Electronic Supplementary Information

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 (4A1/16, WAKO Chemical Industry, Co. Ltd.). Tetrahydrofran (THF), methanol (MeOH), dimethylformamide (DMF), acetonitrile and dichloromethane (CH_2Cl_2) 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 N_2 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 CH_2Cl_2, and then 2 mL of BBr3 solution of CH_2Cl_2 was slowly added into the solution. After stirring for 12 h, 200 mL of 1M HCl aq. was added into the solution, the CH_2Cl_2 phase was corrected after 3 h stirring. The corrected CH_2Cl_2 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%).

^{1}H-NMR: ^{1}H-NMR spectra before/after deprotection of methoxy groups were measured by using JNM-LA400, 400 MHz, Bruker. The polymer was dissolved in $CDCl_3$ 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 δ_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. *Mn*= 25.5 kg/mol, *Mw*= 42.6 kg/mol, *Mw/Mn*= 1.7.

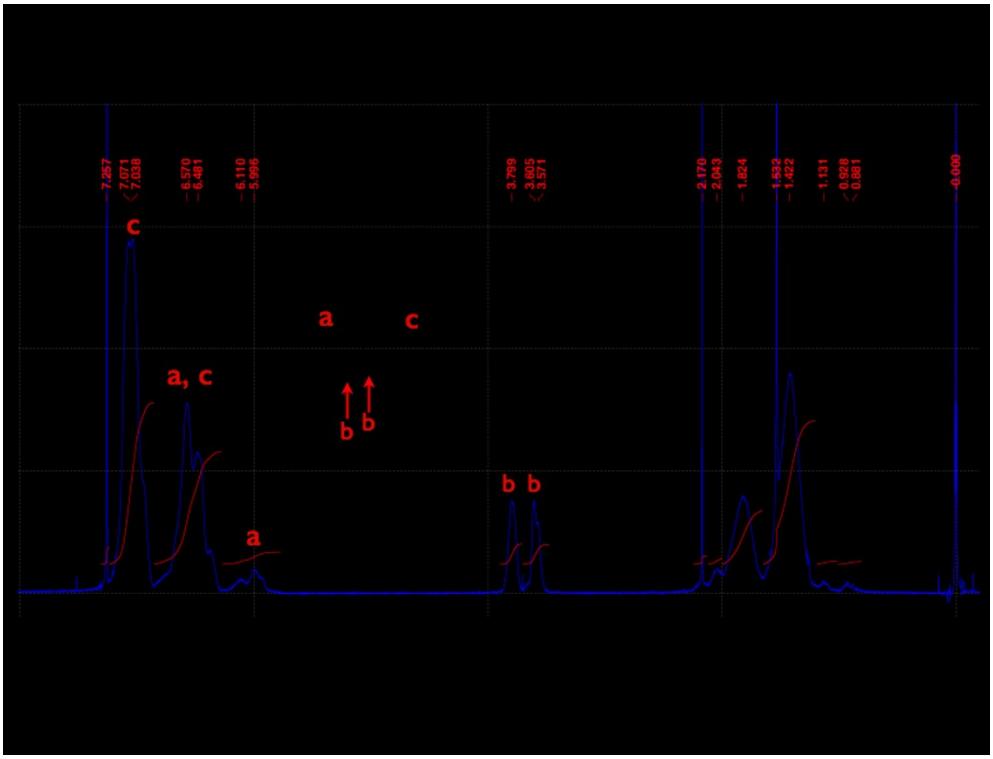

Figure S1. ^{1}H-NMR spectrum of PDMSt-*ran*-PSt.

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.

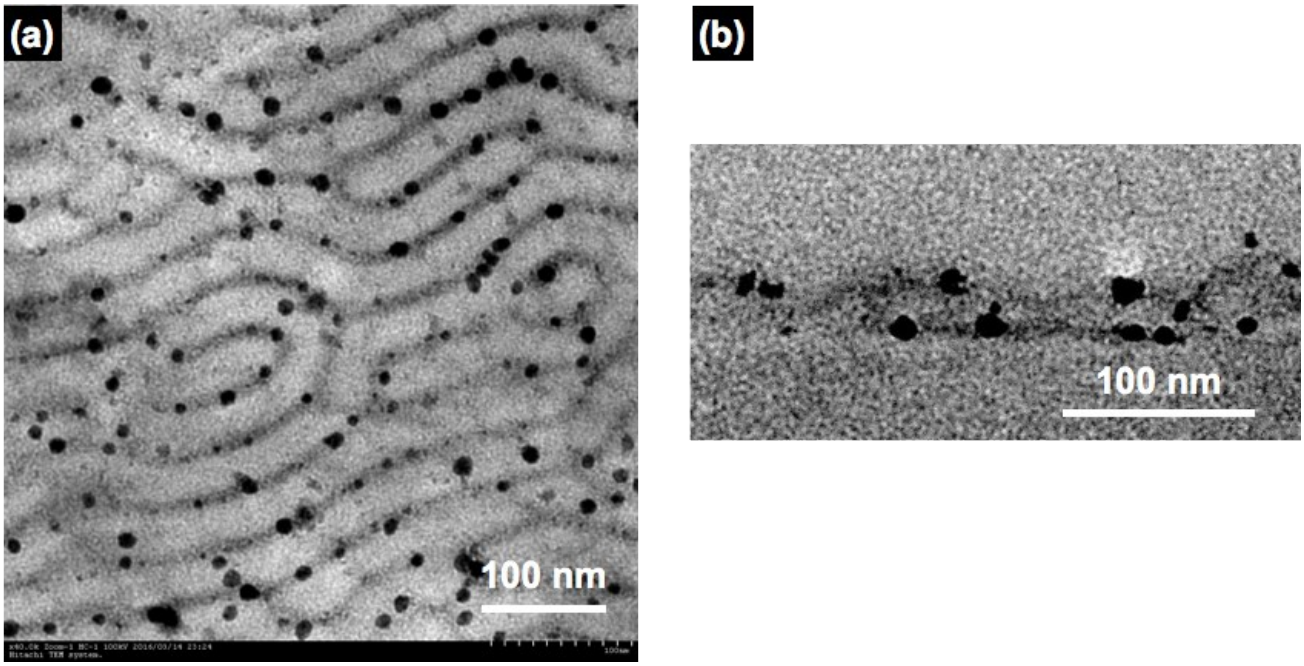

Figure S4. Close-up (a) and cross-sectional (b) TEM images of a silver nanoparticle embedded PVCa-*b*-PSt ultrathin film.