecular self-assembly between y-cyclodextrin (CD) and polyethers in water without temperature change. We revealed the relationships between the guest polymer structures and the resulting microstructure: (1) Short guest homopolymers lead to the formation of rod microstructures, whilst long congeners result in plates. (2) A hydrophilic backbone polymer is necessary to isolate the plates in water, otherwise hydrophobic interaction leads to aggregation of the plates and the formation of polycrystalline  $\gamma$ -CD complexes. (3) Spatial confinement of the  $\gamma$ -CDs on the central segment of a guest triblock copolymer plays a key role in the fabrication of nanosheets with uniform thickness.

## 1. Introduction

Non-covalent supramolecular self-assembly has attracted much research attention because of the potential to produce complicated nanoand micro-sized structures on a large scale via simple experimental procedures [1]. The nano- and micro-structures fabricated via supramolecular self-assembly can be controlled by designing the molecular structure of the components, and change dynamically depending on the surrounding conditions [2-7]. Therefore, supramolecular self-assembly has been utilized for the fabrication of many kinds of applied materials with specific structures, such as lipid bilayer membranes [8,9], selfassembled monolayers [10,11], and metal-organic frameworks [12-15].

Many researchers have dedicated their efforts to fabricating various morphologies by manipulating supramolecular self-assembly behavior

[16-21], as the properties of materials are strongly dependent on the geometry of the nano- and micro-sized structures [22-25]. In general, complicated steps for synthesis of the components, strict temperature control, and sophisticated techniques are required for manipulation of the structures, especially in the case of the self-assembly of organic components [20,26-29]. This is mainly because well-ordered self-assembled microstructures usually arise from the crystallization of a certain part of the components. Because crystallization is a kinetically dominated phenomenon, the rapid formation of microstructures is likely to result in kinetic trapping of the disordered microstructure consisting of polycrystals.

We have focused on the complexation-induced crystallization of cyclodextrins (CDs) in order to form ordered microstructures. CDs are torus-shaped oligosaccharides; there are three kinds of commercially available CDs, i.e.,  $\alpha$ -CD,  $\beta$ -CD, and  $\gamma$ -CD, classified by the ring size. The

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CDs usually adopt a cage-type crystal structure and, in general, these microstructures are disordered [30,31]. On the other hand, after the incorporation of guest compounds into the cavity of the CDs in water, the complexes can crystallize and precipitate with well-ordered microstructures [21,32–34]. Such inclusion complexes consisting of  $\alpha$ -CD,  $\beta$ -CD, and  $\gamma$ -CD adopt hexagonal [35], monoclinic [36], and tetragonal [37] crystal structures, respectively, and the well-ordered microstructures reflect these crystal systems [38–42]. However, control of the geometry of the microstructure of the CD complexes is still challenging, and molecular design strategies for geometry control are not well established.

In this study, we report wide-range control of the aspect ratios of supramolecular self-assembled microstructures of pseudo-polyrotaxane (PPR) consisting of  $\gamma$ -CD and polyethers, from rods to nanosheets, by designing the guest polymer structure. Y-CD was selected with the expectation of a high ability to form single crystals, even during rapid crystallization [43]. Polyethers such as polyethylene oxide (PEO), polypropylene oxide (PPO), and their block copolymers are used as guest polymers. It is well known that y-CD can form double-stranded complexes with PEO [44] and single-stranded complexes with PPO [45]. To obtain various kinds of microstructures, the effect of the structure of the axis polymer (length, hydrophilic/hydrophobic property, and sequence) on the microstructure is investigated systematically. Growth of the microstructures based on the complexation-induced crystallization is observed in real time using an optical microscope (OM). Magnified images of the microstructure are obtained using a scanning electron microscope (SEM). Wide-angle X-ray scattering (WAXS) measurements are used to analyze the crystal structure and to estimate the anisotropy of the microstructures. For aqueous dispersions of the samples, the thickness of the nanosheet structures is analyzed using small-angle X-ray scattering (SAXS), and atomic force microscopy (AFM) is used for the dried state samples.

