Supporting Information

Spreading Dynamics of a Precursor Film of Ionic Liquid or Water on a Micropatterned Polyelectrolyte Brush Surface

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S1. Preparation of Poly(SPMK) Brush/FAS Monolayer Line-Patterned Surface

The glass slides used as a substrate (Matsunami Glass Ind., borosilicate glass, thickness = 0.8–1.0 mm, root mean square roughness was 0.98 nm on area of $30 \times 30 \ \mu\text{m}^2$ by AFM topological measurement) were cut into $26 \times 38 \ \text{mm}^2$ pieces. The substrates were immersed in a H₂SO₄/35% H₂O₂ aq. (70/30 v/v) mixture at 373 K for 1 h to obtain a Si–OH-terminated surface. The substrates were subjected to vacuum ultraviolet (VUV) treatment ($\lambda = 172 \ \text{nm}$, Xe excimer lamp, UER20-172, Ushio Electric, Ltd.) at a pressure of 60–70 Pa for 6 min. The

surface initiator, BHM, was immobilized on the glass substrates by CVA as follows. The substrates and a glass vessel filled with a 5 vol% toluene solution of BHM were packed in a custom-made separable flask (inside diameter: 75 mm, height: 105 mm) purged with N₂ gas. The flask was held in an oven at 418 K for 7 h, after which the substrates were rinsed with ethanol.

The BHM-immobilized substrates were placed in an evacuated vacuum chamber for photolithography. Each substrate was covered with a photomask (L10S5, Mitani Micronics Co., Ltd.) with 10 μ m Cr lines and 5 μ m slits (10 μ m/5 μ m) in an area of 30 × 30 mm² on a quartz glass plate with a thickness of 2.3 mm. Two stainless steel rings (outside diameter: 60 mm, inside diameter: 30 mm, height: 9.5 mm, weight: 160 g per piece) were loaded on the photomask. The surface was irradiated for 360 s by VUV light at 20–40 Pa. To remove the decomposed residue of the BHM monolayers, the patterned surface was rinsed with ethanol. A second organosilane monolayer of FAS was then introduced between the lines of the first patterned monolayer of BHM using a similar CVA method. The substrates and a glass vessel filled with FAS were packed in the separable flask purged with N₂ gas and then heated at 373 K for 3 h, after which the substrates were rinsed with ethanol. By this method, line-patterned BHM monolayer and FAS monolayer surfaces with line widths of 10 and 5 μ m, respectively, were prepared.

Poly(SPMK) brushes were prepared using surface-initiated activators generated by electron transfer (AGET) ATRP of SPMK from the residual BHM monolayer on the line-patterned surface. The SPMK (8.12 mmol), CuBr₂ (8.1 μ mol), bpy (16.6 μ mol), deionized water (6.0 mL), and methanol (14.0 mL) were mixed and applied to the substrate in a glass tube. After the mixture was stirred under a stream of N₂ gas for 30 min, a 0.20 M ascorbic acid aqueous solution (8.2 μ mol) was added as a reducing agent to initiate polymerization. The mixture was stirred under N₂ atmosphere at 303 K for 3 h. Polymerization was terminated by opening the vessel to air. The substrate was rinsed successively with deionized water, ethylene glycol, and deionized water; it was then dried by air blowing.

S2. AFM observation of the Line-Patterned Surface

AFM (NanoWizard 3 Ultra, JPK Instruments AG) was used in the dynamic force mode at room temperature. Imaging was performed under ambient atmosphere to measure the brush thickness in the dry state. Rectangular silicon cantilevers with a backside gold coating (HyperDrive PPP-NCHAuD, Nanosensors, NanoWorld AG, tip radius: 7 nm, spring constant: 42 N m-1, resonance frequency: 330 kHz) were used for imaging. Imaging was performed by scanning an area of $30 \times 30 \text{ µm}2$ transverse to the line pattern.



Figure S1. (a) The AFM topography images and (b) the cross sections of the poly(SPMK) brush and FAS monolayer line-patterned surfaces with line widths of 10 μ m and 5 μ m in the dry state. The brush thicknesses were measured as 39 nm on the surface. The imaging was performed under ambient atmosphere at room temperature.

S3. XPS Analysis of Line-Patterned Surface

XPS (Quantum 2000 Scanning ESCA Microprobe, Physical Electronics, Inc.) was operated with a monochromatized Al $K\alpha$ X-ray source at 1.48 keV at 24.7 W under 1 × 10⁻⁶

Pa. The emission angle of photoelectrons was set to 45° and the beam diameter was 100.0 μ m. The neutralizer was set at 1.0 V and 20.0 μ A. Wide-scan spectra (0–800 eV) were acquired at an energy step of 1.0 and high-resolution spectra (narrow scan) of F_{1s}, K_{2p}, C_{1s} and S_{2p} were at 0.125 eV. As shown in Figure S2, F_{1s}, K_{2p}, and S_{2p} peaks corresponding to the poly(SPMK) brush and FAS monolayer.



