Formation of Unusual Microphase-Separated Ultrathin Films of Poly(vinyl catechol-block-styrene) (PVCa-b-PSt) at the Air-Water Interface by Solution Casting onto Water

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SI 1: Synthesis of Poly(vinyl catechol-random-styrene) (PVCa-ran-PSt)

Polymerization: 3,4-dimethoxy styrene (DMSt, >99%) and styrene (St, GR) was purchased from SIGMA-Aldrich and WAKO Chemical Industry, Co. Ltd., respectively. St was washed with 1M NaOH aq. and then dried over molecular sieves (4Å1/16, WAKO Chemical Industry, Co. Ltd.). Tetrahydrofran (THF), methanol (MeOH), dimethylformamide (DMF), acetonitrile and dichloromethane (CH₂Cl₂) were purchased from WAKO Chemical Industry, Co. Ltd. and used without further purification. 2,2′-azobis(isobutyronitril) (AIBN, WAKO/GR) was recrystallized in MeOH before use.

St (2.5 g, 24 mmol), DMSt (349 mg, 2.1 mmol) and AIBN (43 mg, 0.26 mmol) were dissolved in 4 mL of dried DMF with stirring in a grove box. The solution was degassed by 3 cycles of freeze-thaw-evacuate and finally the atmosphere was filled with N₂ gas. The solution was heated by aluminum block heater at 60 °C for 20 h. The polymerized sample was reprecipitated in MeOH.

After 3 h stirring, the supernatant was removed by decantation and polymer was corrected by centrifugation (3,000 rpm, 15 min), and then, the white precipitates (PDMSt-ran-PSt) were dried in vacuo for overnight.

Deprotection: Yielded white powder (505 mg) was dissolved in 25 mL of CH₂Cl₂, and then 2 mL of BBr₃ solution of CH₂Cl₂ was slowly added into the solution. After stirring for 12 h, 200 mL of 1M HCl aq. was added into the solution, the CH₂Cl₂ phase was corrected after 3 h stirring. The corrected CH₂Cl₂ phase was dropped into the MeOH and the white precipitate was corrected by centrifugation (3,000 rpm, 15 min). The white precipitates (PVCa-ran-PSt) were dried in vacuo for overnight. 384 mg white powder was obtained (yield=76%).

¹H-NMR: ¹H-NMR spectra before/after deprotection of methoxy groups were measured by using JNM-LA400, 400 MHz, Bruker. The polymer was dissolved in CDCl₃ with TMS for NMR measurement. Obtained spectra before and after deprotection of methoxy groups were shown in
Figure S1 and S2, respectively. From the $^1$H-NMR spectra, deprotection of methoxy groups was confirmed since signals at $\delta_H=3.57$ and 3.71, which were attributed to methoxy groups of DMSt moieties, in the spectrum of before BBr$_3$ treatment were disappeared in that of after treatment. Copolymerization ratio between St and DMSt was confirmed as 89:11, which means the content of PVCa was 11%.

**GPC:** Molecular weight of obtained PDMSt-ran-PSt was measured by gel permeation chromatography (GPC, HLC-8320, TOSOH) with using THF as a carrier solvent. $M_n=25.5$ kg/mol, $M_w=42.6$ kg/mol, $M_w/M_n=1.7$.

Figure S1. $^1$H-NMR spectrum of PDMSt-ran-PSt.
Figure S2. $^1$H-NMR spectrum of PVCa-ran-PSt.

SI 2. Close-up cross-sectional TEM image of PVCa-b-PSt ultrathin film.

Figure S3. Close-up cross-sectional TEM image of PVCa-b-PSt ultrathin film.

SI 3. Close-up and cross-sectional TEM images of a silver nanoparticle embedded PVCa-b-PSt ultrathin film.
Figure S4. Close-up (a) and cross-sectional (b) TEM images of a silver nanoparticle embedded PVCa-\textit{b}-PSt ultrathin film.