Supporting Information

Autonomously Isolated Pseudo-Polyrotaxane Nanosheet Fabricated via Hierarchically Ordered Supramolecular Self-assembly

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Materials
β-CD and OH-PEO75PPO30PEO75 (Pluronic F68) were purchased from Fujifilm Wako Pure Chemical Corporation and Sigma-Aldrich, and were used as received.

Equipment
Scanning electron microscopy (SEM) was conducted using a JEOL JSM-7800F. Atomic force microscopy (AFM) was carried out under ambient conditions using a Bruker Nano Multimode 8, operating under the 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⁻¹ were used. Small and wide angle X-ray scattering (SAXS and WAXS) experiments were carried out using a Rigaku NANOPIX with Hypix-3000 detector. The sample-to-detector distance was calibrated with a silver behenate diffraction peak. Grazing incidence wide-angle X-ray scattering (GI-WAXS) experiments were performed using Rigaku SmartLab with Hypix-3000 detector. The wavelength of the X-ray used was 0.154 nm, and the sample to detector distance was 67.15 mm. Measurements were conducted slightly above the critical angle of the samples. Ultraviolet and visible absorption spectra were recorded with a Shimadzu UV-3150 spectrophotometer. The magnetic orientation of the COOH-PPR nanosheet was carried out using a Quantum Design Physical Property Measurement System (PPMS) at International MegaGauss Science Laboratory, The Institute for Solid State Physics, The University of Tokyo, Japan. Polarized and non-polarized microscopy was performed using an Olympus BX51 optical polarizing microscope.

Preparation of the water dispersion sample of pseudo-polyrotaxane nanosheet.
The synthesis of COOH-PEO75PPO30PEO75 followed the procedure reported previously.¹¹) 1 g of OH-PEO75PPO30PEO75 and COOH-PEO75PPO30PEO75 were added to 0.5 L of 18 g/L β-CD water solution. The solutions were stirred for one week and became gradually turbid as the pseudo-polyrotaxane nanosheet was formed. The water dispersions of OH-PPR and COOH-PPR nanosheets were concentrated by centrifugation. The water dispersion of COOH-PPR was deionized using ion exchange resins, Amberlite IRA410J (anion exchange resin) and Amberlite IR120B (cation exchange resin), and the pH was 4.6. The concentration of the water dispersion of the nanosheets was calculated to be 10 wt% by measuring the weight of the sample dried from 200 µL of the water dispersion of PPR nanosheets. The concentration was changed by adding deionized water. The water dispersion of COOH-PPR with NaCl was prepared by adding 6 mg of NaCl to 300 µL of the 5.5 wt% water dispersion of COOH-PPR.

Sample preparation for analysis and experiment
The samples for AFM, SEM, and GIWAXS analyses were prepared by dipping a silicone oxide substrate in the water dispersion of the PPR nanosheet. The water dispersion of the PPR nanosheet was poured into a glass capillary for X-ray measurements (WJM-Glas/Muller GmbH Boro-Silicate capillary: φ = 2.0 mm length = 80 mm) and used for SAXS and WAXS measurements. The samples for polarized and non-polarized optical microscopy were prepared by pouring the water dispersion of PPR nanosheet into the glass cell (13 X 13 X 2 mm).
**Detailed structure of COOH-PPR nanosheet**

From the AFM measurement, the thickness of COOH-PPR nanosheet was determined to be 16 nm, which includes the thickness of the PEO chains. On the other hand, the SAXS profiles of the water dispersion of COOH-PPR indicates the thickness of the $\beta$-CD layer to be 11 nm. Therefore, the thickness of PEO chains on/below the $\beta$-CD layer was evaluated to be ca. 2.5 nm. This is almost equal to the thickness of the PEO chain, 2.68 nm, calculated from the weight density of PEO. The detailed structure of the COOH-PPR nanosheet is depicted in Figure S1.

Figure S1. The schematic illustration of the detailed structure of dried COOH-PPR nanosheets on a silicone oxide substrate.

**WAXS profiles of the PPR nanosheets**

The WAXS profiles of the water dispersion of OH-PPR, COOH-PPR, COOH-PPR with NaCl, and the 1D radial profile, tangentially integrated from the 2D GIWAXS profile of the COOH-PPR on silicone substrate, are shown in Figure S2.

The characteristic peak of PEO crystal was observed at 23° (arrow in Figure S2). However, since the intensity of the peak is very small, it was concluded that a negligible amount of PEO chain crystallized on/below the COOH-PPR nanosheet. This result is similar to the previous report that only 6% of PEO chains of OH-PPR were crystalized.³²)

Figure S2. The WAXS profiles of the 10 wt% water dispersion of (a) OH-PPR and (b) COOH-PPR, (c) the 5.5 wt% water dispersion of COOH-PPR with NaCl, and (d) the 1D radial profile tangentially integrated from 2D GIWAXS profile of COOH-PPR in Figure 2d.
Alignment of the PPR nanosheets in water in a glass capillary

The capillaries filled with the 10 wt% water dispersion of the nanosheet were placed upright and exposed to X-ray radiation. The SAXS 2D profiles of the samples and the schematic illustrations of the nanosheets’ alignments in the glass capillary are displayed in Figure S3. For COOH-PPR, the nanosheets form factor was observed only in the horizontal direction. This means that the nanosheet aligned those faces parallel to the long side of the glass wall of the capillary (Figure S3a). On the other hands, the peaks derived from a lamellar structure factor were observed in a horizontal direction in the case of the OH-PPR. This result indicates that the lattice direction of the lamellae structure was horizontal, and it was concluded that the stacked OH-PPR nanosheets were also faced on the long side of the glass wall of the capillary (Figure S3b).

![Figure S3](image)

Figure S3. The SAXS 2D profiles of the 10wt% water dispersion of (a) COOH-PPR and (b) OH-PPR. The schematic illustrations of the alignments of the PPR nanosheets are described in each figure.

Calculation of the long-range periodic structure using Bragg Snell equation.

According to the Bragg Snell law (eq. S1), the relationship between the reflection peak wavelength $\lambda_R$ and the incident angle $\theta$ of an ordered structure is given by

$$m\lambda_R = 2d(n_a^2 - \sin^2 \theta) \quad (S1)$$

where $m$ is the order of diffraction ($m = 1$), $d$ a spacing of the periodic structure, and $n_a$ a refractive index of the solution obtained by eq. S2:

$$n_a = \left(\sum_i n_i^2 V_i^2\right)^{1/2} \quad (S2)$$

where $n_i$ and $V_i$ are the refractive index and the volume fraction of $i^{th}$ component, respectively. The water dispersion of the COOH-PPR nanosheet contains 95% water. Therefore, the refractive index of water, 1.33, is used for $n_a$ and the incident angle is 90°. The $d$-spacing of the long-range periodic structure was calculated from $\lambda_R$ with these values.

Orientation behavior of COOH-PPR nanosheet’s response to a strong magnetic field

Most of nanosheets align their faces parallel to the direction of an applied magnetic field (Figure S4a). In this case, the nanosheet is capable of rotating around the axis of the magnetic field. On the other hand, the COOH-PPR nanosheet is aligned perpendicular to the direction of the magnetic field (Figure S4b). Although the COOH-PPR nanosheets can rotate around the axis of the magnetic field, the 1D alignment of the PPR nanosheet is maintained.
Figure S4. Orientation behaviors of nanosheet’s response to a strong magnetic field. Nanosheet’s face is aligned parallel (a) or perpendicular (b) to the direction of a strong magnetic field.

**Movie**
The movie of the isolated COOH-PPR nanosheets in water was recorded (Movie S1).