### 2. Result and discussion

### 2.1. Ultrafast formation of microstructure

Formation of the well-ordered microstructures via complexation between  $\gamma$ -CD and PEO was ultrafast compared to the usual microstructure formation of CDs with small host molecules [31,34,39,46,47]. After adding PEO400 (the number approximately indicates the weight average molecular weight) to the aqueous  $\gamma$ -CD dispersion, the solution became turbid within 10 min as the complex crystallized (Fig. 1a). For



PEO2k, crystallization took only 3 min (Fig. 1d). Crystal growth was directly observed by optical microscopy (OM) in real time (movies are presented in the SI; Movies S1 and S2; snapshots extracted from the movies are shown in Fig. 1b and e). Complexation between  $\gamma$ -CD and PEO400 (PPR\_EO400) generated many rod microstructures within 27 min, as shown in Fig. 1b, and almost the same shape was observed for the complex between y-CD and PEO2k (PPR\_EO2k) in Fig. 1e. From these observations, it was found that the well-ordered microstructure was formed within 30 min, although the growth was not completed, as shown in Movie S1 and S2. After aging the solutions for 1 day, the precipitates and liquid phase separated in both cases (Fig. 1a and d). Therefore, growth was mostly completed within 1 day. To investigate the microstructure in detail. SEM observation was performed for PPR\_EO400 and PPR\_EO2k aged for 1 day (Fig. 1c and f). The rod structures appeared to consist of several single crystals for both PPR\_EO400 and PPR\_EO2k. The shapes of the structures were almost the same as those observed by OM, although the particle size increased for the sample aged for 1 day, which indicates further growth of the microstructure after 30 min.

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An ordered microstructure was formed within 30 min by the complexation of  $\gamma$ -CD without temperature change. The crystallization speed increased as the concentration of aqueous  $\gamma$ -CD increased. Although  $\beta$ -CD also has the ability to easily form single crystals [32,42], the water-solubility is not very high, so the concentration cannot be increased. On the other hand,  $\alpha$ -CD has high water-solubility, but disordered microstructures are likely to be formed [48] and re-crystallization is required to obtain an ordered microstructure [34]. Ultrafast formation of the microstructure was achieved based on the characteristic ability of  $\gamma$ -CD to readily form single crystals, even under fast crystallization conditions.

### 2.2. Shape control of microstructure depending on length of polymer axis

The microstructures of the  $\gamma$ -CD complexes with the PEO homopolymer were investigated to reveal the effect of the length of the axis polymer on the higher order structure. Fig. 2 shows SEM images of the  $\gamma$ -CD complexes with the PEO homopolymer. Whereas rod microstructures were observed for both PPR\_EO400 and PPR\_EO2k, a cubic microstructure with a low aspect ratio was observed for the PPR with PEO4k (PPR\_EO4k) (Fig. 2a). For the PPR consisting of PEO6k (PPR\_EO6k) and PEO20k (PPR\_EO20k), plate microstructures were

**Figure 1.** (a) Photographs of the mixed solution of  $\gamma$ -CD and PEO400 (the aging times are shown in the photographs). (b) Images of PPR\_EO400 extracted from the movie recorded by optical microscopy (OM; Movie S1). (c) SEM image of PPR\_PEO400 aged over 1 day. (d) Photographs of the mixed solution of  $\gamma$ -CD and PEO2k (the aging times are shown in the photographs). (e) Images of PPR\_EO2k extracted from the movie recorded by OM (Movie S2). (f) SEM image of PPR\_EO2k aged over 1 day.



Fig. 2. SEM images of (a) PPR\_EO4k, (b) PPR\_EO6k, and (c) PPR\_EO20k.



Fig. 3. WAXS profiles of PPR consisting of PEO.

formed (Fig. 2b and c). These results clearly indicate that a longer axis polymer leads to the formation of thinner microstructures.

