Supporting Information

Azimuthal anchoring coefficients of nematic liquid crystals on polystyrene brushes formed at the air surface of block copolymer monolayers

Naoto Iwata, Yuzuka Yoshioka, Kenta Yazawa, and Masatoshi Tokita\*

# S1. Synthesis of PTESPMA-*block*-PS Copolymer

PTESPMA-*block*-PS were synthesized by two-step atom transfer radical polymerization (Scheme S1). First, a PTESPMA block was synthesized by atom transfer radical polymerization (ATRP). The typical procedure yielding PTESPMA255 is as follows: Ethyl 2-bromoisobutyrate (2-EBiB 115 mg, 0.593 mmol), TESPMA (10.0 g, 40.3 mmol), N,N,N’,N”,N”-pentamethyldiethylene-triamine (PMDETA, 411 mg, 2.37 mmol), anisole (22 g) were added into a 100 ml glass tube. The mixture was bubbled with nitrogen gas for 30 minutes and CuBr (100 mg, 1.19 mmol) was added and purged with nitrogen gas. Then, the tube was placed in an oil bath and kept at 60 ºC for 1 h. The reaction was terminated by opening the tube and exposing the catalyst to air in an ice bath. The reaction mixture was diluted with chloroform and passed through a column filled with alumina to remove the Cu catalyst. The resulted crude product was purified by precipitating into a large amount of methanol and water mixture (7:3 volume ratio) for three times.

PTESPMA-*block*-PS was synthesized by atom transfer radical polymerization (ATRP) method using the PTEPM block as a macronitiator. PTEPM macroinitiator (540 mg) and styrene (2.26 g, 21.7 mmol), PMDETA (231 mg, 1.34 mmol), anisole (2.76 g) were added into a 15 ml glass tube. The mixture was bubbled with nitrogen gas for 15 minutes forming a clear solution. CuBr (39.9 mg, 0.278 mmol) was added and furthermore, purged with nitrogen gas for 5 minutes. The tube was placed in an oil bath at 90 ºC for 57 h. The reaction was terminated by opening the tube and exposing the catalyst to air in an ice bath. The reaction mixture was diluted with chloroform and passed through a column filled with alumina to remove the Cu catalyst. The resulting product was dissolved in tetrahydrofuran (THF) and purified by precipitating into a large amount of methanol and water mixture (8:2 volume ratio) for three times.

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| Scheme S1. Synthesis of PTESPMA-*block*-PS copolymer |
| TESPMA  PTESPMA  PTESPM-*b*-PS |

# S2. Copolymer Composition

The degree of polymerization (DP) of PTESPMA segment was determined by *M*n,PTESPMA measured for a PTESPMA macromonomer by light scattering connected with SEC. The DP of a PTESPMA segment (DPPTESPMA) is equal to Mn,PTESPMA/290, where 290 is the repeat unit molecular weight of PTEPM.

The DP of PS was determined by 1H NMR spectrum measured for the copolymer. Figure S1 shows a typical 1H NMR spectrum measure for a PTESPMA-b-PS copolymer. The ratio of DPPS to DPPTESPMA is equal to the area ratio of the peaks at δ = 6.4 – 7.3 ppm and at δ = 0.7 ppm which are attributed to the five protons on the benzene ring in the PS units (j, k, l) and the two protons bonding to the carbon adjacent to the silicon atom in the PTEPM units (e). Thus,

DPPS : DPPTESPMA = (Ij,k,l/5) : (*I*e/2) (S1),

where *I*j,k,l and *I*e are the area of the peak at δ = 6.4 – 7.3 ppm and at δ = 0.7 ppm, respectively.

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| **Figure S1.** 1H NMR spectrum of a PTESPMA-*block*-PS copolymer with *M*n,PTEPM =25500 and *M*n,PS = 20300 |

# S3. SAXS profile

SAXS (Bruker NanoSTAR-U) was measured for a film sample. The film was prepared by casting THF solution of PTESPMA-*block*-PS copolymer at a concentration of 10 g L−1 on a clean Teflon plate for 7 days at room temperature followed by 48 h annealing at 120 ºC in a vacuum.

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| Figure S2. SAXS profile measured for a PTESPMA-*block*-PS copolymer film. |