Figure S2. XPS spectra of (a) wide scan and high-resolution scan of (b) O_{1s} , (c) F_{1s} , (d) K_{2p} and C_{1s} , and (e) S_{2p} region of the line-patterned poly(SPMK) brush/FAS monolayer surface. The line widths of the brush and monolayer were 10 µm and 5 µm, respectively. The brush thickness in the dry state was 39 nm. Atomic rations of each element measured from peak areas of the high-resolution spectra were shown in (a).

S4. Molecular simulation

Stability energies of solvation were calculated by molecular simulations using a molecular simulation software Materials Studio (Dassault System Co. Ltd.). Structural optimization calculations of each negatively charged sulfopropyl methacrylate (SPM) unit, positively charged EMI, and water molecule were performed based on the density functional theory (DFT). The most stable position and structure of systems containing "SPM and EMI" and "SPM and water" were calculated using classical molecular dynamics (MD), as shown in Figure S3.

More specifically, the stable conformations of SPM unit, EMI, and water molecule were calculated by DFT (DMol³ package, geometry optimization, quality: fine, energy tolerance 1.0x10⁻⁵ Hartree, force and displacement tolerances are 0.002 Hartree/Å and 0.005 Å, functional: GGA/PBE. Solvent was not specified.). The SPM unit and EMI were given charges -1 and +1, respectively. The total energy of the SPM unit was calculated and the value was denoted as ESPM. One molecule of the EMI or water were initially placed 0.4 nm from the sulfonate anion of SPM, and the most stable position and structure were calculated by MD (Forcite, geometry optimization, quality: fine, forcefield: COMPASSII. Charges was used current ESP values calculated by DFT). Subsequently, the structural optimization calculations based on DFT were repeated. Distances of 0.38 and 0.34 nm between the sulfonate anion and the EMI cation and water were obtained, respectively, as shown in the multi-directional diagram of the simulation results (Figure S3). Each atomic charge calculated by DFT shown in Table S1-S3. The total energy of a system containing the SPM and the EMI is denoted as $E_{\text{SPM-EMI}}$, and the energy difference $\Delta E_{\text{SPM-EMI}} = -1.50 \times 10^{-15}$ J between $E_{\text{SPM-EMI}}$ and E_{SPM} was estimated. In addition, the energy difference $\Delta E_{\text{SPM-water}} = -0.33 \times$ 10^{-15} J of a system consisting of the SPM and the water molecule was calculated.

Figure S3. The most stable conformations of (a-1) - (a-4) SPM unit and EMI, and (b-1) - (b-4) SPM unit and water. The objects in Figure (a-1) - (a-4) are same component with same conformation, but captured from different view angles. The objects in Figure $(b-1) \sim (b-4)$ also show the same conformation captured from different view angles. The $D_{\text{SPM-EMI}}$ and $D_{\text{SPM-water}}$ are distance between the sulfur atom in SO³⁻ and the nitrogen atom of EMI, and distance between the sulfur atom and the oxygen atom in water, respectively. The electric charge was shown on each atom.

	Туре	Charge
C1	c4	-0.558
C2	c43	0.252
C3	c3'	0.533
01	o1=	-0.551
C4	c4	-0.569
H1	h1	0.147
H2	h1	0.150
H3	h1	0.148
H4	h1	0.136
H5	h1	0.163
02	o2s	-0.212
C5	c4o	-0.107
C6	c4	-0.086
C7	c4	-0.295
S 1	s4i	0.780
O3	olis	-0.564
O4	olis	-0.553
05	olis	-0.556
H6	h1	0.129
H7	h1	0.089
H8	h1	0.086
H9	h1	0.084
H10	h1	0.107
H11	h1	0.111
H12	h1	0.012
H13	h1	0.126

Table S1. Atomic charges of SPM ^a unit calculated by DFT. ^b

^{*a*} Sulfopropyl methacrylate anion. The total charge was –0.998. ^{*b*} Density functional theory.

	Туре	Charge
H1	h1	0.270
N1	n3a+d	0.369
C1	c3a	-0.251
N2	n3a+d	0.186
C2	c3a	-0.101
C3	c3a	-0.305
H2	h1	0.243
H3	h1	0.217
C4	c4	-0.434
C5	c4	-0.071
H4	h1	0.150
Н5	h1	0.147
H6	h1	0.188
H7	h1	0.135
H8	h1	0.132
C6	c4	-0.581
H9	h1	0.232
H10	h1	0.236
H11	h1	0.239

Table S2. Atomic charges of EMI ^{*a*} calculated by DFT. ^{*b*}

^{*a*} 1-Ethyl-3-methylimidazolium cation. The total charge was 1.001. ^{*b*} Density functional theory.

 Table S3. Atomic charges of water ^a calculated by DFT. ^b

	Туре	Charge
O1	o2*	-0.705
H1	hlo	0.353
H2	hlo	0.353

^{*a*} The total charge was 0.001. ^{*b*} Density functional theory.