The plate microstructures observed for PPR EO6k and PPR EO20k adopted an ordered square shape with almost the same side lengths (indicated by red line in Fig. 2b and c). Because the wide-angle X-ray scattering (WAXS) profiles of all PPRs with PEO (Fig. 3) show the characteristic peaks (filled arrow) derived from the tetragonal lattices with a = b = 23.8 Å, c = 22.9 Å,  $\alpha = \beta = \gamma = 90^{\circ}$  [37,49], it is reasonable to conclude that the shape of the microstructure reflects the tetragonal crystal structure. Although peaks derived from the hexagonal crystal structure could be observed (open arrows) [37,49], there were only a few such peaks. The thin side faces are assigned as the 100 and 010 planes, whereas the thickness direction of the plate corresponds to the 001 plane [32]. The cubic structures observed for PPR\_EO4k apparently reflect the tetragonal crystal structure. The rod microstructures formed for PPR\_EO400 and PPR\_EO2k can be seen to consist of several single crystals, where the side lengths are almost the same (red line in Fig. 1b and c). Therefore, the long side faces of the rod microstructure were assigned as the 100 and 010 planes, whilst the long axis of the rod corresponds to the 001 plane.

The dependence of the crystal growth on the length of the PEO axis is summarized in Fig. 4. It is well known that  $\gamma$ -CD can form doublestranded complexes with PEO, as shown in Fig. 4 [44]. The short axis led to the formation of rod microstructures with the long sides in the *c* axis direction. This indicated that the crystal growth of  $\gamma$ -CD in the *c* axis direction was faster than that along the *a* and *b* axes (Fig. 4a). In contrast, the side lengths in the *c* axis direction of the microstructure became shorter as the polymer axis got longer. This suggests that the crystal growth of  $\gamma$ -CD along the *a* and *b* axes was relatively fast compared to that along the *c* axis in the case of the longer axis polymer.

These results are attributed to the role of rod-like PPR as a building block for constructing the microstructures (Fig. 4). Because well-defined microstructures were formed with PPR\_EO400, PPR\_EO2k, PPR\_EO4k, and PPR\_EO6k, it is thought that the axis of the PEO chains does not protrude in the microstructures, and the length of the PPR unit

is less than the extended length of PEO400 (3.2 nm), PEO2k (16 nm), PEO4k (32 nm), and PEO6k (48 nm). The shorter PPRs undergo weaker transverse interaction than the longer congeners. Thus, the shorter PPRs tend to grow faster along the c axis than along the a and b axes, which results in the rod microstructure (Fig. 4a). In contrast, the longer PPRs form nano-sized plates of the same thickness as PPR because of faster crystal growth along the *a* and *b* axes due to the larger transverse interaction (Fig. 4b). For PPR\_EO20k, Fig. 2c shows the plate microstructures with steps (inset in Fig. 2c, indicated by red arrow) and overlapping, where the thickness of the plates was less than the extended length of the axis (160 nm) and the plates were polydisperse in water based on the SAXS profile (Fig. S1, ESI). This can be explained by the folding of the axis of the PEO chain, as shown in Fig. 4c. It is seen that the folding point disturbs crystal growth along the *c* axis and leads to formation of the plate microstructure. The folding of the axis in longaxis PEO should yield bridging of plates, and steps.

Consequently, the crystal habit of the complexation-induced microstructure formed by  $\gamma$ -CD could be controlled by changing the axis polymer length. The designable geometry of the PPR building unit depending on the axis polymer length is one of the characteristics of the complexes of CDs with polymers that influences the construction of the microstructure.

### 2.3. Effect of the hydrophilicity/hydrophobicity of the axis polymer

We prepared PPRs with PPO and compared the microstructures with those of PPR with PEO to reveal the effect of the hydrophilicity/hydrophobicity of the axis polymer on the higher order structure. For the inclusion complexes of y-CD and PPO400 (PPR\_PO400), PPO2k (PPR\_PO2k), and PPO4k (PPR\_PO4k), a similar dependence of the thickness of the microstructures on the axis length was observed in the SEM images (Fig. 5a, b and 5c). Formation of the tetragonal crystal structure was confirmed from the WAXS profiles (Fig. 6), which show the characteristic peaks (filled arrow) for all PPRs with PPO although the negligible peaks derived from the hexagonal crystal structure were observed (open arrow). The relationship between the crystal planes and the ordered microstructures of PPR\_PO400 (rod), PPR\_PO2k (cube), and PPR\_PO4k (plate) can be interpreted in almost the same manner as that of PPR with PEO. However, the complexes between y-CD and longer PPO became disordered, as seen in the SEM images of the complexes consisting of y-CD and PPO6k (PPR\_PO6k) and PPO14k (PPR\_PO14k) (Fig. 5d and e). Even in these disordered microstructures, the polycrystalline tetragonal crystal structure was formed. Formation of the polycrystalline structure is plausibly due to the competition between the hydrophobic interaction of axis PPO and crystal growth of the  $\gamma$ -CD complexes (Fig. 7b). As the chain becomes longer, PPO loses is hydrophilicity and kinetic trapping of the folding configuration becomes likely. Therefore, PPR\_PO6k and PPR\_PO14k easily formed the kinetically trapped disordered structure. However, in the case of PPR with PEO, there is a weak interaction between the axis PEOs, and PPR does not aggregate in water. Thus, the crystalline  $\gamma$ -CD complex can grow without disturbance from axis aggregation, although axis bridging may occur (Fig. 7a).

The microstructures of the PPRs with PEO and with PPO differed in



Fig. 4. Schematic illustrations of the crystal growth behavior of the PPR consisting of (a) short PEO, (b) relatively long PEO, and (c) much long PEO.

terms of the shapes, as well as the alignment relative to the substrate. In the WAXS profiles of PPR with PEO, only the integral of the (132) peak showed a prominent decrease as the PEO length increased, especially in the case of PPR\_EO6k and PPR\_EO20k. The (132) peak is the sole diffraction peak in this range that contains information about the *c* axis. Therefore, the decreased intensity of the (132) peak integral suggests that the *c* axis of the crystal is parallel to the X-ray direction. Because the X-rays entered the glass substrate vertically in this experiment, it was found that the faces of the plate-type microstructures of PPR\_EO6k and PPR\_EO20k were aligned parallel to the glass substrate.

The magnitude of the alignment of the single crystals was estimated by using the relation R = S(132)/S(200) (Fig. 8a and b), where S(132)and S(200) are the integrals of the (132) and (200) peaks, respectively (the fittings to obtain the integrals are shown in Fig. S2, ESI). The small values of *R* for PPR\_EO6k and PPR\_EO20k (Fig. 8a) indicate the strong alignment of the microstructures with the substrate, consistent with the SEM images, where the microstructures were oriented relative to the substrate. *R* was relatively high in the case of PPR\_EO4k, PPR\_EO2k, and PPR\_EO400. These results are reasonable because the cubic and rod microstructures are not aligned with the substrate, as shown in the SEM



Fig. 6. WAXS profiles of PPR consisting of PPO.



Fig. 5. SEM images of (a) PPR\_PO400, (b) PPR\_PO2k, (c) PPR\_PO4k, (d) PPR\_PO6k, and (e) PPR\_PO14k.



Fig. 7. Schematic illustrations of the aggregation behavior of the plate microstructure consisting of the long linear (a) hydrophilic PEO and (b) hydrophobic PPO.



**Fig. 8.** (a) Ratio (R = S (132)/S (200)) of (132) to (200) peaks in the integrals for PPR consisting of PEO and (b) PPR consisting of PPO.

image.

In contrast, the value of *R* did not decrease for the complexes of  $\gamma$ -CD and PPO (Fig. 8b). In particular, *R* was not reduced for PPR\_PO4k although the plate microstructures were formed. This result is opposite to those for PPR\_EO6k and PPR\_EO20k, and plausibly arises from aggregation of the plate microstructures prior to alignment of the faces to the substrate, as seen in the SEM images. Aggregation of the plate microstructures is probably caused by hydrophobic interaction among the PPO segments protruding from the plate microstructure. By comparing the PPRs obtained with PEO and PPO, it is clear that the hydrophilic axis polymer plays an important role in obtaining the plate microstructure without aggregation. Although high molecular weight PEO was folded in the plate microstructure, the PEO chain near the folding point can interact with water and prevent aggregation of the plate microstructures (Fig. 7a), which resulted in the specific orientation relative to the substrate [50].

It was found that longer PPO segments in PPR lead to aggregation of the plate microstructure and the formation of polycrystalline CD complexes based on the hydrophobic interactions among PPO. On the other hand, weak interaction among the plate microstructures of PPR with longer PEO yields well-ordered plate microstructures that are oriented with the substrate. This is considered as analogous to the design of the oligomer-/polymer-grafted nanoplatelets for isolation in the solvent [51].

# 2.4. Formation of ultrathin microstructure consisting of triblock copolymer as an axis

 $\gamma$ -CD is known to selectively cover the PPO segment of PEO-PPO block copolymers because of the stronger interaction with PPO than that with PEO [52], thereby forming ordered nano- and micro-structures [39,42]. In the present study, the higher-order structure of the inclusion complex consisting of the EO<sub>x</sub>PO<sub>56</sub>EO<sub>x</sub> triblock copolymer (where the subscripts denote the number of units) was investigated by changing the number of PEO units, *x*. The complexes of  $\gamma$ -CD and EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub> (PPR\_EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub>), EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub> (PPR\_EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub>),

and  $EO_{147}PO_{56}EO_{147}$  (PPR\_EO\_{147}PO\_{56}EO\_{147}) were prepared and the structures were analyzed.

For all the triblock copolymer-based PPR samples, the (132) peaks disappeared in the WAXS profiles (Fig. 9a). These results indicate that the plate microstructures were formed and were highly aligned with the substrate in the same manner as those of PPR\_EO6k and PPR\_EO20k. The SAXS profiles of the samples in water show no fringes for PPR\_EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub>, whereas PPR\_EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub> and PPR\_EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub> exhibit clear fringes (Fig. 9b, c, and 9d). By fitting the SAXS profiles to the nanosheet form factor equation, the thicknesses of PPR\_EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub> and PPR\_EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub> were determined to be 22 nm and 31 nm, respectively. The microstructures were observed using SEM: PPR\_EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub> formed the plate microstructure (Fig. 9e), whereas PPR\_EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub> yielded stacked nanosheets (Fig. 9f). Although the PPR nanosheets were isolated in water, the nanosheets were probably stacked during the drying process. Interestingly, PPR\_EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub> clearly comprised many nanosheets (Fig. 9g). The thickness of the nanosheets of PPR\_EO\_{147}PO\_{56}EO\_{147} deduced from AFM analysis was 33 nm (Fig. 9h), which is almost the same thickness as that obtained by SAXS analysis. In all cases, the sheet particles adopted a square shape. Therefore, the thin side faces were assigned as the (100) and (010) planes, while the thickness corresponds to the c axis of the tetragonal single crystal.

The proposed model structure of the axis polymer in the sheet particle is summarized in Figure 10. The thickness of the PPR\_EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub> plates (approximately 100 nm) was larger than the extended length of EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub> (25 nm), therefore suggesting a PPR where the axis was extended, connected with the other PPRs (Fig. 10a). In the case of PPR\_EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub> and PPR\_EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub>, it seems that  $\gamma$ -CD selectively covers the PPO segment, allowing hydration of the PEO chain (Fig. 10b and c). Because the extended length of 56 PPO units is 19 nm, the  $\gamma$ -CDs were considered to be present not only on PPO, but also on PEO to a small extent. It has been reported that the block copolymer containing a PEO segment can form an inclusion complex of  $\gamma$ -CD and a single PEO chain [53,54]. Therefore, single or double PEO chains are covered with  $\gamma$ -CD.

We successfully obtained an isolated PPR nanosheet using  $\gamma$ -CD and PEO-PPO-PEO triblock copolymer. By changing the length of the side PEO chain of the triblock copolymer, it was clearly demonstrated that spatial confinement of the CD on the axis is important for fabricating nanosheets with uniform thickness.

### 3. Conclusion

We reported the ultrafast formation of an ordered microstructure via supramolecular self-assembly of  $\gamma$ -CD and linear polymers. This achievement was possible based on the ability of  $\gamma$ -CD to form single crystals, even under fast crystallization conditions. We further



**Fig. 9.** WAXS profiles of PPR\_EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub>, PPR\_EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub>, and PPR\_EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub> (a). SAXS profiles and fitting results (dashed line) for PPR\_EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub> (b), PPR\_EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub> (c), and PPR\_EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub> (d). SEM images of PPR\_EO<sub>4</sub>PO<sub>56</sub>EO<sub>4</sub> (e), PPR\_EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub> (f), and PPR\_EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub> (g). AFM image and height profile of PPR\_EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub> (h).

demonstrated that the microstructure of the  $\gamma$ -CD complexation-induced crystal with PEO or PPO could be controlled by changing the length of the guest linear polymer. The experimental results indicate that a hydrophilic polymer as the axis is necessary to obtain the plate microstructure without aggregation. Furthermore, it was found that confinement of the position of the CDs on the axis plays a key role for fabricating nanosheets with uniform thickness. Since the nanosheet materials can interact with objects by a large surface area, we expect that the PPR nanosheets can be used to develop a new kind of biomaterials and drug delivery systems that have a high adhesion property.

### 4. Experimental section

### 4.1. Materials

 $\gamma\text{-}CD$  was kindly supplied by CycloChem Co., Ltd. PEO400, PEO2k, PEO4k, PEO4k, PEO20k, PPO400, PPO2k, PPO4k, EO\_4PO\_{56}EO\_4,



Fig. 10. Schematic illustrations of the axis polymer structure of (a) PPR\_EO4PO56EO4, (b) PPR\_EO25PO56EO25, and (c) PPR\_EO147PO56EO147.

EO<sub>25</sub>PO<sub>56</sub>EO<sub>25</sub>, and EO<sub>147</sub>PO<sub>56</sub>EO<sub>147</sub> were purchased from Sigma-Aldrich and Wako Pure Chemical Industries. PPO6k and PPO14k were kindly supplied by Mitsui Chemicals & SKC Polyurethanes Inc. The polydispersity indices of the PEO reagents, PEO2k, PEO4k, PEO6k, and PEO20k, were 1.1, 1.1, 1.2, and 1.5, respectively, and those of the PPO reagents, PPO2k, PPO4k, PPO6k, and PPO14k were 1.1, 1.1, 1.2, 1.3, and 1.3 respectively. All reagents were used as received.

### 4.2. Preparation of PPR

 $\gamma$ -CD was dissolved in the deionized water (pH was approximately 7) at 23  $\pm$  1 °C. The  $\gamma$ -CD concentration was 0.12 g mL<sup>-1</sup>. The 0.25 g of PEO, PPO, and PEO-PPO-PEO triblock copolymer were added into 8.4 mL of aqueous  $\gamma$ -CD, respectively. The mixed solutions were vigorously shaken by a vortex for 1 min. And then the solutions were put on the shaker and aged. In all cases except for PPR\_EO20k, structural analysis was conducted for the samples aged over 1 day since the precipitates and liquid phase separated and the complexation seemed almost completed within 1 day. For PPR\_EO20k, structural analysis was conducted for the sample aged over 1 week because the complexation required a long time for separation of the precipitate and liquid phase.

### 4.3. Sample preparation for structural analysis

The samples for the AFM and SEM experiments were prepared by dipping a silicone oxide substrate into an aqueous dispersion of PPR. The aqueous dispersion of PPR was poured into a glass capillary for X-ray measurements (WJM-Glass/Muller GmbH Boro-Silicate capillary:  $\phi = 2.0 \times \text{length} = 80 \text{ mm}$ ) and used for SAXS analysis. After drying the sample for 1 day at room temperature, the WAXS experiment was performed by targeting the particle attached to the glass wall.

### 4.4. Measurement

WAXS and SAXS experiments were carried out using a Rigaku NANOPIX instrument with a Hypix-3000 detector. The sample-to-detector distance was calibrated relative to the silver behenate diffraction peak. SEM observation was conducted with a JEOL JSM-7800F instrument. The AFM experiment was carried out under ambient conditions using a Bruker Nano Multimode 8 instrument, operating in tapping mode. Antimony-doped silicon cantilever tips (Bruker RTESPA-300) with a resonance frequency of around 300 kHz and a spring constant of 40 Nm<sup>-1</sup> were used. The *in-situ* crystal growth induced by complexation was recorded by using a Nikon ECLIPSE Ts2R phase contrast microscope with a Nikon DS-Fi3 camera.

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### Appendix A. Supplementary data

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